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HANDBOOK OF Preparative Inorganic Chemistry

VOLUME 2 · SECOND EDITION

Edited by **GEORG BRAUER**

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TRANSLATED BY SCRIPTA TECHNICA, INC.

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Translation Editor's Preface

The English version of Volume II of Brauer's "Handbook" follows the path of the very well received translation of Volume I. Again, some of the material and particularly the bibliography has been corrected and brought up to date. The nomenclature has been revised where necessary, with the Stock and the Stock-Werner systems (the practice of using Roman numerals to define oxidation states of atoms) adopted as much as possible. This conforms with current I.U. P. A. C. and Chemical Abstracts practice {for details of this, see Robert C. Brasted, J. Chem. Education <u>35</u>, 136 (1948)]. The references to laboratory equipment and techniques reflect current U.S. usage, but useful European methods have been retained.

It is hoped that this volume will be as well received as the preceding one. Comments from users are invited to help improve future editions.

Paul G. Stecher

Rahway, N. J. May 1965

Contents

TRANSLATION EDITOR'S PREFACE

Part II (continued)

Elements and Compounds

| SECTION 19. COPPER, SILVER, GOLD | 1003 |
|---|------|
| Copper (Pure Metal) | 1003 |
| Colloidal Copper | 1003 |
| Copper Hydride CuH | 1004 |
| Copper (I) Chloride CuCl | 1005 |
| Copper (I) Bromide CuBr | 1006 |
| Copper (I) Iodide Cul | 1007 |
| Copper (II) Chloride CuCl ₂ | 1008 |
| Copper (II) Bromide CuBr ₂ | 1009 |
| Copper Oxychloride CuCl ₂ · Cu(OH) ₂ | 1010 |
| Copper (I) Oxide Cu ₂ O | 1011 |
| Copper (II) Oxide CuO | 1012 |
| Copper (II) Hydroxide Cu(OH) 3 | 1013 |
| Potassium Cuprate (III) KCuO ₂ | 1014 |
| Schweizer's Reagent | 1016 |
| Copper (I) Sulfide Cu ₂ S | 1016 |
| Copper (II) Sulfide CuS | 1017 |
| Copper (I) Selenide Cu ₂ Se | 1019 |
| Copper (I) Telluride CuaTe | 1019 |
| Copper (I) Sulfate Cu ₂ SO ₄ | 1020 |
| Tetraamminecopper (II) Sulfate [Cu(NH ₃) ₄]SO ₄ - H ₂ O | 1021 |
| Copper (I) Nitride Cu ₃ N | 1021 |
| Copper (II) Azide Cu(N ₃) ₂ | 1022 |
| Copper Phosphide Cu ₃ P | 1023 |
| Copper Diphosphide CuP ₂ | 1024 |
| Basic Copper Carbonates CuCO ₂ · Cu(OH) ₂ (Green | |
| Cupric Carbonate) | 1024 |
| 2 CuCO ₃ · Cu(OH) _a (Blue Cupric Carbonate) | 1025 |
| Copper (I) Acetylide $Cu_2C_2 \cdot H_2O$ | 1026 |
| Paris Green (Copper Acetoarsenite) | 1027 |
| Fehling's Solution | 1027 |
| Very Pure Silver | 1028 |
| Silver Powder | 1029 |
| Silver from Residues | 1029 |
| Silver Mirrors | 1031 |
| Colloidal Silver | 1034 |
| Silver Iodide AgI | 1035 |
| Silver Chlorate AgClO3 | 1037 |
| | |

| | 1037 |
|--|------|
| Silver Oxide Ag ₃ O | 1038 |
| Silver Peroxide AgaO2 | 1039 |
| Silver Peroxide Ag ₈ O ₂ Sodium Orthoargentite Na ₃ AgO ₂ | 1039 |
| Sodium Orthoargentite Na ₃ AgO ₂ Silver (1) Sulfide Ag ₂ S | 1041 |
| Silver (1) Sulfide $Ag_{2}S$. Silver (1) Selenide $Ag_{2}Se$. | 1042 |
| Silver (I) Selenide Ag ₂ Se Silver (I) Telluride Ag ₂ Te | 1042 |
| Silver (I) Teliuride Ag ₂ 10 Silver Sulfate Ag ₂ SO ₄ | 1043 |
| | 1043 |
| | 1045 |
| | 1046 |
| | 1047 |
| | 1047 |
| | 1048 |
| and the demonstration of the state of the st | 1048 |
| oblige Mitelto AdMille | 1049 |
| | 1050 |
| ~ Dhenanthrolinesilver (II) Persultate [Ag phen2]0306 | 1000 |
| Trie-w w'-dinvridvisilver (II) Perchiorate | 1050 |
| $[\Lambda_{c}(d)nyn]_{c}(C[O_{c})_{c}, \ldots, c, c,$ | 1050 |
| Very Dure Gold | |
| Colloidal Gold | 1053 |
| Gold from Residues | 1054 |
| Gold (I) Chloride AuCl | 1055 |
| Gold (III) Chloride AuCl ₃ | 1056 |
| Hydrogen Tetrachloroaurate (III) HAuCl. · 4 HgO | 1057 |
| Potassium Tetrachloroaurate (III) KAuCl ₄ · ¹ / ₂ H ₂ O | 1058 |
| Gold (III) Oxide Au ₂ O ₃ | 1059 |
| Gold (III) Hydroxide Au(OH) ₃ | 1060 |
| Potassium Aurate KAuO ₂ · 3H ₂ O | 1061 |
| Gold (I) Sulfide Au ₂ S | 1061 |
| Gold (II) Suifide AuS | 1062 |
| Gold (III) Sulfide Au _a S ₃ | 1063 |
| Gold (I) Acetylide Au _a C _a | 1063 |
| Gold (I) Cyanide AuCN | 1064 |
| Potassium Dicyanoaurate (I) K[Au(CN) ₂] | 1065 |
| | |
| SECTION 20. ZINC, CADMIUM, MERCURY | 1067 |
| Zinc Zn | 1067 |
| Zinc Hydride ZnH2 | 1069 |
| Zinc Chloride ZnCl _a | 1070 |
| Zinc Hydroxychloride Zn(OH)Cl | 1071 |
| Ammonium Tetrachlorozincate (NH4) 2nCl4 | 1072 |
| Zinc Bromide ZnBr ₂ | 1072 |
| Zinc Iodide ZnIa | 1073 |
| Zinc Hydroxide (crystalline) <-Zn(OH) 2 | 1074 |
| Ziac Sulfide ZnS | 1075 |
| Zinc Formaldehydesulfoxylate Zn(SO2 · CH2OH)3. | 1076 |

| CONTENTS | 1. | ŧ |
|---|-------------|---|
| Ammonium Zinc Sulfate (NH4) 3Zn(SO4) 3.6H2O | 1077 | |
| Zinc Selenide ZnSe | 1078 | |
| Zinc Amide Zn(NH _g); | 1079 | |
| Zinc Nitride Zn ₃ N ₂ | 1080 | |
| Zinc Phosphides Zn ₃ P ₂ , ZnP ₃ | 1080 | |
| Zinc Phosphate Zn ₃ (PO ₄) ₂ · 4H ₂ O | 1081 | |
| Zinc Hydroxyphosphate Zn ₂ (OH)PO4 | 1082 | |
| Zinc Arsenides Zn ₃ As ₂ , ZnAs ₂ | 1083 | |
| Zinc Thioantimonate Zn ₃ (SbS ₄) ₂ , | 1063 | |
| Diethylzinc Zn(C ₂ H ₆) | 1084 | |
| Zinc Carbonate ZnCO ₃ , | 1086 | |
| Zinc Acetate Zn(CH ₃ COO) _a | 1087 | |
| Zinc Cyanide Zn(CN)a | 1087 | |
| Potassium Tetracyanozincate K ₂ Zn(CN) | 1088 | |
| Zine Silicate Zn ₂ SiO ₄ | 1089 | |
| Zinc Fluorosilicate ZnSiFs · 6 RgO | 1090 | |
| Zinc Ferrate (III) ZnFe ₃ O ₄ | 1090 | |
| Rinmann's Green | 1092 | |
| Cadmium (needles) Cd | 1092 | |
| Cadmium Chloride CdCl ₂ | 1093 | |
| Cadmium Hydroxychloride Cd(OH)Cl | 1094 | |
| Potassium Cadmium Chloride CdCl ₂ · KCl · H ₂ O | 1095 | |
| Cadmium Bromide CdBra | 1096 | |
| Cadmium Iodide CdI2 | 1096 | |
| Cadmium Hydroxide Cd(OH) 2 | 1097 | |
| Cadmium Sulfide CdS | 1098 | |
| Cadmium Nitride Cd ₃ N _a | 1100 | |
| Cadmium Amide Cd(NH _a) _a | 1100 | |
| Cadmium Phosphides Cd ₃ P ₃ , CdP ₂ , CdP ₄ | 1101 | |
| Cadmium Arsenides Cd ₃ As ₂ , CdAs ₂ | 1103 | |
| Diethylcadmium Cd(C ₂ H ₅) ₃ | 1103 | |
| Cadmium Carbonate CdCO3 | 1104 | |
| Cadmium Acetate Cd(CH ₃ COO) ₂ | 1105 | |
| Cadmium Cyanide Cd(CN) ₂ | 1105 | |
| Potassium Tetracyanocadmate KaCd(CN) | 1106 | |
| Cadmium Thiocyanate Cd(SCN)a | 1106 | |
| Cadmium Silicate Cd ₂ SiO ₄ | 1107 | |
| Cadmium Ferrate (III) CdFe ₃ O ₄ | ,1107 | |
| Mercury (II) Oxychloride HgCla · 4 HgO | 1108 | |
| Mercury (II) Bromide HgBr ₃ | 1109 | |
| Potassium Trilodomercurate (II) KHgI3 - HaO | 71110 | |
| Copper (I) Tetraiodomercurate (II) CugHgI | UTIO | |
| Mercury (II) Sulfide HgS | 1111 | |
| Mercury (II) Selenide HgSe | 1113 | |
| Mercury (II) Amide Chloride HgNH ₂ Cl | 1114 | |
| Diamminemercury (II) Dichloride HgCl ₂ · 2NH ₃ · · · · · | ·1114 | |
| Mercury (II) Iminobromide Hg ₂ (NH)Br ₂ | 1115 | |

| | 1116 |
|--|------|
| Millon's Base NHg OH . XH O | 1117 |
| Bromide of Millon's Base NHg_Br | 1117 |
| Mercury (D Thionitrosylate [Hga(NS)2]x. | 1118 |
| | 1118 |
| man an a | 1120 |
| The second of the second of the state of the second of the | 1120 |
| Second and Apple Ref Mar States and the States and the second stat | 1121 |
| Mananany (IB Cranide Eg(Colla | 1122 |
| Detection Tetracyanomercurate (III Dans(VII)4 **** | 1122 |
| Merouwy (D. Thiocyanate Hga(SCN) a | 1123 |
| Herenry (II) Thiocyanate Hg(SCN) a · · · · · · · · · · · · · · · · · · | 1123 |
| Potassium Tetrathiocyanomercurate (II) K ₂ Hg(SCN) ₄ . | |
| SECTION 21. SCANDIUM, YTTRIUM, RARE EARTHS | 1125 |
| Pure Scandium Compounds | 1125 |
| Treatment of Monazite Sand | 1127 |
| Treatment of Gadolinite | 1129 |
| Pure La. Pr and Nd Compounds from Cerium Earths by | |
| Ion Exchange | 1131 |
| Pure Cerium Compounds | 1132 |
| Pure Samarium Compounds | 1135 |
| Pure Europium Compounds | 1136 |
| Pure Ytterbium Compounds | 1138 |
| Metallic Rare Earths | 1141 |
| Rare Earth Trichlorides LnCl ₃ (anhydrous) | 1146 |
| Rare Earth Tribromides LnBr ₃ (anhydrous) | 1148 |
| Rare Earth Triiodides Lnl ₃ (anhydrous) | 1149 |
| Rare Earth Dihalides LnX ₂ (anhydrous) | 1150 |
| Cerium (III) Oxide Ce ₃ O ₃ | 1151 |
| Praseodymium (IV) Oxide PrO2 | 1151 |
| Rare Earth Hydroxides Ln(OH)3 (crystalline) | 1152 |
| Lanthanum Sulfide La ₂ S ₃ | 1153 |
| Lanthanum Selenides La ₂ Se ₃ , La ₂ Se ₄ | 1154 |
| La. Ce, Pr and Nd Monochalcogenides LnS, LnSe, LnTe | 1165 |
| Europium (II) Chalcogenides EuS, EuSe, EuTe | - |
| Rare Earth Sulfates Ln ₂ (SO ₄) ₃ • nH ₂ O | 1155 |
| Rare Earth Nitrides LnN. | 1156 |
| Rare Sarth Nitrates 1 - (AC) 1 (a-b-dama) | 1157 |
| Rare Earth Nitrates Ln(NO ₃) ₃ (anhydrous) | 1158 |
| Rare Earth Cyclopentadienides Ln(C ₅ H ₅) ₂ | 1159 |
| SECTION 22. TITANIUM, ZIRCONIUM, HAFNIUM, THORIUM | 1161 |
| Titanium Ti | 1161 |
| Zireomuni, naimum Zr. Hf | 1172 |
| | 1174 |
| reparation of circonium and Hamium | 1179 |
| | 1184 |
| - months (II) UNIOTICE. Brownide and Indide Tich The | |
| Tilg | 1185 |
| | |

| CONTENTS | | |
|--|--------|-----|
| Titanium (III) Chloride, Bromide and Iodide TiCla. | | |
| TiCl ₃ · 6 H ₂ O; TiBr ₃ , TiBr ₃ · 6 H ₂ O; Til ₃ | 1187 | |
| Titanium (IV) Chloride TiCl. | 1195 | |
| Ammonium Hexachlorotitanate (NH4) [TiCla] | 1199 | |
| Titanium (IV) Bromide TiBr4. Zirconium (IV), Hafnium (IV) and Thorium (IV) Chlorides and Bromides ZrCl4, HfCl4, ThCl4; ZrBr4, HfBr4, | 1201 | |
| ThBr | 1203 | |
| Thorium Chloride ThCl ₄ · 8 H ₂ O. | 1204 | |
| Titanium (IV), Zirconium (IV) and Thorium (IV) lodides Til ₄ (ZrI ₄ , ThI ₄). | 1205 | |
| Titanium (III) Oxychloride TiOCl | 1209 | |
| Titanium (IV) Oxychloride TiOCl | 1209 | |
| Zirconium Oxychloride ZrOCl ₂ · 8 H ₂ O | 1210 | |
| Hafnium Oxychloride | 1213 | |
| Lower Titanium Oxides TiO, Ti ₂ O ₃ | 1214 | |
| Titanium (IV) Oxide TiO ₂ | 1216 | |
| Titanium (IV) Oxide Hydrate TiO, - n H ₂ O | 1218 | |
| Peroxotitanic Acid H_TiO5 | 1219 | |
| Zirconium (IV) Oxide ZrO ₂ | 1220 | |
| Hafnium (IV) Oxide HfO ₃ | 1221 | |
| Thorium (IV) Oxide ThO ₂ | 1221 | |
| Titanium, Zirconium and Thorium Sulfides TiS ₃ , TiS ₈ , TiS _{<3} , | 1222 | |
| Zirconium Sulfides. | 1226 | |
| Thorium Sulfides | 1226 | |
| Titanium (III) Sulfate Ti ₂ (SO ₄) ₃ | 1226 | |
| Titanoxy Sulfate TIOSO4 | 1228 | |
| Zirconium Sulfates. | 1231 | |
| Purification of Zr Salts via the Tetrahydrate, | 1232 | I. |
| Titanium, Zirconium and Hainium Nitrides TiN, ZrN, HIN | 1233 | i |
| Thorium Nitride Th ₃ N ₄ | | |
| Titanium Tetranitrate Ti(NO3)4 | 1237 | |
| Thorium Nitrate Th(NO3)4 - B H2O | 1238 | 5 |
| Titanium Oxonitrate, Zirconium Oxonitrate TiO(NO3) | | |
| ZrO(NO ₃) _a | 1241 | |
| Titanium Phosphide, Zirconium Phosphides, Thorium | | |
| Phosphide TiP, ZrP ₂ , ZrP, Th ₃ P ₄ | 1241 | - |
| Zirconium and Hafnium Phosphates. | 1244 | |
| Titanium, Zirconium and Hafnium Carbides TiC, ZrC, HfC | 1245 | i i |
| Thorium Carbides ThC, ThC, | . 1248 | |
| Titanium, Zirconium and Thorium Silicides TiSi , ZrSi , | | 1 |
| ThSi ₂ | 1249 | e . |
| SECTION 23. VANADIUM, NIOBIUM, TANTALUM | 1252 | |
| Vanadium V | 1262 | |
| | | £ |

| | 1255 |
|--|--------------|
| Vanadium (II) Chloride VCl | 1256 |
| | 1259 |
| | 1260 |
| | 1260 |
| The second descent of the second | 1261 |
| The second difference of the second sec | 1262 |
| The stars (III) Indide Views as a start start of the start | 1262 |
| strandburn Owyobloride VOCL | 1262 |
| Vanadium Ovydichloride VOCLa | |
| Manadouro Owytrichloride VOCIs | 1264 1265 |
| Venedium Dioxychloride VO ₂ Cl. | |
| Lower Vanadium Oxides | 1266 |
| Vanadium (III) Bydroxide V(OH)3 | 1268 |
| Vanadium (V) Oxide V ₂ O ₅ | 1270 |
| Ammonium Metavanadate NH, VO3 | 1272 |
| Alkali Vanadates | 1273 |
| Vanadium Sulfides | 1274 |
| Vanadium Selenides | 1276 |
| Vanadium (II) Sulfate VSO4 · 6 H2O | 1277 |
| Hydrogen Disulfatovanadate (III) HV(SO ₄) ₂ · 4 H ₂ O | 1282 |
| Ammonium and Potassium Disulfatovanadate (III) | |
| $\mathrm{NH}_{4}\mathrm{V}(\mathrm{SO}_{4})_{2}, \mathrm{KV}(\mathrm{SO}_{4})_{2}, \ldots, \ldots, \ldots, \ldots, \ldots, \ldots$ | 1283 |
| Vanadium (IV) Oxysulfate (Vanadyl Sulfate) VOSO4 | 1285 |
| Vanadium Nitrides | 1286 |
| Vanadium Phosphides VP ₂ , VP, VP _{<1} | 1287 |
| Vanadium Carbides VC, V ₂ C | 1288 |
| Dibenzenevanadium (0) V(C _e H ₆) ₂ | 1289 |
| Potassium Hexathiocyanatovanadate (III) K ₃ V(SCN) ₆ | 1291 |
| Niobium Metal, Tantalum Metal | 1292 |
| Vanadium, Niobium and Tantalum Hydrides | 1295 |
| Niobium (II) Chloride NbCl ₂ | 1296 |
| Niobium (III) Chloride NbCl | 1297 |
| Niopium (IV) Chloride NbCl | 1299 |
| Tantaium (IV) Chloride TaCl | 1301 |
| mootum (v) and Tantaium (v) Chiorides NoCle. TaCle. | 1302 |
| Nicolum Oxytrichloride NhOCl | 1307 |
| Nicolum (III) Bromide NbBra | 1309 |
| IAHAIUH (IV) Bromide TaBr. | 1310 |
| Noorum (V) and Tantalum (V) Bromides NbBr- | |
| | 1311 |
| $\lambda = 0$ | 1313 |
| The state of the s | |
| | 1314 |
| | 1315 |
| | 1316 |
| | 1317 |
| Niobium (IV) Oxide NbOg. | 1318 |
| | |

| Niodium (V) and Tantalum (V) Oxides Nb_2O_6 , Ta_3O_6 . Alkali Niobates and Tantalates | 13 18 1323 |
|--|----------------------|
| Peroxyniobic and Peroxytantalic Acids $HNbO_4 \cdot n H_2O_4$ HTaO ₄ · n H ₂ O | 1324 |
| Potassium Peroxyniobate, Potassium Peroxytantalate | 1000 |
| K ₃ NbO ₉ , K ₃ TaO ₈ | 1325 |
| Nioblum and Tantalum Sulfides | 1327 |
| Niobium and Tantalum Nitrides. Niobium and Tantalum Phosphides NbP2, TaP2, NbP, | 1328 |
| ToD | 1330 |
| TaP Niobium and Tantalum Carbides | |
| Mobility and Thicality Carolides | 1391 |
| SECTION 24. CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM. | 1334 |
| Chromium Cr | 1334 |
| Chromium (II) Chloride CrCl ₂ | 1336 |
| Chromium (III) Chloride CrCi3 | 1338 |
| Chromium (II) Bromide CrBr2 | 1340 |
| Chromium (III) Bromide CrBr ₃ | 1341 |
| Chromium (II) Iodíde CrI ₂ | 1341 |
| Chromium (III) Iodide CrI ₃ , | 1344 |
| Chromium (III) Hydroxide Cr(OH) ₃ · n H ₃ O | 1345 |
| Chromium Sulfides CrS, Cr ₂ S ₃ | 1346 |
| Chromium Nitride CrN | 1347 |
| Hexasquochromium (III) Chloride [Cr(OH ₂) ₆]Cl ₃ | 1348 |
| Chloropentaaquochromium (III) Chloride | |
| [CrCl(OH ₃) ₈]Cl ₂ · H ₂ O. | 1350 |
| Hexaamminechromium (III) Chloride and Nitrate | |
| $[Cr(NH_3)_3]Cl_3, [Cr(NH_3)_4](NO_3)_3, \dots, \dots$ | 1351 |
| Chloropentaamminechromium (III) Chloride | 1004 |
| | 1352 |
| [CrCl(NH ₃)6]Cl ₂ Triethylenediaminechromium (III) Sulfate, Chloride and | 100% |
| Thiocyanate $[Cr en_3]_2(SO_4)_3$, $[Cr en_3]Cl_3 \cdot 3.5 H_2O_3$ | |
| Thiocyanate [CF en_{3}] ₂ (aO_{4}) ₃ , [CF en_{3}] O_{4}] ₃ , [CF en_{3}] O_{4}] ₃ , [CF en_{3}] O_{4} | 1354 |
| $[Cr en_3](SCN)_3 \cdot H_2O$ | TOOA |
| cis-Dichlorodiethylenediaminechromium (III) Chloride | 1356 |
| $[CrCl_2 en_2]Cl \cdot H_2O_1$ | 1000 |
| trans-Dithiocyanatodi(ethylenediamine)chromium (III) | 1357 |
| Thiocyanate [Cr(SCN) 2 en 3]SCN. | · · · · · · · · · |
| trans-Dichlorodi (ethylenediamine)chromium (III) | 1357 |
| Chloride [CrCl_gen_]Cl | |
| Dichloroaquotriamminechromium (III) Chloride | 1950 |
| [CrCl ₂ (OH ₂)(NH ₃) ₃]Cl | 1996 |
| Hexaureachromium (in) omoride (or (oor an 4) biors | |
| 3 H ₂ O | 1359 |
| Rhodochromium Chloride [(NH3)5Cr(OH)Cr(NH3)5]Cls . | 1359 |
| Erythrochromium Chloride | 1000 |
| [(NH ₃) ₅ Cr(OH)Cr(NH ₃) ₄ (OH ₂)]Cl ₅ | 1396 |
| | 20) |

xiti

| the Deschloreta | |
|---|------|
| Tris (2,2 - dipyridyl)chromium (II) Perchlorate | 1361 |
| [Cr(dipy)_s](ClO ₄) ₂ . | |
| Tris (2,2 - dipyridyl)chromium (II) Perchlorate [Cr(dipy) ₃](ClO ₄) ₂ . Tris (2,2 - dipyridyl)chromium (I) Perchlorate | 1362 |
| [Cr(dipy) ₃]ClO ₄ [Cr(dipy) ₃]ClO ₄ Tris{2,2 -dipyridyl)chromium (0) [Cr(dipy) ₃] | 1363 |
| Tris(2,2-dipyridyl)chromium (0) [Cr(C _g H _g NC) _g] | 1363 |
| Hexaphenylisonitrilochronium (0) for (0 gater) at the Chromium Orthophosphate CrPO4. | 1364 |
| Chromium (II) Sulfate CrSO ₄ · 5 H ₂ O | 1365 |
| Chromium (II) Sulfate CrSoft Strate Chromium (II) Salt Solutions. | 1366 |
| Chromium (II) Sait Solutions. Chromium (II) Acetate $Cr_2(CH_3COO)_4 \cdot 2H_2O_4$. | 1368 |
| Chromium (II) Addite $CrC_2O_4 \cdot 2H_2O_4$ | 1370 |
| Hexaaquochromium (III) Acetate [Cr(OH ₂) _e](CH ₃ COO) ₃ | 1371 |
| Dihydroxohexaacetatotrichromium (III) Acetate and | |
| Chloride [Cr ₃ (OH) ₂ (CH ₃ COO) ₆](CH ₃ COO) • n H ₂ O, | |
| $[Cr_3(OH)_2(CH_3COO)_8]CI \cdot 8 H_2O$ | 1371 |
| Potassium Trioxalatochromate (III) K ₃ [Cr(C ₂ O ₄) ₃] - | |
| 3 H ₂ O | 1372 |
| Potassium Hexacyanochromate (III) $K_3[Cr(CN)_6]$ | 1373 |
| Potassium Hexathlocyanatochromate (II) | |
| K-ICT/SCN)-I + 4 H-Q | 1374 |
| $K_3[Cr(SCN)_6] \cdot 4 H_2O$ Trilithium Hexaphenylchromate (III) $Li_3Cr(C_8H_5)_6$. | |
| 2.5 (C ₂ H ₅) ₂ O | 1375 |
| Ammonium Tetrathiocyanatodiamminechromate (III) | |
| $NH_4[Cr(SCN)_4(NH_3)_7] \cdot H_2O$ | 1376 |
| Tetrathiocyanatodiamminechromic (III) Acid | |
| H(Cr(SCN) ₄ (NH ₃) ₃] | 1377 |
| Ammonium Tetrathiocyanatodianilinochromate (III) | |
| $NH_4[Cr(SCN)_4(C_9H_5NH_2)_2] \cdot 1^{1/2} H_3O$ | 1378 |
| Potassium Tetrathiocyanatodipyridinochromate (III) | |
| $K[Cr(SCN)_{4}py_{3}] \cdot 2 H_{3}O$ | 1379 |
| Trichlorotriaquochromium [CrCl ₂ (OH ₂) ₂] | 1380 |
| Trichlorotriethanolochromium [CrCl_(C_H_OH)] | 1380 |
| Trichlorotriamminechromium [CrCl_/NH_). | 1381 |
| Trichlorotripyridizechromium [CrClanya] | 1381 |
| Caromium (III) Glycinate (HeNCHeCOO), Cr | 1382 |
| Chromium (III) Xanthate [C_H_OCS__C_] | 1383 |
| Varomium (ill) Acetviscetonate (C | 1383 |
| Unromyl Chloride CrO-Cl- | 1384 |
| | 1385 |
| | 1386 |
| WARVANTA REREINUPRIE CPCIENCII).I_ | 1387 |
| | 1388 |
| | 1388 |
| | 1389 |
| | 1389 |
| | 1390 |
| Potassium Chlorochromate K[CrO ₃ Cl] | 1390 |
| | 2000 |

| Potassium Tetraperoxochromate (V) K3CrOa | 1391 |
|--|--------------|
| Ammonium Pentaperoxodichromate | |
| $(NH_4)_2 Cr_4 O_{12} \cdot 2 H_2 O$ | 1392 |
| Diperoxotrianminechromium (IV) (NH ₃) ₃ CrO ₄ | 1392 |
| Barium Orthochromate (IV) Ba CrO. | 1399 |
| Barium Chromate (V) Ba ₃ (CrO ₄) ₂ . | 1394 |
| Sodium Thiochromite NaCrS ₂ . Dibenzenechromium (0) ($C_{eH_{g}}$) ₂ Cr | 1394 1395 |
| Bis(diphenyl)chromium (0) (C ₁₂ H ₁₀) ₂ Cr | 1396 |
| Dibenzenechromium (I) Iodide [(C _g H _g) ₂ Cr]I. | 1397 |
| Bis(diphenyl)chromium (I) Iodide [Cr(C ₁₃ H ₁₀) ₂]I | 1397 |
| (Diphenyl)(benzene)chromium (I) Iodide | 1001 |
| [(C ₁ ₉ H ₁₀)Cr(C ₆ H ₈)]I | 1398 |
| Molybdenum Mo | 1401 |
| Dibenzenemolybdenum (0) (C eH a) Mo. | 1402 |
| Molybdenum (II) Chloride Mo ₃ Cl ₆ | 1403 |
| Molybdenum (III) Chloride MoCla | 1404 |
| Molybdenum (V) Chloride MoCl 5 | 1405 |
| Molybdenum (ill) Bromide MoBrs | 1407 |
| Tribromotripyridinemolybdenum [MoBr ₃ py ₃] | 1408 |
| Potassium Hexachloromolybdate (III) KaMoCle | 1408 |
| Molybdenum (IV) Oxide MoO2 | 1409 |
| y-Molybdenum Oxide Mo ₄ O ₁₁ , | 1410 |
| Lower Molybdenum Hydroxides | 1411 |
| Molybdenum (VI) Oxide MoO ₃ | 1412 |
| Molybdic Acid H ₂ MoO ₄ · H ₂ O | 1412 |
| Ammonium Oxopentachloromolybdate (V) | |
| (NH ₄) ₂ [MoOCl ₅] | 1413 |
| Potassium Hydrogen Diperoxomonomolybdate | |
| КНМоО ₅ • 2 Н ₂ О | 1414 |
| Tetraamminezinc Tetraperoxomolybdate (VI) | |
| $[Zn(NH_3)_4]MoO_B$ | 1414 |
| Molybdenum (IV) Sulfide MoS , | 1415 |
| Ammonium Tetrathiomolybdate (NH4)2MoS4 | 1416 |
| Potassium Octacyanomolybdate (IV) | |
| $K_4[Mo(CN)_{\theta}] \cdot 2 H_2O$, | 1416 |
| Tungsten W | 1417 |
| Tungsten (V) Chloride WCl5 | 1419 |
| Tungsten (VI) Chloride WCI 6 | 1420 |
| Tungsten (IV) Oxide WOa. | 1421 |
| γ-Tungsten Oxide W ₁₆ O ₄ s | 1422 |
| Tungsten Blue Ho.s WO3. | 1423 |
| Tungsten (VI) Oxide WO ₃ | 1423 |
| Yellow Tungstic Acid H ₂ WO4 | 1425 |
| Tungsten Oxytetrachloride WOCl4 | |
| Tungsten (IV) Sulfide WS: Tungsten Hexaphenoxide W(OC gHs): | 1426 |
| Tungsten nexaphenoxide n (00 645) 8 | |
| | Â |

-

| ATL | |
|--|--|
| Potassium Enneachloroditungstate (III) K ₃ W ₂ Cl ₂ | 1427 |
| | 1429 |
| | 1429 |
| Potassium Octacyanotungstate (V) $K_{3}[W(CN)_{3}] \cdot H_{3}O$. | 1430 |
| Potassium Octacyanotangotato (1) Lai 144101 | 1431 |
| Uranium U | 1434 |
| Uranium Hydride Ufig. | 1435 |
| Uranium (III) Chloride UCl ₃ | 1436 |
| Uranium (IV) Chloride UCl4. | 1438 |
| Uranium (V) Chloride UCls | 1439 |
| Uranyl Chloride UOgCla. | 1440 |
| Uranium (IV) Bromide UBr. | 1442 |
| Uranium (IV) Oxide UO2 | 1442 |
| Uranium (VI) Oxide UO3 | |
| Alkali Uranates (VI) LigUO4, NagUO4, KgUO4 | 1445 |
| Alkali Uranates (V) LiUO3, NaUO3 | 1445 |
| Uranium Peroxide UO4 · 2 H 2O | 1446 |
| Uranium (IV) Sulfide US | 1446 |
| Uranium (IV) Sulfate U(SO4)2 · 8 H2O or 4 H2O | 1447 |
| Ammonium Uranyl Carbonate (NH ₄) ₄ [UO ₂ (CO ₃) ₃] | 1449 |
| Uranium (IV) Oxalate $U(C_3O_4)_2 \cdot 6 H_3O_{1}$ | 1449 |
| Potassium Tetraoxalatouranate (IV) | |
| $K_4[U(C_2O_4)_4] + 5 H_2O_4$ | 1450 |
| Uranium (V) Ethoxide U(OC _a H ₅) _B | 1451 |
| Uranium (VI) Ethoxide U(OC ₂ H ₅) ₈ , | 1452 |
| Uranyldibenzoyimethane UO ₂ (C ₁₅ H ₁₁ O ₂) ₂ , | 1453 |
| | |
| | |
| SECTION 25. MANGANESE | 1454 |
| Manganese Mn. | 1454 |
| Manganese (II) Oxide MnO | 1455 |
| Manganese (II) Hydroxide Mn(OH) 2 | 1456 |
| Manganese (III) Oxide γ -Mn ₂ O ₃ , γ -MnO(OH). | |
| Manganese (IV) Ovide Ma $_2O_3$, γ -MIIO(OR),, Manganese (IV) Ovide Ma $_2O_3$, γ -MIIO(OR),, | 1457 |
| Manganese (IV) Oxide MnOg. | 1458 |
| Manganese (VII) Oxide Mn _a O ₇ | 1459 |
| Sodium Manganate (V) Na ₃ MnO ₄ · 0.25 NaOH · 12 H ₂ O . | 1460 |
| Potassium Manganate (VI) K ₃ MnO ₄ | 1461 |
| r_{M} r_{M | 1462 |
| | |
| | 1463 |
| | |
| Potassium Manganaga (111) Chlorida V. M. C. | 1463 |
| Potassium Manganese (III) Chloride KaMnCla. | 1463 1463 |
| Potassium Manganese (III) Chloride K _a MnCl ₅ Potassium Hexachioromanganate (IV) K _a MnCl ₆ Manganese (II) Sulfide MnS | 1463 1463 1464 |
| Potassium Manganese (III) Chloride K _a MnCl ₅ Potassium Hexachloromanganate (IV) K _a MnCl ₆ Manganese (II) Sulfide MnS. Manganese (III) Sulfata Mn ₋ (SO ₋). | 1463 1463 1464 1464 |
| Potassium Manganese (III) Chloride K _a MnCl ₅ Potassium Hexachloromanganate (IV) K _a MnCl ₆ Manganese (II) Sulfide MnS. Manganese (III) Sulfate Mn ₂ (SO ₄) ₃ . | 1463 1463 1464 1464 1465 |
| Potassium Manganese (III) Chloride K ₂ MnCl ₈ Potassium Hexachloromanganate (IV) K ₂ MnCl ₈ Manganese (II) Sulfide MnS. Manganese (III) Sulfate Mn ₂ (SO ₄) ₂ . Cestiam Manganese (III) Sulfate CsMn(SO ₄) ₂ . 12 H ₂ O. | 1463 1463 1464 1464 1465 1465 1467 1468 |
| Potassium Manganese (III) Chloride K ₃ MnCl ₈ Potassium Hexachloromanganate (IV) K ₃ MnCl ₈ Manganese (II) Sulfide MnS, Manganese (III) Sulfate Mn ₃ (SO ₄) ₃ . Cestum Manganese (III) Sulfate CsMn(SO ₄) ₃ · 12 H ₂ O. Manganese Nitride Mn ₄ N. | 1463 1463 1464 1464 1465 1465 |
| Potassium Manganese (III) Chloride K _a MnCl ₅ Potassium Hexachloromanganate (IV) K _a MnCl ₆ Manganese (II) Sulfide MnS. Manganese (III) Sulfate Mn ₂ (SO ₄) ₃ . | 1463 1463 1464 1464 1465 1465 1467 1468 |

| CONTENTS | *** |
|---|---|
| Potassium Trioxalatomanganate (III) | |
| $K_{3}[Mn(C_{2}O_{4})_{3}] \cdot 3 H_{2}O_{4}$ | 1470 |
| Potassium Dioxalatodibydroxomanganate (IV) | |
| $K_{2}[Mn(C_{2}O_{4})_{2}(OH)_{2}] \cdot 2 H_{2}O_{4}$ | 1471 |
| Potassium Hexacyanomanganate (I) KaMn(CN) | 1472 |
| Potassium Hexacyanomanganate (II) K Mn(CN) . 3 H O | 1473 |
| Potassium Hexacyanomanganate (III) KaMn(CN) | 1474 |
| | 1476 |
| | |
| Rhenium Metal. | 1476 |
| Rhenium (III) Chloride ReCl ₃ | 1476 |
| Rhenium (V) Chloride ReCls. | 1477 |
| Potassium Rhenium (IV) Chloride K ₃ ReCl ₆ | 1478 |
| Rhenium (VI) Oxychloride ReOCl4 | 1479 |
| Rhenium (VII) Oxychloride ReO ₃ Cl | 1480 |
| Rhenium (IV) Oxide ReO2 | 1480 |
| Rhenium (VI) Oxide ReO3 | 1481 |
| Rhenium (VII) Oxide Re ₂ O7 | 1482 |
| Rhenium Rhenate (IV) Na 2ReO3 | 1483 |
| Ammonium Perrhenate NH4ReO4 | 1484 |
| Barium Perrhenate Ba(ReO ₄) ₂ | 1485 |
| Barium Rhenate (VI) BaReO4 | 1485 |
| Rhenium (IV) Sulfide ReS ₂ | 1486 |
| Rhenium (VII) Sulfide Re ₃ S ₇ | 1487 |
| Barium Mesoperrhenate Ba ₃ (ReO ₆) ₂ | 1487 |
| Workup of Rhenium Residues | 1488 |
| SECTION 27. IRON | 1490 |
| Metallic Iron. | 1490 |
| Iron (II) Chloride FeCl ₂ , | 1491 |
| Iron (III) Chloride FeCl ₃ | 1492 |
| Iron (II) Bromide FeBr ₂ | 1493 |
| Iron (III) Bromide FeBr ₃ | 1494 |
| Iron (II) Iodide Fel ₂ | |
| Iron (II) Oxide FeO | 1497 |
| Iron (II) Hydroxide Fe(OH)2 | 1498 |
| Iron (II, III) Oxide Fe_3O_4 | 1499 |
| Iron (III) Hydroxide FeO(OH) | |
| Iron (III) Oxychloride FeOCl | |
| | 1502 |
| Iron (II) Sulfide FeS | 150%- |
| Iron Carbide Feat | 1509 |
| Lithium Ferrate (III) LiFeOg | 1504 |
| Potassium Ferrate (VI) K ₂ FeO ₄ | |
| Potassium Ferrate (VI) RaceO4 | 1507 |
| | 1. S. |
| Basic Iron (III) Sulfate Fe ₃ (SO ₄) ₃ (OH) ₅ - 2 H ₂ O or 3 Fe ₂ O ₃ - 4 SO ₃ - 9 H ₂ O | |
| SKegUs + 2 DUs + 2 MgO + + + + + + + + + + + + + + + + + + + | 1997 - 1998 - 1998 - 1998 - 1998 - 1998 - 1998 - 1998 - 1998 - 1998 - 1998 - 1998 - 1998 - 1998 - 1998 - 1998 - |
| | |

| Basic Iron (III) Acetate | 1508 |
|--|------|
| Basic Iron (III) Acetate $[Fe_3(CH_3COO)_8(OH)_9]CH_9COO + H_3O$ | 1509 |
| (Fe ₃ (CH ₃ COO) ₆ (OH) ₂)CH ₃ COO H ₃ Hexacyanoferric (II) Acid H ₄ Fe(CN) ₆ , Fe(CN) ₆ | 1509 |
| Hexacyanoferric (II) Acta $H_4Fe(CN)_8$. Aramonium Hexacyanoferrate (II) $(NH_4)_4Fe(CN)_6$. | 1510 |
| | 1910 |
| | 1511 |
| | 1011 |
| | |
| Ma (Fa(CN), NHa) + 3 D V | 1511 |
| Sodium Pentacyanoamminoferrate (III) | |
| Sodium Pentacyanoamminorerrate (III) Na <u>a</u> [Fe(CN) _E NH ₃] · H ₂ O | 1512 |
| Madia(Cri)Enral 1.5. 1.1.1 | |
| SECTION 28. COBALT, NICKEL | 1513 |
| Metallic Cobalt | 1513 |
| Metallic Cobait | 1515 |
| Cobalt (II) Chloride CoCla | 1516 |
| Hexaamminecobalt (II) Chloride [Co(NH ₃) ₆]Cl ₂ | 1517 |
| Cobalt (II) Bromide CoBr ₂ , CoBr ₂ · 6 H ₂ O | 1518 |
| Cobalt (II) Iodide α -CoI ₂ , β -CoI ₂ , CoI ₂ · 6 H ₂ O | 1518 |
| Cobalt (II) Oxide CoO | |
| Cobalt (II, III) Oxide Co ₃ O ₄ | 1520 |
| Cobalt (III) Hydroxide CoO(OH) | 1520 |
| Cohalt (II) Hydroxide Co(OH)2 | 1521 |
| Cobalt Sulfides CoS, CoS ₂ , Co ₃ S ₄ , Co ₃ S ₈ | 1523 |
| Cobalt (III) Sulfate Co ₂ (SO ₄) ₃ · 18 H ₂ O | 1524 |
| Cobalt Aluminate CoAl ₂ O ₄ | 1525 |
| Hexaammminecobalt (III) Nitrate [Co(HN3)6](NO3)3 | 1526 |
| Cobalt (III) Amide Co(NH ₂) ₃ | 1526 |
| Dicobalt Nitride CoaN | 1529 |
| Cobalt Nitride CoN | 1529 |
| Cobalt Phosphides CoP3, CoP, Co2P | 1530 |
| Dicobalt Carbide Co ₂ C | 1531 |
| Hexaamminecobalt (III) Chloride [Co(NH ₃) _a]Cl ₃ | 1531 |
| Chloropentaamminecobalt (III) Chloride [Co(NH ₃) ₅ Cl]Cl ₂ , | 1532 |
| Nitropentaamminecobait (III) Chloride | ADON |
| [Co(NH ₃) ₆ NO ₂]Cl ₂ | 1534 |
| Nitritopentaamminecobalt (III) Chloride | TOOT |
| {Co(NH ₃)6ONO]Cl ₃ | 1000 |
| Carbonatotetraamminecobalt (III) Sulfate | 1535 |
| Constructed and the construction of the construction of the constructed and the constr | |
| [Co(NH ₃) ₄ CO ₃] ₂ SO ₄ · 3 H ₂ O Dichlorotetraamminecobalt (III) Chloride | 1535 |
| (Co(NH) CL)() | |
| [Co(NH ₃) ₄ Cl ₂]Cl | 1536 |
| Triethylenediaminecobalt (III) Bromide [Co en3]Br3 | 1538 |
| Decastamine-µ-peroxocobalt (III) Cobalt (IV) Sulfate | |
| $[(NH_a)_{g}Coll(O_{g})ColV(NH_{a})_{g}](SO_{4})_{2} \cdot SO_{4}H \cdot 3H_{2}O.$ | 1540 |
| EVALUATE DESCRIPTION OF STATE (III) No $-100/MO_{10}$ (| 1541 |
| Potassium Hexacyanocobaltate (III) Ka[Co(CN)a] | 1541 |
| | |

Actent

Evili

| CONTENTS | 18 19 19 |
|---|------------------|
| Hexacyanocobaltic (III) Acid. | 1542 |
| Metallic Nickel | 1548 |
| Nickel (II) Chloride NiCla | 1544 |
| nexaamminenickei (II) Chioride (Ni(NH _a) _a)C) | 1545 |
| Nickel (II) Bromide NiBra | 1545 |
| NICKEI (II) IODIDE NIL | 1547 |
| Nickel (II) Oxide NiO | 1548 |
| NICKei (II) Hydroxide Ni(OH) | 1549 |
| $\beta \sim \text{Nickel}$ (III) Hydroxide NiO(OH) | 1549 |
| y-Nickel (III) Hydroxide NiO(OH) | 1550 |
| Nickel (II, III) Hydroxide Ni ₂ O ₂ (OH) | 1551 |
| Nickel (II) Sulfide NIS | 1551 |
| Nickel (IV) Sulfide NiS ₂ | 1554 |
| Nickel (II) Amide $N_i(NH_2)_{a}$ | 1554 |
| Trinickel Dinitride NiaNa | 1555 |
| Trinickel Nitride Ni ₃ N | 1555 |
| Nickel Carbide Ni ₃ C | 1556 |
| Nickel (II) Carbonate | 1556 |
| Nickel (II) Thiocyanate Ni(SCN)2. | 1558 |
| $Di - \mu$ -sulfido-tetrakis(dithiobenzoato)dinickel (IV) | |
| $(C_{e}H_{5} \cdot CSS)_{2}NiS_{2}Ni(SSC \cdot C_{e}H_{5})_{2}$ | 1558 |
| Potassium Tetracyanonickelate (II) | 1000 |
| $K_2[Ni(CN)_4] \cdot H_2O_1$ | 1559 |
| | |
| SECTION 29, THE PLATINUM METALS | 1560 |
| Pure Platinum Pt. | 1560 |
| Reclaimed Platinum | 1561 |
| Platinum Sponge | 1562 |
| Platinum Black | 1562 |
| Platinized Asbestos | 1563 |
| Handling of Platinum Equipment | 1564 |
| Platinum Electroplating | 1565 |
| Platinum Chlorides | 1567 |
| Hexachloropiatinic (IV) Acid H_PtCl 8 · 6 H_O | 1569 |
| Tetrachloroplatinic (II) Acid HaPtCl. | 1570 |
| Ammonium Hexachloroplatinate (IV) (NH ₄) ₃ PtCl ₅ | 1570 |
| Potassium Hexachioroplatinate (IV) K ₂ PtCl ₆ | 1571 |
| Sodium Hexachloroplatinate (IV) Na PtCl 8. | 1574 |
| Na ₂ PtCl ₈ · 6 H ₂ O | |
| Potassium Tetrachloroplatinate (II) KaPtCl4 | 1572 |
| Plotinum (II) Orde PtO. | 10/3 |
| Platinum (IV) Oxide PtO ₂ · xH ₂ O | 1574 |
| Hexabydroxyplatinates (IV) Na $_{2}$ Pt(OH) $_{6}$ · XH $_{2}$ O, | 1575 |
| $K_3Pt(OH)_6 \cdot x H_3O$ | |
| Platinum (II) Sulfide PtS | 1545 |
| Platinum (IV) Sulfide PtS 2 | 1990 B |
| | <u>د الأرشيد</u> |
| | 6230 |

| a sture (II) and Barium Tetra- | |
|--|-------------------|
| Potassium Tetracyanoplatinate (II) and Barium Tetra- | |
| cyanoplatinate (II) Est (CIIIA | 1576 |
| (HaO | |
| | 1577 |
| | 1578 |
| | 1578 |
| m | 1579 |
| - is be-itendiamminenistinum (II) [F((NO2/2))] | 1580 |
| | 1581 |
| Colloidal Palladium | 1581 |
| The Dealth and Dealth and the second se | 1582 |
| Dalladiand Ashestos | 1582 |
| D -Dation (B) Chloride PfCla | 1582 |
| PdCl ₂ Solution for the Detection of CO. | 1583 |
| Palladium (II) Oxide PdO | 1909 |
| Tetrachloropalladates (II) K ₂ PdCl ₄ , Na ₂ PdCl ₄ , | 1004 |
| (NH ₄) ₂ PdCl ₄ | 1584 |
| Hexachloropalladates (IV) K ₂ PdCl ₆ , (NH ₄) ₂ PdCl ₆ | 1584 |
| Diamminepalladium (II) Salts [PdCl ₂ (NH ₃) ₂]. | |
| $[PdBr_{a}(NH_{3})_{a}]$ | 1585 |
| Pure Rhodium Rh | 1585 |
| Rhodium (III) Chloride RhCl ₃ , | 1587 |
| Hexachlororhodates (III) | 1587 |
| Rhodium (III) Oxide Rh ₂ O ₃ , | 1588 |
| Rhodium Sulfate | 1589 |
| Chloropentaamminerhodium Salts [RhCl (NH ₃) ₅]Cl ₂ , | |
| [RhCl(NH ₃) ₅](NO ₃) ₂ | 1590 |
| Pure Iridium Ir | 15 9 0 |
| Iridium (IV) Oxide IrO ₃ , | 1590 |
| Hydrated Iridium (IV) Oxide IrO ₂ · 2 H ₂ O,, | 1591 |
| Hydrated Iridium (III) Oxide $Ir_2O_3 \cdot x H_2O_3$ | 1592 |
| Iridium (III) Chloride (rC) | 1592 |
| Hexachloroiridic (IV) Acid HairCla | 1593 |
| Potassium Hexachloroiridate (IV) KalrCla | 1593 |
| Ammonium Hexachioroiridate (IV) (NH .) sIrCl . | 1594 |
| Potassium Hexachioroiridate (III) KalrClassium Hexachioroiridate (III) KalrClassium | 1595 |
| Pure Ruthenium Ru | 1595 |
| Ruthenium (IV) Hydroxychloride Ru(OH)Cla | 1597 |
| Ruthenium (III) Chloride RuCla, RuCla + HaO | 1597 |
| Ammonium Hexacalororuthenate (IV) (NH,) - RuCl. | 1599 |
| Ruinenium (IV) Oxide Ruft- | 1599 |
| Nullenium (VIII) Oxide RuO | 1599 |
| - Verolum numenate and Polassinte Dopwithoneto | 2000 |
| | 1600 |
| | 1601 |
| | 1601 |
| Sodium Hexachloroosmate (IV) Na 2OsCl 6 · 2 H 2O. | 1602 |
| | 1002 |

2-

| Ammonium Hexachioroosmate (IV) (NH4) 20sCl 8 | 1402 |
|--|------|
| Osmum (17) Oxide OsO | 1602 |
| Osmlum (VIII) Oxide OsO | 1000 |
| Potassium Osmate (VI) K ₂ OsO ₄ · 2 H ₂ O | 1000 |
| Potassium Osmiamate K(OsO3N), | 1009 |
| a the bran oblitamate K(OSO3N) | 1605 |

Part III

Special Compounds

| SECTION). ADSORBENTS AND CATALYSTS | 1609 |
|---|------|
| Introduction | 1609 |
| Active Metals | 1613 |
| Pyrophoric Cobalt | 1615 |
| NI-Mg Mixed Oxalate Catalyst (1:1) | 1615 |
| Tungsten | 1622 |
| "Molecular" Silver | 1623 |
| Habey Nickel | 1625 |
| Nickel Formate-Paraffin Catalyst | 1631 |
| Active Copper | 1633 |
| Carbonyl Iron | 1636 |
| Explosive Antimony | 1638 |
| Silver (Active Agent for Reductors) | 1641 |
| Deposition of Metals from the Vapor Phase | 1643 |
| Hydrated Oxide Gels | 1646 |
| Hydrated Chromium Oxide Gel | 1648 |
| Silica Gel | 1648 |
| Aluminum Hydroxide Gel | 1652 |
| "Glimmering" Hydrated Iron (III) Oxide | 1654 |
| Active Metal Oxides | 1656 |
| Aluminum Oxide,, | 1660 |
| α-Iron (III) Oxide | 1661 |
| Magnesium Oxide | 1663 |
| Zinc Oxide | 1664 |
| Lead (IV) Oxide | 1668 |
| Colloidal Suspensions of Oxides in Gases (Smokes) | 1669 |
| Copper-Chromium Oxide | 1672 |
| Hopkalite (Hopcalite) | 1674 |
| | |
| SECTION 2. HYDROXO SALTS | 1677 |
| General | 1677 |
| Handling of Concentrated Alkali Hydroxides | 1679 |
| Sodium Hydroxozincaies | 1681 |
| Sodium Tetrahydroxomagnesate Na 2[Mg(OH)4] | 1683 |
| Sodium Tetrahydroxocuprate (II) Na [Cu(OH)4] | 1684 |
| Barium Hexahydroxocuprate (II) Bas(Cu(OH)s] | 1685 |
| Sodium Tetrahydroxoferrate (II) Na [Fe(OH)4] | 1686 |
| | 1 |

| | 1686 |
|--|------|
| Streatium Hexabydroxonickelate (II) Srs[Ni(OH)s] | 1687 |
| | 1688 |
| A. M | 1689 |
| Or above Independent ales (111) | |
| Based and Badeovoferrates (111) | 1690 |
| AND AN AN AN ANALASY AND AN | 1692 |
| $\alpha_{1} \rightarrow \alpha_{2} \rightarrow \alpha_{2$ | 1694 |
| $\sigma_{i} \rightarrow \phi_{i}$ there had a variation of (iV) Na $i V(V) B_{i} \rightarrow \cdots$ | 1694 |
| Barium Oxohydroxostannate (II) Ba[Sn ₂ O(OH) ₄] | 1696 |
| | 1698 |
| SECTION 3. ISO- AND HETEROPOLY ACIDS AND THEIR SALTS | 1698 |
| Introduction. | 1700 |
| General Methods | 1702 |
| Isopoly Compounds | 1702 |
| Isopolyvanadates | 1702 |
| Isopolyniobates | |
| Isopolytantalates | 1707 |
| Isopolyarsenates | 1709 |
| Isopolymolybdates | 1710 |
| Isopolytungstates | 1712 |
| Isopolysulfates | 1714 |
| Heterpoly Compounds | 1716 |
| 12-Tungstic Acid-1-Borates | 1716 |
| 12-Tungstic Acid-1-Silicates | 1717 |
| 10-Tungstic Acid-1-Silicates | 1719 |
| 12-Tungstic Acid-1-Phosphates | 1720 |
| 22-Tungstic Acid-2-Phosphates | 1722 |
| 21-Tungstic Acid-2-Phosphates | 1722 |
| 18-Tungstic Acid-2-Phosphates | 1723 |
| 12-Tungstic Acid-1-Arsenates | 1724 |
| 16-Tungstic Acid-2-Arsenates | 1725 |
| 6-Tungstic Acid-1-Tellurates | 1726 |
| Metatungstates, Dodecatungstates | 1727 |
| 12-MOIVDdic Acid-1-Silicates | 1729 |
| 44 mulyburg Actor 1+ Phosphotog | 1730 |
| | 1732 |
| | 1734 |
| | 1734 |
| | 1736 |
| | 1737 |
| | 1738 |
| | 1190 |
| Phosphates. | 1700 |
| SECTION A COMPANY OF A COMPANY | 1739 |
| SECTION 4, CARBONYL AND NITROSYL COMPOUNDS | 1741 |
| | 1741 |
| Chromiam, Melybdeaum, Tungsten Carbonyls Cr(CO)e, | |
| Mo(CO) . W(CO) . | 1741 |

| CONTERIS | |
|--|----------|
| Iron Pentacarbonyl Fe(CO)6. | 1743 |
| DUIDT NODACATOONY FAR(CO) | 7744 |
| IIIIIOU LOGOCACETDONVIIFe(CO),], OF FA.(CO), _ | 1746 |
| $\nabla O D A T D D T P D T T B [C O (C C) A] A [C O (C O) A] .$ | 1746 |
| Nickel Carbonyl Ni(CO)4 | 1747 |
| Dipyridine Chromium Tetracarbonyl, Tripyridine Chro- | 1/4/ |
| mium Tricarbonyl Cr(CO) 4 py 2, Cr(CO) 3 py 2 | 1749 |
| o-Phenanthroline Nickel Dicarbonyl Ni(CO) 2C 12H N2. | 1750 |
| Iron Tetracarbonyl Halides Fe(CO) ₄ X ₂ | 1751 |
| Iron Tetracarbonyl Dihydride Fe(CO)4H ₂ | 1751 |
| Cobalt Tetracarbonyl Hydride Co(CO) H | 1753 |
| fron Carbonyl Mercury Fe(CO) Hg | 1755 |
| Cobalt Carbonyl Mercury [Co(CO)] Hg | 1755 |
| Ethylenediamine Iron Carbonyl [Fe en ₃] [Fe ₂ (CO) _e] | 1750 |
| Pyridine Iron Carbonyi [Fe py e] [Fe 4(CO)19] | 1756 |
| Detection Mitnery Trieschard Detection 100 1001 | 1758 |
| Potassium Nitrosyl Tricarbonyl Ferrate (Fe(CO) ₃ NO]K | 1759 |
| Iron Dinitrosyl Dicarbonyl Fe(NO) ₂ (CO) ₂ | 1760 |
| Cobalt Nitrosyl Tricarbonyl Co(NO)(CO)s | 1761 |
| Dinitrosyl Cobalt Halides (NO) 2CoCl, (NO) 2CoBr, | |
| (NO) ² Col | 1761 |
| Sodium Dinitrosyl Thioferrate Na[(NO) 3FeS] • 4 H 20 | 1763 |
| Ammonium Heptanitrosyl Trithiotetraferrate | |
| $NH_4[(NO), Fe_4S_3] \cdot H_2O$ | 1764 |
| Ethyl Dinitrosyl Thioferrate [(NO) = FeSC = H =] = | 1765 |
| Potassium Dinitrosyl Thiosulfatoferrate | |
| $K[(NO)_{2}FeS_{2}O_{3}] \cdot H_{2}O$ | 1766 |
| Potassium Nitrosyl Cyanomolybdate | |
| $K_4[(NO)Mo(CN)_B] \cdot H_2O$ | 1766 |
| Potassium Nitrosyl Cyanomanganate K ₃ [(NO)Mn(CN)s] | |
| Sodium Nitrosyl Cyanoferrate Na 2(NO)Fe(CN) 5] · 2 H 20 | 1768 |
| Sodium Carbonyl Cyanoferrate Na ₃ [(CO)Fe(CN)s] | 1769 |
| | |
| SECTION 5. ALLOYS AND INTERMETALLIC COMPOUNDS | |
| General Remarks | 1771 |
| Purity of the Starting Materials | |
| Form of the Starting Materials | 1773 |
| Preparation of Starting Mixtures | 1773 |
| Crucible and Ampoule Methods | 1774 |
| Heating and Cooling | 1782 |
| Allow Synthesis under Pressure | 1784 |
| Melting Without a Container | 1786 |
| Comminution in the Absence of Air | TLDD. C. |
| Distillation Method | 1789 |
| Regime Methods | 1791 |
| Special Processes | |
| Silioidag | |
| Borides | A (13 4 |
| | |

725111

| Amalganas | 1801 |
|--|------|
| Amalgams Poinssium-Sodium Alloy (liquid). Low-Melting Alloys | 1808 |
| FORMULA INDEX | 1811 |
| SUBJECT INDEX | 1828 |
| MOEX OF PROCEDURES, MATERIALS AND DEVICES | |
| ERNATA FOR VOLUME 1 | 1859 |

SECTION 19

Copper, Silver, Gold

O. GLEMSER AND H. SAUER

Copper (Pure Metal)

 $CuO + H_g = Cu + H_gO$ 79.5 22.41. 63.5 18.0

A solution of electrolytic copper in 30% nitric acid is evaporated to dryness. The resultant nitrate is converted to the oxide by heating for 15 hours in an electrical furnace at 850°C. The oxide is then reduced at low temperature (250-300°C). The product is finely divided metallic copper.

Alternate method: Reduction of copper oxalate with hydrogen [K. Fischbeck and O. Dorner, Z. anorg. allg. Chem. <u>182</u>, 228 (1928)]. For preparative directions, see subsection on CuS, p. 1018.

PROPERTIES:

Atomic weight 63.54; m.p. 1084°C, b.p. 2595°C; d²₄° 8.93. Crystal structure: type A1.

REFERENCE:

H. Haraldsen. Z. anorg. allg. Chem. 240, 339 (1939).

Colloidal Copper

An ammoniacal solution of $CuSO_4$ (1:1000) is treated with a dilute solution of hydrazine hydrate (1:2000) in the presence of acacia (gum arabic). The hydrosol obtained upon heating is immediately poured into a parchment paper bag which has been presoaked in water for some time; it is dialyzed against water for four days.

PROPERTIES:

The hydrosol is copper-red under incident light and blue under transmitted light. If protected from air, it is stable for a limited time. REFERENCE:

A. Guthier and G. Hofmeier. Z. anorg. allg. Chem. 44, 227 (1905).

Copper Hydride

CuH

L

| 4 Cul | + | LiAlH | = Lil | + Alls | + | 4 CuH |
|-------|---|-------|-------|--------|---|-------|
| 761 5 | | 38.0 | 133.9 | 407.7 | | 258.3 |

A pyridine solution of CuI is made to react at room temperature with a solution of LIAIH, in ether-pyridine (the latter being prepared by mixing a concentrated ether solution of LiAlH4 with absolute pyridine), yielding a blood-red pyridine solution of CuH. The mixture is allowed to stand at room temperature for 4-6 hours to complete the reaction. The Alls co-product is sparingly soluble in pyridine and precipitates to a large extent. It is then readily separated from the clear supernatant liquor by centrifugation. The residual AII, and the soluble Lil are separated from the Cull by addition of an at least equal volume of other to the pyridine solution. The resultant red-brown precipitate of CuH is separated by centrifugation, washed with ether, dissolved in pyridine, and reprecipitated with ether. This purification procedure is repeated twice. The ether is then evaporated in a high vacuum.

The reaction may also be carried out by treating a solution of Cul in pyridine-tetrahydrofuran-ether with an other solution of lithium aluminum hydride. In this case, CuH precipitates as soon as the two solutions are mixed, while both All, and Lil remain in solution. The CuH precipitate is then purified as above (by dissolving in pyridine and reprecipitating with other).

IL PREPARATION OF COPPER HYDRIDE BY REDUCTION OF SOLUTIONS OF COPPER SALTS WITH HYPOPROSPHOROUS ACID

A 65°C mixture of 25 g. of CuSO₄.5 H₂O in 100 ml, of water and 20 ml. of 2N H₂SO₄ is added to a solution of 21 g. of H₂PO1 in 300 ml. of water. After standing for 24 hours, the resultant precipitate is filtered and washed successively with water, alcohol and ether. Although the precipitation is not quantitative under these conditions, the product is relatively pure.

Small amounts of iron salt or halogen ion impurity interfere with the precipitation.

PROPERTIES:

Formula weight 64.55. Light red-brown color. Anhydrous when chitained by method I. Undecomposed (metastable) up to about C; decomposes into the elements above this temperature, and

rapidly at 100°C. Quite stable in 0°C water; just as in the thermal decomposition, dissociates into metallic copper and H_2 from 45°C on, rapidly at 65°C. Dark red pyridine solution. Crystal structure: type B4 (expanded Cu lattice). Heat of formation: 5.1 kcal./mole.

REFERENCES:

- I. E. Wiberg and W. Henle. Z. Naturforsch. 7b, 250 (1952).
- II. O. Neunhoeffer and F. Nerdel. J. prakt. Chem. 144, 63 (1935); G. F. Hüttig and F. Brodkorb. Z. anorg. allg. Chem. 153, 235, 242 (1926).

Copper (I) Chloride

CaCl

 $2 \text{ CuSO}_4 + 2 \text{ NaCl} + \text{SO}_2 + 2 \text{ H}_2\text{O} = 2 \text{ CuCl} + \text{ Na}_2\text{SO}_4 + 2 \text{ H}_2\text{SO}_4$ (5 H₂O)

499.4 116.9 22.41. 36.0 198.0 142.1 196.2

Gaseous SO_2 is bubbled through an acquous solution of 50 g, of $CuSO_4 \cdot 5 H_2O$ and 24 g, of NaCl at 60-70°C until CuCl ceases to precipitate. The product is suction-filtered and washed with sulfurous acid, then with glacial acetic aciduntii the latter becomes colorless. The moist product is placed in a shallow dish or on a large watch glass and heated on a water bath until the odor of acetic acid is no longer detectable. It is stored in a tightly closed container.

Alternate methods: a) Acetyl chloride is added in drops to a boiling solution of cupric acetate in glacial acetic acid containing at least 50% of acetic anhydride by volume. When the color changes to yellow, the addition is stopped and the mixture is refluxed for 15 minutes. The resultant white solid is suction-filtered, washed with acetic anhydride, and dried at 140-150°C (D. Hardt, private communication).

b) Cupric chloride is heated to 150-200°C in glycerol. The CuCl obtained is filtered, washed with alcohol, and dried in vacuum (B, K, Vaidya, Nature (London) <u>123</u>, 414 (1928)).

c) Reduction of CuCl₂·2 H₂O in a Na₂SO₃ solution (R. N. Keller and H. D. Wycoff in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 1).

d) A solution of crystalline $CuCl_2$ in hydrochloric acid is reduced over copper with exclusion of air (use a Bunsen valve; for a description of the valve, see Hackh's Chemical Dictionary, 3rd ed., the Blakiston Co., Phila.-Toronto, 1944). The product is poured into water [M. Denigés, Compt. Rend. Hebd. Séances Acad. Sci. <u>108</u>, 567 (1889)].

e) A mixture consisting of 1 part of CuSO₄-5 H_aO, 2 parts of NaCl and 1 part of Cu turnings is heated (use a Bunsen valve) with 10 parts of H_sO until the color disappears completely. The mixture is poured into water, and CuCl crystallizes out (M. Denigés, Comptes Rendus Hebd, Séances Acad. Sci. <u>108</u>, 567 (1889)].

Comptes mencus neou, seances Adad. Joi. 100, 001 (1000).
 f) Sublimation of commercially pure CuCl over copper in a stream of HCl and argon at 900°C [J. B. Wagner and C. Wagner, J. Chem. Physics <u>26</u>, 1597 (1957)].

SYNONYM:

Cuprous chloride.

PROPERTIES:

Formula weight 99.00. White crystalline material, M.p. 432° C, b.p. 1490°C; d_{4}^{25} 4.14, d_{4}^{422} 3.677. Sparingly soluble in water (25°C): 1.53 g./100 g. (partial decomposition in water: 2CuCl = Cu + CuCl₂). Forms a green basic chloride in air. Soluble in hot conc. hydrochloric acid, conc. alkali chloride solutions, conc. aqueous ammonia. Crystal structure: type B3. Conversion into high-temperature modification of type B4 at 410°C. Heat of formation (25°C): - 32.2 kcal./mole.

REFERENCE:

M. Rosenfeld. Ber. dtsch. chem. Ges. 12, 954 (1879).

Copper [] Bromide

CuBr

 $2 \text{ CuSO}_4 - 2 \text{ KBr} + \text{SO}_2 + 2 \text{ H}_2 \text{O} = 2 \text{ CuBr} + 2 \text{ H}_2 \text{SO}_4 + \text{K}_2 \text{SO}_4$ (5 H₂O) 499.4 238.0 22.47. 38.0 286.9 196.2 174.3

Stoichiometric quantities of pure $CuSO_4 \cdot 5 H_2O$ and KBr are dissolved in boiled distilled water and the solution is filtered through hard filter paper. It is then heated to a moderate temperature and a fast stream of pure SO_3 is passed through, with stirring, for about two hours. The passage of gas is continued until the mixture has cooled completely; the CuBr precipitates in the form of fine yellowish-white crystals. The solid is filtered while carefully excluding all light, resuspended 5-7 times in boiled distilled water into which some SO_3 is bubbled, and filtered again. The product is finally washed with SO_2 -containing alcohol, followed by SO_3 -containing ether. The salt is dried for 3-4 days over H_2SO_4 and KOH in a hydrogen atmosphere, and then in vacuum.

Alternate methods: a) Acetyl bromide is added in drops to a boiling solution of cupric acetate in glacial acetic acid, containing at least 50% of acetic anhydride by volume, until the solution becomes light green and a pure white precipitate appears (D. Hardt, private communication). b) Another starting material consists of the mixture used in the preparation of ethyl bromide from alcohol, Br_2 and red phosphorus. The mixture is filtered and an excess of $CuSO_4 \cdot 5 H_3O$ is added to the clear solution. The dark green solution is brought to a boil; crystallization soon follows [D. B. Briggs, J. Chem. Soc. (London) 127, 496 (1925)].

c) Synthesis from the elements [J. B. Wagner and C. Wagner, J. Chem. Physics <u>26</u>, 1597 (1957)].

SYNONYM:

Cuprous bromide.

PROPERTIES:

Formula weight 143.46. Colorless crystals. M.p. 498°C, b.p. 1345°C; d_4^{25} 4.72. Insoluble in H₂O; soluble in hydrogen halide solutions, nitric acid and aqueous ammonia. Heat of formation (25°C): - 24.9 kcal./mole.

CuBr exists in three modifications: y-CuBr (type B3) below 391°C, β -CuBr (type B4) between 391 and 470°C, α -CuBr (cubic) above 470°C.

REFERENCE:

J. N. Frers. Ber. dtsch. chem. Ges. 61, 377 (1928).

Copper () lodide

CuI

 $2 C_{u}SO_{4} + 2 KI + SO_{2} + 2 H_{2}O = 2 CuI + 2 H_{2}SO_{4} + K_{2}SO_{4}$ (5 H₂O)

499.4 332.0 22.4 I. 36.0 380.9 196.2 174.3

The compound is obtained as a pure white solid by precipitation of a solution of $CuSO_4 \cdot 5 H_2O$ with KI in the presence of a slight excess of sulfurous acid. The product is washed with water containing a small amount of SO_3 , then (with exclusion of air) with pure alcohol, and finally with anhydrous ether. It is then filtered with suction and freed in vacuum of the last traces of ether. Residual strongly adhering traces of water are best removed in a high vacuum, first at 110°C and finally somewhat above 400°C. A better product is obtained if a small quantity of iodine is added to the material after it has been dried at 110°C: This iodine is entirely removed at 400°C.

Alternate methods: a) Analogous to the preparation of CuBr from the reaction mixture used in the synthesis of ethyl indide. Crystalline CuI is obtained [D. B. Briggs, J. Chem. Soc. (London: 127, 496 (1925)]. b) Synthesis from the elements [J. B. Wagner and C. Wagner,
 J. Chem. Physics <u>26</u>, 1597 (1957)].

STNONYN:

Cuprous iodide.

PROPERTIES:

Formula weight 190.45. Pure white crystalline powder. M.p. 605°C, b.p. 1936°C; d_4^{35} 5.63. Quite stable in light and air, melts without decomposition in high vacuum and in a stream of oxygenfree N₂. The solidified melt is clear and colorless (impure materials yield dark melts). Insoluble in H₂O; soluble in acids and squeous ammonia; soluble in alkali fodides. Heat of formation (25°C): - 16.2 kcal./mole.

Cul exists in three modifications: γ -Cul (type B3) below 402°C, 8-Cul between 402 and 440°C, and α -Cul (cubic) above 440°C.

REFERENCE:

C. Tubandt, E. Rindtorff and W. Jost. Z. anorg. allg. Chem. <u>165</u>, 195 (1927).

Copper (li) Chloride

CuCl₂

I. DEHYDRATION OF THE HYDRATE IN A STREAM OF HCI

Pure $CuCl_2 \cdot 2$ H₂O is recrystallized from dilute hydrochloric acid to remove traces of basic salt, and is then heated to constant weight at 140-150°C in a stream of dry HCI. The CuCl₂ is stored in a desiccator over H₂SO₄ and NaOH until all remaining traces of athering HCl have been absorbed by the NaOH.

L. $Cu(CH_{3}COO)_{2} + 2 CH_{3}COC) = CuCl_{2} + 2 (CH_{3}CO)_{3}O$ **181.6** 157.0 134.5 204.2

A) CUPRIC ACETATE SOLUTION

Glacial acetic acid containing a small quantity of acetic anhydride is placed in the solvent flask of a Soxhlet extractor. The extraction section of the apparatus is filled with copper turnings, aix is introduced, and the solvent is brought to a boil. The solution becomes saturated with copper acetate after 1-2 hours.



B) ANHYDROUS CUPRIC CHLORIDE

The solution prepared in the Soxhlet via (A) is allowed to cool to 35° C, decanted from the solid which crystallizes out, and precipitated at $40-50^{\circ}$ C with the stolchiometric quantity of acetyl chloride. Calculation of the stolchiometric quantity may be based on the solubility of cupric acetate in glacial acetic acid: 20 g./liter at 35° C. The precipitate is washed with either hot glacial acetic acid or cold acetic anhydride, both of which may be removed by a final washing with anhydrous ether. The product is dried at 120° C.

Alternate methods: a) High-vacuum dehydration of CuCi₂ · 2 H₂O at 100°C [W. Biltz, Z. anorg. allg. Chem. <u>148</u>, 207 (1925)].

b) Refluxing of $CuCl_2 \cdot 2 H_2O$ in SOCl₂. Removal of the excess SOCl₂ by distillation and evaporation of residual solvent in vacuum [H. Hecht, Z. anorg. allg. Chem. <u>254</u>, 37 (1947)].

SYNONYM:

Cupric chloride.

PROPERTIES:

Formula weight 134.45. Yellow, deliquescent mass. M.p. 630°C, b.p. 655°C; d_4^{35} 3.387. Soluble in H₂O and alcohol. Solubility in ethyl alcohol (0°C) 31.9 g.; in methyl alcohol (15.5°C) 67.8 g./100 ml. Soluble in acetone, yielding a dark green solution, which becomes yellow at high dilution. Heat of formation (25°C): - 49.2 kcal./mole.

REFERENCES:

- I. H. C. Jones and W. R. Veazey. Z. phys. Chem. 61, 654 (1908).
- II, D. Hardt. Z. anorg. allg. Chem. (in press); private communication.

Copper (II) Bromide

CuBr₂

ĩ.

 $CuO + 2 HBr = CuBr_1 + H_2O$ 79.5 161.8 223.4 18.9

The stoichiometric quantity of CuO [or Cu(OH)₃] is dissolved in aqueous hydrobromic acid and the solution is evaporated in vacuum over H_2SO_4 .

 $II. \begin{array}{c} Cu(CH_{3}COO)_{2} \cdot H_{2}O + 3 CH_{3}COBt \\ 199.6 & 368.9 \\ = CuBr_{2} + 2 (CH_{3}CO)_{2}O + CH_{3}COOH + HBt \\ 228.4 & 204.2 & 60.1 & 60.9 \end{array}$

Finely divided $Cu(CH_3COO)_2 \cdot H_3O$ (4.0 g.) is placed in a Pyrex tube (18 × 200 mm.) which is closed off with a rubber stopper

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provided with a dropping funnel and a filtering tube. Agitation (magnetic stirrer) is started; 15 ml. of benzene is added, followed slowly by a 10% excess of CH_3COBr . The mixture is stirred for some supernatant is siphoned off through the filtering tube. The reaction is brought to completion by treating the residue with additional benzene and CH_3COBr . The supernatant liquid is removed by filtration and the CuBr₃ is washed 3-4 times with anhydrous benzene. The product is dried at 150°C for two hours under nitrogen.

SYNONYM:

Cupric bromide.

PROPERTIES:

Black crystals, very deliquescent. M.p. 498°C, b.p. 900°C; $d_1^{2\circ}$ 4.710. Highly soluble in H₂O, yielding a green solution; solubility (15°C) 122 g./100 g. H₂O; soluble in acetone, alcohol and pyridine. Dry heating causes decomposition into CuBr and Br₂. Evaporation of an aqueous solution also causes decomposition (at the b.p.). Depending on the temperature, CuBr₂ crystallizes from aqueous solutions with two or four molecules of water of crystallization, yielding highly deliquescent, brownish-green crystals. Crystal structure: monoclinic. Heat of formation (25°C): - 33.2 kcal./mole.

REFERENCES:

- I. L. Vanino, Handbuch der präp. Chemie [Handbook of Preparative Chemistry], Part I, 2nd Ed., Stuttgart, 1921.
- II. G. W. Watt, P. S. Gentile and E. P. Helvenston. J. Amer. Chem. Soc. <u>77</u>, 2752 (1955).

Copper Oxychloride

CuCl₁ · Cu(OH)₂

| 2 CuCl ₂ | + CaCO ₃ $+$ | HtO | $= CuCl_2 \cdot Cu(OH)_2$ | Ŧ | CaCl ₂ | ÷ | CO₁ |
|---------------------|-------------------------|------|---------------------------|---|-------------------|---|--------|
| 268.9 | 100.1 | 18.0 | 232.0 | | 111.0 | | 22.41. |

Stoichiometric quantities of cupric chloride, calcium carbonate (marble) and water are allowed to react in a bomb tube for 48 hours at 200°C. The product is filtered, freed from unreacted $CuCl_2$ by washing with boiling alcohol, and dried in a desiccator.

Alternate method: A conc. solution of $CuCl_2$ is boiled for several hours with CuO. The liquid is decanted; the product is washed with accord and dried [E. Hayek, Z. anorg. alig. Chem. 210, 241 (1933)].

PROPERTIES:

Dark yellowish-green powder, decomposed by boiling water, Crystal structure: monoclinic.

REFERENCE:

G. Rousseau. Compt. Rend. Hebd. Séances Acad. Sci. <u>119</u>, 1262 (1890).

Copper (I) Oxide

Cu₂O

I.

П.

| 4 C | u(CH 3CO O |),₂ + | N ₂ H ₄ + | 2 H _t O |
|-----|-----------------------|-------|---------------------------------|--------------------|
| | (1 H ₂ O) | | (1 H ₁ O) | |
| | 798.6 | | 50.1 | 36.0 |
| = | 2 Cu ₂ O - | + N₁ | + 8 CH | соон |
| | 286.2 | 28.0 | 4 | 80.4 |
| | 3 | | 4 | e |

A 20% hydrazine hydrate solution (3-5 ml.) is added to 50 ml. of concentrated copper acetate solution. The solution turns green, nitrogen evolves, and a yellow to orange precipitate of Cu_2O separates on standing. The product is washed with H_2O , followed by alcohol and ether. Care must be exercised to avoid an excess of hydrazine in the reduction, since such an excess causes reduction to metallic copper.

> $4 Cu + O_2 = 2 Cu_2O$ 254.2 22.4 l. 286.2

Small copper plates (e.g., 5 mm. \times 20 mm. \times 10 μ) are hung from platinum wires placed in a vertical tubular furnace; the latter is then heated to 1000°C in an atmosphere of technical grade N₂ (1% O₂). While bringing to the desired temperature and cooling down, use only pure N₂. The reaction is completed after about 24 hours. The product composition corresponds approximately to Cu₂O [cf. C. Wagner and H. Hammen, Z. physik, Chem. <u>B40</u>, 197 (1938)].

Alternate methods: a) Equivalent amounts of CuO and Cu are heated in vacuum for five hours at 1000°C. The product is homogenized and reheated [F. W. Wrigge and K. Meisel, Z. anorg. allg. Chem. 203, 312 (1932)].

b) Reduction of Fehling's solution with hydrazine suffate... [M. C. Neuburger, Z. Physik 67, 846 (1931)].

c) Electrolysis of a weakly alkaline solution of NaCl at 80°C, using copper electrodes [B. B. Dey, A. Jorgarao, H. V. K. Udura, S. Sampath and R. Viswanathan, J. Sci. Ind. Research (India) 12B, 424 (1955).
219 (1954); Hira Lal, J. Sci. Ind. Research (India) 12B, 424 (1955).

SYNONYN:

Cuprous oxide.

PROPERTIES:

Formula weight 143.08. Yellow powder. Red Cu₂O is identical with the yellow variety, the difference in color being caused by particle size. M.p. 1232°C; d²⁵ 6.04. Insoluble in H₂O; soluble in aqueous ammonia, conc. aqueous hydrogen halide solutions, markedly soluble in alkali hydroxides. Soluble in dilute oxyacids, with formation of Cu and Cu++. Crystal structure: type C3. Heat of formation (from 2 Cu + 1/2 O2): -40.0 kcal./mole (25°C).

REFERENCES:

- I. M. Straumanis and A. Cirulis. Z. anorg. allg. Chem. 224, 110 (1935).
- II. H. Dünwald and C. Wagner. Z. phys. Chem. <u>B22</u>, 215 (1933); E. Engelhard, Ann. Phys. (V) 17, 501 (1933).

Copper (il) Oxide

CuO

The starting material, cupric nitrate, may be obtained by dissolving electrolytic copper in nitric acid and evaporating the solution to dryness on a steam bath:

> $2 Cu(NO_3)_2 = 2 CuO + 4 NO_2 + O_2$ (3 H₂O) 483.2 159.1 184.0 32.0

The cupric nitrate is dried in a drying oven, in which the temperature is raised very slowly from 90 to 120°C. After the material has been completely converted to the green, loose basic salt (24 hr.), it is boiled with water and filtered. The dried salt is first heated slowly to 400°C, resulting in removal of most of the nitric acid; it is then pulverized, slowly heated further to 850°C, and maintained at this temperature for one hour. It is again ground to a fine powder, reheated for several hours to about 700°C, and allowed to cool in a desiccator.

Alternate methods: a) Precipitation of $Cu(OH)_{g}$ from a $CuSO_{4}$ solution with ammonia, followed by calcination to CuO. The product is free of sulfate. Calcination temperature 600-700°C [A. A.

Kazantsev, Khim. Zh., ser. B (Zh. Prikl, Khim.) 77, 1108 (1938)]. b) Oxidation of very pure thin copper foll at 1000°C in a stream of pare O2 [H. H. von Baumbach, H. Dinwald and C. Wagner, Z. phys. Chem. B22, 226 (1933); K. Hauffe and P. Kofstand, Z. Elektrochem. 59, 399 (1955)],

c) Precipitation from $CuCi_2 \cdot 4 H_2O$ with sodium hydroxids in the presence of CH_3OH [R. Fricke and J. Kubach, Z. Elektrochem. 53, 76 (1949)].

SYNONYM:

Cupric oxide.

PROPERTIES:

Formula weight 79.54. Black powder. M.p. 1336°C; $d_4^{1+}6.315$. Soluble in acids and ammonia. After calcination at high temperatures, soluble only in boiling conc. acids. Crystal structure: type B26. Heat of formation (25°C): -37.1 kcal./mole.

REFERENCE:

R. Ruer and J. Kuschmann. Z. anorg, allg. Chem. 154, 69 (1926).

Copper (II) Hydroxide

Cu(OH)_t

CuSO₄ + 2 NaOH = Cu(OH)₂ + Na₂SO₄ (5 H₁O) 249.7 80.0 97.6 142.1

I. A solution of $CuSO_4 \cdot 6 H_3O$ is treated at 70°C with 10% aqueous ammonia until a deep blue color appears. The solution is then allowed to react with the stoichiometric quantity of NaOH, yielding a precipitate which settles well. This is filtered, washed repeatedly with warm water, and dried in vacuum over conc. H_3SO_4 .

H. Aqueous ammonia is added in drops to a boiling solution of $CuSO_4 \cdot 5 H_2O$ until the initially green precipitate acquires a blue color. The crystalline basic sulfate thus obtained is filtered and carefully washed with water. It is then digested with a moderately concentrated NaOH solution, filtered, washed, and dried in vacuum over CaO or H_2SO_4 .

SYNONYM:

Cupric hydroxide.

PROPERTIES:

Light blue, crystalline powder. Insoluble in H_BO ; soluble in acids and aqueous ammonia; fairly soluble in concentrated NaOH. The crystalline form is stable at 100°C. Heating of the freshly

precipitated hydroxide results in conversion to black, watercontaining supric oxide. d_4^{30} 3.368. Heat of formation (18°C); -106.7 kcal./mole.

REFERENCES:

- I. A. N. Agte and N. S. Golynko. Trudy Leningr. Khim.-Tekh. Inst. 8, 140 (1940).
- I. Vanino and E. Engert. Chemiker-Ztg. 48, 144 (1927);
 B. Röttger. J. prakt. Chem. <u>73</u>, 491 (1858); R. Fricke and J. Kubach. Z. Elektrochem. <u>53</u>, 76 (1949).

Potassium Cuprate (III)

KCuO₂

A mixture of any available finely divided potassium oxide with CuO is heated to 400-500°C in carefully dried oxygen at 760 mm. Hg.

A) POTASSIUM OXIDE, KO_x

The sealed (20 cm. long) glass tube d containing distilled potassium is placed in the constricted side tube b of the apparatus depicted in Fig. 276; the system is evacuated and flame-dried, then filled with dry nitrogen; tube a is fixed so that it slopes somewhat toward c. Tube d is raised above b and its lower end broken in a stream of nitrogen; it is then replaced in b by means of a wire attached to hook c. The system is again evacuated; the potassium inside b is melted and allowed to flow into a, care being taken to avoid plugging of the gas inlet.

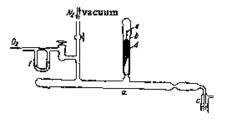


Fig. 276. Preparation of finely divided potassium oxide.

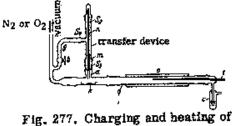
Oxidation of the potassium is achieved by admixing increasing amounts of oxygen to the nitrogen. The quantity of O_2 is adjusted by means of flowmeter *j*. When the reaction is complete, the resultant loose powder is homogenized in a vacuum ball mill (Fig. 55, p. 76) in a stream of dry N_2 , and stored in sealed glass amponies.

ANALYSIS:

Potassium is determined as KClO₄; the product may also be hydrolyzed and titrated as KOH.

B) REACTION OF KOx WITH CuO

The potassium oxide prepared in (A) is ground with the stoichiometric amount of CuO (K: Cu = 1:1) in the vacuum ball mill mentioned above. The grinding is carried out with careful exclusion of moisture, and is continued until the powder clings to the walls. This usually takes 5-20 minutes. The inner ground joint s_2 of the ball mill is then connected to the outer joint s_2 of the transfer device shown in Fig. 277 in such a manner that the Tshaped transfer piece is horizontal. It contains a movable aluminum pin n which fits fairly loosely into opening so. To start with, s3 is closed off with a ground cap. The mixture of oxides is transferred from the ball mill to the transfer device by shaking and knocking at the walls. The transfer device is disconnected from the mill in a stream of dry N₂ and joint s₂ is closed with a ground stopper; cap s3 is then removed and s3 is connected to joint ., on the side tube a of the main apparatus of Fig. 277. A silicon carbide boat k is located exactly below sa. Stopper sa is removed, dry N₂ is introduced through s4, and a small portion of the material is pushed into the boat by raising and lowering the aluminum pin n. Careful shifting of the boat followed by repeated movement of the pin allows the boat to be filled completely.



the KOx-CuO mixture.

While the stream of dry N_3 continues to flow, the boat is shifted to reactor tube q, placed in furnace o (Fig. 277), which consists of an electrically heated quartz tube surrounded by a transparent protective tube. The mixture is heated to 450°C in very pure Q_2 the formation of KCuO₂ is complete after 24 hours.

PROPERTIES:

Formula weight 134.64. Crystalline powder, steel blue to deep blue. Decomposes vigorously in water, yielding a brown black

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precipitate. Decomposes in dilute acids, evolving O_B and forming cupric salts. Evolves chlorine and oxygen in conc. hydrochloric acid. Decomposes with loss of weight on heating above 500°C in a stream of oxygen. Nonmagnetic; shows a characteristic x-ray diffraction pattern.

REFERENCE:

K. Wahl and W. Klemm, Z. anorg. allg. Chem. 270, 69 (1952).

Schweizer's Reagent

L. Copper turnings are covered with 20% ammonia containing some NH₄Cl, and air is bubbled through the suspension. An azureblue solution of $[Cu(NH_3)_4]$ (OH)₂ is formed. Evaporation of the solution in a stream of dry NH₃ yields long, azure-blue needles of $[Cu(NH_3)_4]$ (OH)₂.

II. Freshly precipitated $Cu(OH)_3$ is dissolved in 20% ammonia solution.

PROPERTIES:

Formula weight 165.68. Schweizer's reagent dissolves cellulose.

REFERENCE:

M. E. Schweizer. J. prakt. Chem. 72, 109, 344 (1857).

Copper (i) Sulfide

Ca₂S

 $2 Cu + S = Cu_2 S$ 127.1 32.1 159.1

I. A mixture of stoichiometric quantities of Cu and S is placed in a quartz tube, which is scaled in high vacuum. The tube is heated until the mixture melts.

II. An evacuated, sealed glass tube contains very pure Cu at one cad, while the other is charged with the stoichiometric quantity of 8 purified by the method of von Wartenberg (p. 342). The reaction is complete after heating 1-2 days at 400° C.

Atternate methods: a) Cupric sulfide is heated in vacuum to the melting point of cuprous sulfide. The reaction is preferably carried out in a graphite crucible inside an evacuated tube [E. Posnjak, E. T. Allen and H. E. Merwin, Z. anorg. allg. Chem. 94, 95 (1916)].

b) Cupric sulfide obtained by precipitation from a $CuSO_4$ solution with H₂S is reduced in a stream of H₂/H₂S. The optimum conditions are: a temperature of 700°C, a gas composition of 4.6% H₂ and 95.4% H₂S, and a reaction time of one hour. The product is crystalline and quite pure [N. P. Diyev and E. M. Yakimets, Izv. Ural. Fil. Akad. Nauk SSSR 1955, No. 3, 5; abstract in Chem. Abstr. 13.638al.

SYNONYM:

Cuprous sulfide.

PROPERTIES:

Blue to blue-black, M.p. 1127°C; d²° 5.6. Solubility (18°C): 4.95×10^{-5} g./100 g. H_gO. Very sparingly soluble in hydrochloric acid. Heat of formation (25°C): -19.6 kcal./mole.

Exists in two modification: 8-Cu₂S (hexagonal) below 91°C, α -Cu₂S (type C 1) above 91°C. The latter exists only with a copper deficiency, the composition being approximately CuileS.

REFERENCES:

- I. P. Rahlfs. Z. phys. Chem. (B) 31, 157 (1936); P. Ramdohr. Z. prakt. Geol. <u>51</u>, 1 (1943). II. C. Wagner. Private communication,

Copper [II] Sulfide

CuS

$$Cu + S = CuS$$

63.5 82.1 95.6

The sulfide precipitated when cupric salt solutions are treated with H₈S is not uniform. A better product is obtained from the reaction of a solution of sulfur in CS , with pure copper powder obtained from copper oxalate, Copper from CuO is unsuitable; it strongly absorbs H₂O vapor and thus still contains some oxygen.

A) COPPER OXALATE

A solution of $CuSO_4 \cdot 5 H_2O$ in water is reacted with an equal volume of conc. H_2SO_4 . The solution is brought to a boil, and a slight excess of boiling aqueous oxalic acid is introduced in a thin stream. The crystalline, easily filtered oxalate is repeatedly

washed with pure water, filtered through a filter crucible, and further washed until no acid can be detected.

B) COPPER POWDER

The copper oxalate is heated at 130° C to remove as much water of crystallization as possible. It is then placed in an electric furnace and heated to 320° C in a stream of purified H₃. The decomposition starts suddenly and is accompanied by a rise in temperature. Heating is continued at $220-260^{\circ}$ C, and the product is then allowed to cool (both operations are conducted under a stream of H₃). The copper powder is stored under hydrogen.

C) COPPER SULFIDE

The copper powder obtained above is finely ground and covered with CS_2 in a beaker. Somewhat more than the theoretical amount of S is dissolved in a large volume of CS_2 and added to the contents of the beaker (the sulfur required may be obtained in sufficiently pure form by dissolving pure S in CS_2 , filtering the solution through a glass filter crucible, and precipitating the filtrate with low-boiling petroleum ether). The resultant Cu_2S is transferred with the adhering CS_2 to a bomb and covered with twice the amount of S required for the formation of CuS. The bomb is filled as completely as possible with CS_2 and sealed. Then it is rotated along its long axis for four hours while surrounded with steam. The bomb is opened and contents filtered through a glass filter crucible and washed with CS_2 ; the residual, adhering CS_2 is removed in vacuum. The product is dried for 1-2 hours at 90-100°C in a vacuum of 0.1-1 mm. Hg.

STNONYM:

Cupric sulfide.

PROPERTIES:

Black. M.p. (dec.) 200°C; d_4^{20} 4.6. Insoluble in H₂O, alcohol and dilute acids. Solubility (18°C): 33.6 × 10⁻⁶ g./100 g. H₂O. Somewhat soluble in solutions of (NH₄)₂S and alkali polysulfides. Soluble without residue in KCN solution. Crystal structure: type B 18. Heat of formation (25°C): -12.1 kcal./mole.

ELTERENCE:

K. Fischbeck and O. Dorner. Z. anorg. allg. Chem. <u>182</u>, 228 (1928).

Copper (i) Selenide

Cu_sSe

 $2 Cu + Se = Cu_2Se$ 127.1 79.0 206.0

Selenium vapor carried in a stream of nitrogen is passed over Cu placed in a porcelain boat. The Se is also in a porcelain boat located ahead of the Cu in the quartz reaction tube. A thermai gradient is obtained by means of two electric heaters which maintain the temperature of the Cu at about 400°C and that of the Se at about 300°C. A well-crystallized product is obtained.

Alternate methods: a) Heating a stolchiometric mixture of Cu and Se in an evacuated, sealed quartz tube [P. Rahlfs, Z. phys. Chem. (B) <u>31</u>, 1957 (1936)].

b) Preparation of Cu₂Se and CuSe from Cu and Se in a Cu₂SO₄ solution [C. Goria, Gazz, Chim, Ital. <u>70</u>, 461 (1940)].

c) Passage of H₂Se through solutions of Cu saits. Formation of CuSe and Cu₂Se [L. Moser and K. Atynski, Mh. Chemie <u>45</u>, 235 (1925)].

d) Reduction of the basic selenite CuO • CuSeO₃ [W. Geilmann and F. R. Wrigge, Z. anorg. allg. Chem. <u>210</u>, 373 (1933)].

SYNONYM:

Cuprous selenide,

PROPERTIES:

Black. d_4^{21} 6.84. Exists in two modifications: tetragonal β -Cu₂Se (below 110°C), cubic α -Cu₂Se (above 110°C) (essentially a defect lattice deficient in copper). Heat of formation (25°C): -14.2 kcal./mole.

REFERENCES:

P. Rahlfs. Z. phys. Chem. (B) <u>31</u>, 157 (1936); W. Borchert. Z. Kristallogr. <u>106</u>, 5 (1945); G. Gattow and A. Sohneider. Z. anorg. alig. Chem. <u>286</u>, 296 (1956).

Copper (I) Telluride

Cu₃Te

2 Cu + Te = Cu₂Te 127.1 127.8 254.7

Obtained by fusing electrolytic Cu with pure Te in a crusible under a protective layer of NaCl and KCl. STRONYN:

Cuprous telluride.

PROPERTIES:

Gray-blue, brittle; homogeneous; contains 33 and 35 atom %Te. M.p. about 900°C. d²⁶ 7.338. Crystal structure: bexagonal (special type), defect lattice at Cu <₂ Te.

REFERENCE:

H. Nowotny. Z. Metallforsch. (Metallkunde) 1, 40 (1946).

Copper (1) Sulfate

Cu₂SO₄

 $2 C_{0} + 2 H_{2}SO_{4} = C_{0}SO_{4} + 2 H_{2}O + SO_{2}$ 127.1 196.2 223.1 36.0

Copper turnings are placed in conc. H_2SO_4 at a temperature of 200°C. The resultant green solution is added dropwise, through an asbestos filter, to an alcohol-ether mixture (1:1) or to methanol, causing Cu₂SO₄ to precipitate in the form of almost white crystals. The product is decanted, washed with alcohol, and dried in vacuum. It cannot be prepared by treating CuCl or CuI with H_2SO_4 .

Alternate method: Double decomposition of Cu₂O with neutral dimethyl sulfate under anhydrous conditions [A. Recoura, Comptes Rendus Hebd. Séances Acad. Sci. <u>148</u>, 1105 (1909)].

SYNONYM:

Cuprous sulfate.

PROPERTIES:

Nearly white crystals or grayish powder. Decomposes in water to $CuSO_4$ and Cu. Stable in dry air; decomposes slowly in moist air. Easily decomposed by heating; oxidizes at 200°C to CuO and $CaSO_4$, licat of formation (25°C): -197.2 kcal./mole.

REFERENCE:

J. G. F. Druce and G. Fowles. Chem. News 137, 385 (1928).

Tetraamminecopper (II) Sulfate

[Cu{NH₄}₄]SO₄ · H₂O

$CuSO_4 \cdot 5 H_2O + 4 NH_3 = [Cu(NH_3)_4]SO_4 \cdot H_2O + 4 H_2O$ 249.7 68.1 245.8 72.1

A solution of 50 g, of finely divided CuSO + 5 H₂O in 75 ml, of conc. ammonia and 50 ml, of water is filtered and precipitated by slow addition of 75 ml. of alcohol. After standing for several hours in the cold, the crystals are filtered on a Büchner funnel, washed with a mixture of alcohol and conc, ammonia (1:1) and then with alcohol and ether, and dried by suction.

Large crystals may be obtained by covering a layer of alcohol with a layer of an ammonia solution of CuSO, (G. Bornemann, Anorgan. Praparate [Inorganic Preparations], Leipzig, 1926, p. 156).

SYNONYM:

Cuprammonium sulfate.

PROPERTIES:

Deep blue crystals. d2° 1.81. Solubility (21,5°C): 18.5 g./100 g. H₂O. Decomposes in air. Loses H₂O and 2 NH₃ on heating to 120°C; the remaining ammonia is evolved at 160°C.

REFERENCES:

H, and W. Biltz. Übungsbeispiele aus der anorg. Chemie [Exercises in Inorg. Chem.], Leipzig, 1920; F. Mazzi, Acta Cryst. 8, 137 (1955); M. Simerská. Czechosl. J. Phys. 4, 3 (1954).

Copper (|| Nitride

Cu₂N

This compound is prepared by treating CuF₃ with NH₃.

A) STARTING MATERIALS

1. According to L. Balbiano [Gazz. Chim. Ral. 14. 78 (1884)] CuF . 2 H .O is prepared by dissolving CuO in 40% hydrofluoric acid, precipitating the fluoride with alcohol, and drying in a 1. D. C. 10 vacuum. ÷

2. NH₄F is dried in vacuum over NaOH.

3. NH3 and N2 are carefully dried.

B DENYDRATION OF CuF2 - 2H2O

About 1.5 g. of a mixture of 5 parts of $CuF_2 \cdot 2H_2O$ and 1 part of NH₄F, in a corundum boat placed in a quartz tube set in an electric resistance furnace, is slowly heated for two hours to 280°C in a stream of N₂. (The NH₄F serves to depress hydrolysis during the dehydration.)

C) PREPARATION OF Cu3N

The anhydrous CuF_{2n} at 280°C (see above), is immediately reacted for three hours at the same temperature with a fast stream of NH_3 . Heating above 300°C gives products deficient in nitrogen.

STNONYM:

Cuprous nitride.

PROPERTIES:

Formula weight 204.63. Dark green powder, stable in air at room temperature; oxidizes at 400°C in a stream of O_2 with pronounced incandescence. Decomposes spontaneously in vacuum at about 450°C. Soluble in dilute mineral acids and conc. hydrochloric acid with formation of the corresponding ammonium sait and partial formation of Cu metal. Decomposes violently with conc. H_2SO_4 and HNO_3 . d_4^{26} 5.84. Crystal structure: type DO_8 . Heat of formation (25°C): +17.8 kcal./mole.

REFERENCES:

R. Juza and H. Hahn. Z. anorg. allg. Chem. <u>239</u>, 282 (1938); <u>241</u>, 172 (1939); R. Juza. Ibid. <u>248</u>, 118 (1941).

Copper (ii) Azide

Cu(N₃)₁

 $\begin{array}{rll} Cu(NO_{5})_{2} \ + \ 2 \ NaN_{5} \ = \ Cu(N_{5})_{2} \ + \ 2 \ NaNO_{5} \\ (3 \ H, O) \\ 241.6 \\ 130.0 \\ 147.6 \\ 170.0 \end{array}$

A solution of 5 g. of $Cu(NO_3)_3 \cdot 3 H_3O$ in 200 ml. of H_3O is treated in the cold with 50 ml. of a solution containing 2.5 g. of NaN₃. The resultant precipitate is suction-filtered and washed several times with cold water. The wet product is left to stand 24 hours in 50 ml. of a 2% solution of hydrazoic acid, suctionfiltered, washed with alcohol and ether, and dried at room temperature. The yield is 2.5 g. of azide in the form of a brownblack mass with a reddish shine.

Alternatively, finely powdered basic $CuCO_3$ may be treated with an excess of 2% HN₃, after which the workup is the same as above.

Alternate methods: a) Reaction between $Cu(NO_3)_3 \cdot 3 H_3O$ and $LiN_3 \cdot H_3O$ in alcoholic solution and decomposition of the $Cu(N_3)_2 \cdot 2 NH_3$ [M. Straumanis and A. Cirulis, Z. anorg. allg. Chem. <u>251</u>, 315 (1943)].

b) Determination of azide nitrogen according to F. Feigl and E. Chargaff, Z. anal. Chem. 74, 376 (1928).

SYNONYM:

Cuprous azide.

PROPERTIES:

Black-brown powder or black-brown, opaque crystal needles, depending on the method of preparation. Very sparingly soluble in H_2O and organic solvents. Readily soluble in acids, including CH_3COOH , and in ammonia. Decomposes on heating in air into Cu and N_2 . Can be easily reduced to white CuN_3 in an aqueous solution of hydrazine. Crystal structure: orthorhombic.

Explosive properties: Harmless when moist, quite sensitive to rubbing when dry or moistened with ether. Explodes when placed in a flame. Six times stronger than $Pb(N_3)_3$ and 450 times stronger than mercury fulminate when used as a detonator.

REFERENCE:

M. Straumanis and A. Cirulis. Z. anorg. allg. Chem. 251, 315 (1943).

Copper Phosphide

Cu₁P

 $3 Cu + P = Cu_3 P$ 190.6 31.0 221.6

Stoichiometric amounts of Cu and red P are heated for 20 hours at 640°C in an evacuated, sealed Vycor glass tube. The reaction product is homogenized, melted in a sealed quartz tibe and heated for five hours at 1000°C.

PROPERTIES:

Silvery, shiny material with metallic appearance. Insoluble is nitric acid. d²⁵ 7.147. Crystal structure: hexagonal. Heat of fact mation (25°C): - 36.0 kcal./mole. REPERSNER:

H. Haraldsen, Z. anorg. allg. Chem. <u>240</u>, 337 (1939).

Copper Diphosphide

CuPr

 $Cu_{3}P + 5P = 3CuP_{2}$ 221.6 154.9 376.5

A mixture of Cu₃P with the calculated amount of red phosphorus is heated in a quartz tube for 24 hours at 600°C.

PROPERTIES:

Formula weight 125.49. Gray-black, grainy powder. Slowly dissolves in boiling nitric acid (1.2). d_4^{25} 4.201. Heat of formation (25°C): --23.5 kcal/mole.

REFERENCE:

H. Haraldsen, Z. anorg. allg. Chem. 240, 337 (1939).

Basic Copper Carbonates

CuCO₁-Cu(OH), (Green Cupric Carbonate)

 $2 \operatorname{Cu}(\operatorname{NO}_{3})_{2} + 2 \operatorname{Na}_{2}\operatorname{CO}_{3} + H_{2}O$ (3 H₂O) 483.2 212.0 18.0 = CuCO_{3} \cdot Cu(OH)_{1} + CO_{2} + 4 \operatorname{NaNO}_{3} 221.2 44.0 340.0

An aqueous solution of $Cu(NO_3)_2 \cdot 3 H_2O$ is allowed to react at room temperature with a solution containing the equivalent amount of acdium or potassium carbonate. The greenish blue, partially colloidal precipitate of varying composition that forms is gradually transformed under the mother liquor into crystalline $CuCO_3 \cdot Cu(OH)_2$. Instead of $Cu(NO_3)_2 \cdot 3 H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$ or $CuSO_4 \cdot 5 H_2O$ may be used.

Alternate methods: a) Precipitation of 100 ml, of 1N CuSO₄ with 110 ml, of 1N Na₂CO₃, followed immediately by filtering, water, and drying after standing for 24 hours [14. Gröger, Z. anorg. allg. Chem. <u>24</u>, 127 (1900)].

b) Hot CuSO₄ solution is precipitated with sodium hydroxide. The precipitate is decanted and washed until the solid is free of alkali. It is then dissolved in acetic acid, the solution is evaporated to dryness, and the residue is taken up in water and added to a 100°C solution containing 4/5 of the equivalent quantity of K_2CO_3 . The supernatant is decanted and the precipitate is washed with hot water and dried [W. C. Reynolds, Proc. Chem. Soc. (London) 190, 53 (1897/98)].

PROPERTIES;

Malachite-green powder, insoluble in H_2O , soluble in aqueous ammonia. On boiling in water, particularly when the latter contains alkali carbonate, deposits brown oxide. Stable to 150°C in the absence of alkali, decomposes at 220°C. Unstable toward H_2S . d_4^{25} 3.85.

REFERENCE:

G. Bornemann. Anorg. Präparate [Inorganic Preparations], Leipzig, 1926, p. 156.

2 CuCO₃ · Cu(OH), (Blue Cupric Carbonate)

 $3 \operatorname{Cu(NO_3)_2} + 3 \operatorname{CaCO_3} + H_2O$ $(3 H_9O)$ $724.8 \quad 300.3 \quad 18.0$ $= 2 \operatorname{Cu(CO_3} \cdot \operatorname{Cu(OH)_3} + 3 \operatorname{Ca(NO_3)_2} + \operatorname{CO_2}$ $344.7 \quad 492.3 \quad 22.4 l.$

A solution of copper nitrate is mixed with an excess of pieces of chalk, and the mixture is placed in a large-diameter tube of strong glass connected to a mercury manometer. The tube is then sealed. The azurite forms at room temperature when the liberated CO_2 creates a pressure of 5-8 atm.

Alternate methods: a) From precipitated green basic copper carbonate under a CO₂ pressure of 4 atm. The reaction is markedly accelerated by the addition of azurite [V. Auger, Comptes Rendar Hebd. Séances Acad. Sci. <u>158</u>, 944 (1914)].

b) A soluble copper salt is added in portions to a solution containing Na_2CO_3 , $NaHCO_3$ and suspended blue copper carbonate. A new portion is added only after the previous one has been converted from the green basic carbonate to the blue [V. Auger, loc. cit.].

c) Formation from CuCO₃ · Na₂CO₃ · S H₂O (from saturated NaHCO₃ solution and precipitated basic CuCO₃) and moist CO₃ at 40 atm. [V. Auger, loc. cit.].

(62)

PROPERTIES:

Amre-blue crystalline powder, M.p. (dec.) 220°C; d³⁰ 3.88. hsoluble in water. Converts to the green compound in humid air. Soluble in ammonium salt solutions. Crystal structure: orthorhombic.

REFERENCE:

H. J. Debray. Comptes Rendus Hebd. Séances Acad. Sci. 49, 218 £859).

Copper (I) Acetylide

Cu₂C₁ H₂O

 $2\operatorname{CuCl} + \operatorname{H}_{s}\operatorname{C}_{z} = \operatorname{Cu}_{z}\operatorname{C}_{z} + 2\operatorname{HCl}$ $(H_{1}O)$ 198.0 22.4 l. 72.9 169.1

Pare CuCl (10 g.) is added in vacuum to a solution of 30 g. of NH Cl in 100 ml, of H2O; it dissolves after addition of 50 ml. of conc. ammonia. A solution of 20 g. of hydroxylammonium chloride in 100 ml. of H₂O is then added, and the entire mixture is diluted with 150 ml. of H₂O. The solution becomes completely colorless after a few minutes. It is then siphoned into an evacuated vessel. and acetylene is introduced. The acetylene (from a steel cylinder) passes through a purification train consisting of sealed wash bottles equipped with fritted glass plates and filled (in succession) with HgCl_solution, 2N NaOH, Cu (NO3) , in nitric acid and 2N H_SO4. followed by two wash bottles filled with 2% leuco-indigo carmine solution (made from indigo carmine and zinc dust), for the detection and absorption of O₂, and a glass-bead trap for catching any entrained liquid droplets. Upon contact with the cuprous salt solution, acetylene produces a bright red, flocculent and very voluminous precipitate. The product is suction-filtered on a fritted-glass funnel and washed with boiled water and acetone, all operations being carried out in vacuum. After thorough suctiondrying, it is dried at 100°C (in high vacuum) in a drying pistol, The product contains about 95% Cu₂C₂. H₂O and is stored in scaled ampoules filled in high vacuum,

PROPERTIES.

Brownish-red powder. Insoluble in H₂O, soluble in HCl and KCN solutions. On heating with HCl, moist, freshly prepared Cafe . H O decomposes into C H and CuCl (and a small amount of vinyl chloride). Oxidizes in air to Cu₂O, C and H₂O, the color changing to dark brown.

REFERENCES:

R. Klement and E. Köddermann-Gros. Z. anorg. Chem. 254, 201 (1947); L. Ilosvay. Ber. dtsch. chem. Ges. 32, 2697 (1899).

Paris Green (Copper Acetoarsenite)

 $4 \operatorname{CuO} + 3 \operatorname{As}_{\mathfrak{g}} \operatorname{O}_{\mathfrak{z}} + 2 \operatorname{CH}_{\mathfrak{z}} \operatorname{COOH} = 3 \operatorname{Cu}(\operatorname{AsO}_{\mathfrak{z}})_{\mathfrak{z}} \cdot \operatorname{Cu}(\operatorname{CH}_{\mathfrak{z}} \operatorname{COO})_{\mathfrak{z}} + \operatorname{H}_{\mathfrak{z}} \operatorname{O}_{\mathfrak{z}}$ 593.5 120.1 1013.7 318.2 18.0

Cupric oxide is heated with 8% acetic acid. As 2O a is added, and the mixture is refluxed for two hours. The product is allowed to cool for half an hour, filtered, washed and dried.

Alternate method: Dilute acetic acid is allowed to react with an excess of freshly precipitated Cu(OH), and the product is separated by filtration. Dilute acetic acid is added to a solution of As₂O₃ in boiling NaOH until the color of phenolphthalein disappears. The hot solutions are mixed (mole ratio of CuO:As2Os = 4:3) and allowed to stand for several days [S. Avery, J. Amer. Chem. Soc. 28, 1159 (1906)).

PROPERTIES:

Emerald green, crystalline powder, stable to air and light. Insoluble in H₂O. Decomposes on prolonged heating in H₂O. Unstable in acids, bases and toward H.S. Toxic.

REFERENCE:

G. D. Luchinskiy and U. F. Churilkina. Zh. Prikladnoy Khim. 13, 558 (1940).

Fehling's Solution

SOLUTION 1

34.6 g. of CuSO₄ \cdot 5 H_gO dissolved in 500 ml, of H₂O.

SOLUTION 2

173 g. of crystalline potassium sodium tartrate (Rochelle salt) and 53 g. of NaOH are dissolved in H₂O and diluted to 500 mł. Equal volumes of the two solutions are mixed before use.

1.2

11

1.1

.0 F 1 7 74 3 PROPERTIES:

Deep blue solution, reduced to Cu_2O on heating with reducing agents (sugar test in urine).

REFERENCE:

J. D'Ans and E. Lax, Taschenbuch für Chemiker und Physiker [Pocket Book for Chemists and Physicists], Berlin, 1943, p. 1779.

Very Pure Silver

Crude silver (e.g., from silver residues, see p. 1029) is dissolved in conc. nitric acid, and the diluted solution is precipitated in the cold with a solution of very pure NaCl. The precipitate is washed several times with cold water and dissolved in freshly prepared ammonia solution. After several hours of standing, the solution is filtered. Silver chloride is precipitated from the filtrate with very pure nitric acid, washed with H₂O until no further nitrate can be detected, and reduced in a silver dish with invert sugar* and NaOH (from Na metal) at 60°C, with sucrose and NaOH. or with a boiling alkaline solution of formaldehyde (the formaldebyde should be distilled prior to the preparation; sugar solutions should be filtered through bone charcoal and recrystallized). The resultant silver slurry is filtered, carefully washed free of chloride ion with water, dried and melted down to small ingots over pure CaO. If the metal is heated no longer than absolutely necessary for melting, and if the resultant metal grains are cooled in a reducing flame, the silver obtained is quite pure; it contains about 0.001% S and traces of C. AgCl and O.

The silver obtained in this manner is further purified by electrolysis. The greater part of the grains is used as the anode firited glass finger filled with the Ag) against a cathode of pure silver (wire or sheet). The electrolyte is a 10% AgNO₃ solution prepared from the remaining melted silver and very pure nitric acid. The power supply lead is a strip of fine sheet silver whose upper surface is protected by a layer of asphalt or Bakelite lacquer. The electrolysis is carried out at a constant voltage of 1.39 v. across the terminals. The silver flakes depositing on the cathode are removed from time to time, carefully washed, dried and fused to ingots in a stream of pure hydrogen in a boat made of very pure CaO.

^{*}A 1:1 mixture of dextrose and levulose.

PROPERTIES:

Atomic weight 107.88. M.p. 960.5°C, b.p. 2170°C; d2° 10.497. Crystal structure: type A 1.

REFERENCES:

O. Hönigschmid and R. Sachtlehen. Z. anorg. alig. Chem. <u>195</u>, 207 (1931); Th. W. Richards and R. C. Weils. Z. anorg. alig. Chem. <u>47</u>, 56 (1905); O. Hönigschmid, E. Zintland M. Linhard. Z. anorg. alig. Chem. <u>136</u>, 263 (1924).

Silver Powder

Pure AgCl is stirred with water, allowed to react with sodium hydroxide, and reduced with glucose, which is added to the boiling suspension in small portions. Samples are removed from time to time, filtered and carefully washed. If the Ag yields a completely clear solution on heating in chloride-free HNO₃, the reduction is complete. The medium must be kept alkaline throughout the reaction; an excess of glucose should be avoided. The product is filtered, washed free of base, and dried at 100°C.

Alternate methods: a) Reduction of AgCl with aqueous formaldehyde [L. Vanino, Ber. dtsch. chem. Ges. 31, 1764 (1898)].

b) Heating finely powdered Ag₂O to 500°C [F. Jirsa and J. Jelinek, Z. anorg. allg. Chem. <u>158</u>, 63 (1926)].

c) Reduction of Ag₃O with H_3O_3 and drying at 250°C [F. Jirsa and J. Jelinek, loc. cit.].

PROPERTIES:

Gray, crumbling powder. According to Vanino, the product of the reduction is a loose, black powder.

REFERENCE:

G. Bornemann. Anorg. Präparate [Inorganic Preparations], Leipzig, 1926, p. 161.

Silver from Residues

I. The collected residues are allowed to react with hydrochloric acid (1:1). The precipitate is allowed to settle and the supernatant is siphoned off. The precipitate is washed free of iron by repeated decantation with hydrochloric acid and water, filtered with success.

. .

- 51**4**

placed in a large porcelain dish, mixed with HCl (1:1), and reduced with Zn rods with stirring. After disappearance of the white **particles of AgCl**, the Ag slurry is washed free of acid and Zn with **bot water and filtered**. The washings should be tested for the **presence** of Zn. The resultant sliver slurry can be processed further either to Ag or AgNO₃ (when only pure AgCl is required, an ammonia solution of the salt may be reduced with 20% hydrazine **bydrate**).

a) The silver slurry is dried and fused with a small quantity of borax in a Hessian crucible. The fused Ag is made into granules by careful pouring into water.

b) The silver slurry is dissolved in nitric acid (1:1); the solution is filtered and evaporated in a porcelain dish on a steam bath until crystallization. The last traces of nitric acid are removed by drying in a vacuum or by fusion.

Alternate methods: The silver obtained from the reduction with Zn is dissolved in dilute nitric acid. The solution is filtered and AgCl is precipitated by addition of dilute hydrochloric acid to the hot solution. The precipitate is filtered, carefully washed with warm water, and dried. Then 20 parts of AgCl are mixed in a mortar with 10 parts of Na₂CO₃ and 3 parts of KNO₃. The mixture is placed in a red-hot Hessian crucible. The reduction proceeds according to 2 AgCl + Na₂CO₃ = 2 Ag + 2 NaCl + CO₂ + $\frac{1}{2}$ O₂. The AgCl may also be added in portions to the mixture heated slightly above 960°C. A melt of Ag Is formed immediately. The Ag ingot is cleaned by boiling in water containing sulfuric acid (G. Bornemann, Anorg. Präparate [Inorganic Preparations], Leipzig, 1926, p. 160).

REFERENCES;

Handbuch für das Eisenhüttenlaboratorium [Handbook for the Iron Works Laboratory], Vol. I, p. 317 (1939). F. Specht. Quantitative anorganische Analyse in der Technik [Quantitative Inorganic Analysis in Engineering], 1953.

B. SILVER FROM PHOTOGRAPHIC SOLUTIONS

The photographic solution is made alkaline with ammonia and allowed to react with a slight excess of ammonium sulfide. The mixture is allowed to stand overnight and the supernatant liquid is siphoned off. The residue is suction-filtered and washed with water. The precipitate, after addition of a small amount of anhydrous borax, is placed in a Hessian crucible, dried and calcined at 960°C. The borax is leached out of the product with bot water.

Alternate methods: a) Zinc rods are placed in exhausted fixing solutions and allowed to stand for about one week with frequent agitation. The precipitated Ag slurry is filtered off and cupellated with lead (H. Grubitsch, Anorg. präparative Chemie [Inorganic Preparative Chemistry]. Vienna, 1950, p. 454; for description of cupellation, see also Hackh's Chemical Dictionary, 3rd ed., The Blakiston Co., Philadelphia-Toronto, 1944).

b) The pH of the solution is adjusted to 6.9-7.2 with soda, and $CuSO_4$ or $Al_2(SO_4)_3$ is added. Silver precipitates with the corresponding hydroxide (when the Ag is not present as AgCl, FeCl₃ is added). The voluminous precipitate is treated after 3-4 days with sulfuric acid of increasing concentration (up to 96%), which removes hydroxides, gelatin and other impurities and concentrates the Ag to 20-50% of the total. The Ag is fused in a crucible after adding some borax (U.S. Pat. 2, 131,045).

REFERENCE:

Handbuch für das Eisenhüttenlaboratorium (Handbook for the Iron Works Laboratory], Vol I, p. 318 (1939).

Silver Mirrors

Of the two methods given below, the first is best for flat surfaces, while the second is used for concave surfaces, such as vacuum jackets. With variations, however, they may also be used in other applications. Careful and thorough cleaning of the mirror surface (glass, quartz, porcelain, mica, plastic, etc.) is a necessary condition for any successful silvering effort.

1. A) PREPARATION OF THE MIRROR SURFACE

The silver coating on old mirrors is dissolved with nitrie acid and the surface is rinsed with water. The hands are scrubbed with soap, and the soap foam is transferred to the surface, which is then scrubbed for some time with the foam. Scrubbing is continued while the surface is rinsed, first with tap water, then with distilled water. In the end, the units surface must be perfectly wetted by the water. If any greasy, water-repellent area remains, the entire operation must be repeated. After rinsing, the piece to be mirrored is placed in a dish of distilled water.

If it is desired to polish the silver mirror after deposition, the surface is first covered with a thin paste prepared from equal parts of alcohol, ammonia and precipitated calcium carbonate, and the paste is rubbed in vigorously with cellulose pulp. This cleaning mixture may then be removed with some fresh cellulose,

B PREPARATION OF THE SOLUTION

The following are weighed into three clean test tubes: 1) 5 \pm 0.1 g. of AgNO₃, 2) 1.1 \pm 0.05 g. of AgNO₃, 3) 0.9 \pm 0.05 g. of Rochelle salt. The second and third of these compounds are dissolved in a few milliliters of distilled water.

The following are held in readiness: two dark brown bottles (\$00 ml.) with ground stoppers; three beakers or Erlenmeyer flasts with capacities of a) 800, b) 300, c) 100 ml.; a 20-ml. burette; a glass funnel.

C) SILVER SOLUTION

The 5 g. of $AgNO_3$ (test tube 1) is dissolved in 50-100 ml. of distilled water in vessel b; one third of the solution is held in reserve in c. Ammonia is added (with vigorous swirling) from the burette to the larger portion in b until the resultant deep brown precipitate just dissolves. Some $AgNO_3$ solution is then added from the reserve, ammonia is again added in drops, and the procedure is repeated until the reserve has been exhausted. The last solution added should be $AgNO_3$, and the mixture should be somewhat turbid. If the solution is clear at the end of the operation, a few crystals of $AgNO_3$ are dissolved in distilled water and added to the mixture until turbidity sets in. The Ag solution is diluted to 500 ml. with distilled water and transferred without filtering to one of the brown bottles. Thus protected against light, it may be stored almost indefinitely.

D) REDUCING SOLUTION

The solution of Rochelle salt (test tube 3) is added to 500 ml. of distilled water in vessel a; the mixture is brought to a boll, and the AgNO₃ solution from test tube 2 is added, first in drops **the addition** causes a boiling point elevation and thus a delay in **boiling**—do not add the AgNO₃ too fast!), then more rapidly. The resultant brown-colored turbidity gradually transforms into a greenish-gray precipitate. The solution is boiled over a small flame for six additional minutes, filtered and stored in the second brown bottle. In this bottle the solution is stable for several **months**.

E) SELVERING

Small mirrors are best made in a thoroughly cleaned crystallizing disk or a photographic developing tray. Larger mirrors prefined paper at the edge of the surface, so that the surface itself serves as the bottom of the dish.

Equal volumes of the silver-containing and reducing solutions are measured out in a graduated cylinder in amounts sufficient to cover the mirror surface with a layer of liquid 1 cm. deep. The mixture is then immediately poured on to the surface and the dish is vigorously rocked. A bluish, rapidly thickening deposit is formed after a few minutes on the mirror and the glass walls. The solution becomes turbid and small silver particles appear on the surface of the liquid. The solution is poured off, the mirror rinsed with distilled water, and the silvering process repeated with fresh solution. Finally, the silvered piece is rinsed with distilled water followed by alcohol, and the mirror is allowed to dry while standing on end. It is advisable to grip the mirror with lab. tongs or forceps and not to touch it with the fingers.

In the case of mirrors silvered on the back, the silver layer is protected with a lacquer coating (shellac, varnish). The Ag precipitated on the glass side is removed with a cotton pad moistened with highly diluted nitric acid.

F) POLISHING

The operation is carried out on the day following the silvering. A piece of dust-free chamois leather is tightened around a ball of wool ("polishing ball"). The surface is then carefully gone over with the ball and is then rubbed with increasing pressure. If this does not produce the desired result, some jeweler's rouge is spread on the ball, the excess is brushed off, and polishing is continued.

The mirror prepared as above has a golden sheen (on the back side).

(I. A) PRETREATMENT

The glass surface to be treated, such as the inner space of a jacket, is cleaned for 30 minutes at 60°C with freshly prepared cleaning solution and is then thoroughly rinsed with water. This is followed by a 10-minute treatment with 1.4% hydrofluoric acid and another rinse with water. Then the surface is treated for 10 minutes with technical grade conc. nitric acid (d 1.52) and rinsed with water; the final rinse is distilled water. £ŝ 1.11.1

B) SILVERING

The following three solutions are prepared separately:

1) 50 g, of AgNO₃ in two liters of water; stored in the dark in a ground-joint bottle;

2) 90 g. of very pure, chlorine-free KOH in two liters of water; 4.5.5 rubber-stoppered bottle;

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3) 80 g. of sugar in 800 ml. of water; a mixture of 100 ml, of set alcohol and 3.5 ml. of very pure, chlorine-free nitric acid (a) 1.42) is added to this solution, which is then stored for at least one week before use in a ground-joint bottle.

The three solutions (16:8:1) are mixed as follows: conc. aramonia is added in drops with stirring to solution (1) until the initially formed precipitate just dissolves. Solution (2) is then added, yielding a dark brown to black precipitate (a green precipitate indicates a deficiency of ammonia and the material must be rejected). If the precipitate is of the right color, ammonia is again added slowly with stirring until the precipitate just disappears. A slight excess of ammonia delays the deposition of silver in the next stage, but does not prevent it. The resultant mixture of (1) and (2) may be stored, at most, for one hour. Solution (3) is added immediately before use. The deposition of silver lasts 10 to 30 minutes, depending on the excess of ammonia. Its completion is recognizable by the appearance of a flocculent precipitate. The solution must be removed at this point to avoid harm to the mirror. The surface is thoroughly rinsed with distilled water to remove all residues (including silver slurry) and dried, preferably in vacuum. The silver layer and the glass do not separate on heating to 450° C in a high vacuum of 10^{-5} mm., which is particularly important in silvering of vacuum jackets for distillation columns.

REFERENCES:

- W. Bothe, J. prakt. Chem. <u>42</u>, 191 (1863); R. Böttger. Polytechn. Notizbl. <u>38</u>, 217 (1883); <u>39</u>, 324 (1884); H. Kreusler, Die Sterne <u>9</u>, 42 (1929); E. von Angerer. Techn. Kunstgriffe [Industrial Techniques], 5th ed., Braunschweig, p. 61.
- II. P. W. Schenk. Private communication.

Colloidat Silver

A mixture of 200 ml. of 30% FeSO₄ solution, 280 ml. of 40% solution citrate, and about 50 ml. of 10% NaOH is added to 200 ml. of 10% AgNO₃ solution. The resultant colloidal ailver precipitate is allowed to settle and washed 4-5 times with 10% ammonium mitrate solution and finally twice with 96% alcohol. The mixture is centrifuged and the product carefully dried on a water bath or in a desiccator.

Alternate methods: a) A 0.001N AgNO₃ solution (100 ml.) is treated with a few drops of freshly prepared tannin solution and one drop of 1% sodium carbonate solution. Heating the mixture results in formation of a sol (W. Ostwald, Kleines Praktikum der Kelleichemie [Lab. Manual for Colloid Chem.], 7th ed., 1930, p. 4). b) A warm 0.001N solution of AgNO₂ is reduced by dropwise addition of 0.005% hydrazine hydrate solution (Ag sol according to Gutbler, cited in W. Ostwaid, loc. cit.).

c) Silver sol by electrical atomization: Two silver rods, 2-3 mm. in diameter, are bent at right angles 2 cm. from their ends and the bent sections immersed in a beaker with distilled water so that they form a U figure. A current of 4-6 amp. should flow at 110 volts through the short-circuited electrodes (rheostat control). Clouds of colloidal Ag are formed when an electric arc is passed through the gap between the two ends. Addition of a few drops of 2% sodium carbonate solution is recommended [G. Bredig, Angew. Chem. 951 (1898)].

PROPERTIES:

Black, grainy powder containing about 97% Ag. Soluble in water, yielding a red-brown to black, extremely finely divided Ag sol.

REFERENCE:

M. Carey Lea. Amer. J. Sci. 37, 476 (1889).

Silver Iodide

Agĭ

 $AgNO_{3} + KI = AgI + KNO_{3}$ 169.9 168.0 234.8 101.1

At atmospheric pressure silver iodide exists in three modifications: α -form (cubic, type B3), β -form (hexagonal, type B4) and γ -form (cubic, type B3). At room temperature, the rate of interconversion between the α - and β -forms is so low that the two forms are stable when stored alone or as a mixture. The silver iodide precipitated from solutions usually consists of a mixture of these two modifications. When physical uniformity of the product is not a factor, chemically pure AgI may be prepared in large quantities by the following method.

Very pure KI (83 g.) is dissolved in 8.3 liters of distilled water, and 85 g. of very pure $AgNO_3$ in 8.5 liters of water. The KS solution is added, with constant stirring, to the $AgNO_3$ solution. A milky liquid is initially formed; flocculation occurs only later. The supernatant is siphoned off after standing 2-3 hours, the precipitate is transferred to a three-liter bottle, two liters of distilled water is added, and the mixture is shaken vigoroually to disperse the small olumps of iodide. The flocculent precipitate setties rapidly, and the clear supernatant may be siphoned off after about five minutes. The product is cleaned by decantation until all the KNO₃ has been removed. The wash water is allowed to remain in contact with the precipitate overnight to remove all of the possibly adsorbed electrolyte (which is hard to dislodge). (Test for KNO₃: evaporation to dryness of 200 ml. of the wash water in a platinum dish. Blank test with the distilled water used for washing.) The precipitate is placed on a piece of hard filter paper and dried at 110-120°C. The dry AgI is easily ground to a fine powder.

The mixing of the solutions and the washing operations must be carried out in the absence of daylight. The product may be exposed to daylight only when it is completely free of impurities.

PROPERTIES:

Yellow, crystalline. M.p. 556.8°C, b.p. 1506°C. Insoluble in H₂O; solubility (25°C): $0.25 \cdot 10^{-6}$ g./100 g. H₂O; almost insoluble in ammonia; appreciably soluble in conc. hydriodic acid and conc. solutions of alkali iodides, particularly when hot; soluble in Na₂S₂O₃ solution. Heat of formation -14.95 kcal, per mole.

HENAGONAL & Agl

Silver iodide as precipitated above is dissolved in a conc. solution of potassium iodide. The solution is filtered and poured into water. The AgI precipitates as a thick flocculate. It is washed with water (by decantation) until the iodide ion is no longer detectable by the AgNO₃ test. The AgI is filtered and dried at room temperature.

da° 5.696; crystal structure: type B4.

CUBIC a - Agi

a) Cubic Agl is always formed when hexagonal or mixed Agl is pulverized.

b) Silver iodide is dissolved in a conc. solution of AgNO₃. The solution is filtered and poured into water. Fine-grained, slowly coagulating AgI is formed. It is washed by decantation until the filtered and the product dried at room temperature.

d2° 5.680; crystal structure: type B3,

REFERENCE:

H. H. Kolkmeijer and J. W. A. van Hengel. Z. Kristallogr. <u>A 88</u>, 317 (1934).

Silver Chlorate

AgClO₁

 $AgNO_3 + NaClO_3 = AgClO_3 + NaNO_3$ 169.9 106.4 191.3 85.0

Solutions of 170 g of AgNO₃ and 106 g of NaClO₃, each dissolved in 100 ml. of 85°C water, are combined and cooled to 0°C. The supernatant is carefully decanted and 50 ml. of H_2O (0°C) is added to the residue. The resultant crystals are suction-filtered; they are 95% pure.

A purer product may be obtained by dissolving the residue remaining after the above decantation in 125 ml. of H_2O at 90°C, cooling to 0°C, and suction-filtering. The crystals are redissolved in 120 ml. of H_2O at 90°C, cooled to 0°C, suction-filtered, and dried in a desiccator. The yield is about 118 g. of 99.7% AgClO₃.

The compound should be stored in dark flasks. Since $AgClO_3$ is a strong oxidant, extreme care should be exercised when it is brought into contact with easily oxidized materials, especially organic substances.

PROPERTIES:

White crystals. M.p. 230°C, decomposes at 270°C; d 4.43.

REFERENCE:

D. G. Nicholson and C. E. Holley in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 4.

Silver Oxide

Ag₂O

 $2 \text{ AgNO}_{3} + 2 \text{ NaOH} = \text{Ag}_{2}\text{O} + 2 \text{ NaNO}_{3} + \text{H}_{2}\text{O}$ 369.8 80.9 231.8 170.0 18.0

Equivalent quantities of a conc. solution of $AgNO_3$ and a dilute solution of NaOH (both prepared with CO_2 -free water) are mixed; the resultant precipitate is decanted and washed with CO_2 -free water. The precipitate is centrifuged, suction-filtered, and dried at 85-88°C in a stream of CO_2 -free air.

Alternate methods: a) Precipitation of a dilute AgNO₃ solution with Ba(OH)₂, with careful exclusion of CO_2 [E. Laue, Z. anorg. allg. Chem. 165, 336 (1927)].

b) Electrolytic preparation: A 25-30% NaNO's solution is electrolyzed at room temperature at minimum current density (anode current density is important), using a silver anode and a nickel cathods positioned as close as possible. [K. Merei, Magyar. Chem. Folyoirat 45, 197 (1913)].

PROPERTIES:

Dark brown to brown-black powder. M.p. (dec.) 300°C; d45 7.320. Insoluble in water [solubility (20°C): 2.14 · 10⁻³ g./100 g. H₂O]; somewhat soluble in NaOH. Moist Ag₂O is quite insensitive to light. Some decomposition occurs on drying. Crystal structure: type C3. Heat of formation (25°C): -7.3 kcal./mole.

REFERENCE:

E. H. Madsen. Z. anorg. allg. Chem. 79, 197 (1913).

Silver Peroxide

Ag₂O₇

$Ag_{2}O + 2KOH + 2KMnO_{4} = Ag_{2}O_{2} + 2K_{2}MnO_{4} + H_{2}O_{3}$ 247.8 394.2 18.0 316.1 231.8 112.2

Solutions of AgNO3 and KMnO4 are combined and an excess of KOH is added. The resultant precipitate is filtered in a glass filtering crucible, washed with ice-cold water until the filtrate is colorless, dried for two hours at 110°C, and placed for 24 hours in a desiccator over P₂O₅. An anhydrous product containing up to 60% Ag₂O₂ is obtained.

Alternate methods: a) Treatment of AgNO3 solution with a solution of potassium or ammonium persulfate [H. Marshall, J. Chem. Soc. (London) 59, 775 (1891)].

b) Reaction of metallic Ag with ozone-containing Oz at 240°C; use of lower temperatures is also possible if FegO3 or Pt is used as catalyst (W. Manchot and W. Kampschulte, Ber. dtsch. chem. Ges. 40, 2891 (1907)].

c) Reaction of NaOCl with Ag 20 at 75-80°C [R. L. Dutta, J. Indian Chem. Soc. 32, 95 (1955)].

d) Hydrolysis of Ag₂NO₁₁ (from anodic oxidation of AgNO₃ solutions) and thermal decomposition of Ag7NO11 [G. M. Schwab and G. Hartmann, Z. anorg. allg. Chem. 281, 183 (1955)].

PROPERTIES

Gray-black powder. Decomposes above 100°C into Ag and O₂; 42 7.483. Boluble in conc. HNO3, from which it precipitates

on dilution. Decomposes in hot cone. H_2SO_4 with evolution of O_2 . Strongly oxidizing.

REFERENCE:

F. Jirsa. Z. anorg. allg. Chem. 225, 302 (1935).

Sodium Orthoargentite

Na₃AgO₁

 $Ag_2O + 3Na_2O = 2Na_3AgO_2$ 231.8 186.0 417.7

Stoichiometric quantities of pure, absolutely dry Na₂O and dry Ag₂O (dried in vacuum at 80° C) are weighed in the absence of moisture and CO₂. The two starting materials are ground to a fine powder and intimately mixed in the vacuum ball mill shown in Fig. 55, p. 76. The mixture is transferred (with exclusion of air) to a sintered magnesia boat placed in a protective tube of Fe or Ag which itself is positioned in a heating tube (Vycor or quartz). The heating tube is evacuated and the mixture heated to 400°C. The product is homogenized by grinding and reheating.

PROPERTIES:

Formula weight 208.85. Light green powder, highly sensitive to moisture. Decomposed to a black substance even by small quantities of water vapor. Stable up to 450°C in vacuum.

REFERENCE:

E. Zintl and W. Morawietz, Z. anorg. allg. Chem. 236, 372 (1998).

Silver (I) Sulfide

Ag₂S

 $2 \text{ Ag} + \text{S} = \text{ Ag}_{\text{s}} \text{S}$ 215.8 32.1 247.8

I. Pure sulfur vapor, carried in a stream of N_{cr} is passed over pure Ag at 250 °C. The S and Ag are in two separate boats placed in a quartz tube. Alternatively the S may be placed in a quartz take 18 cm. long and 16 mm. I.D. with a constriction in the middle (Fig. 278). That tube is open at one end and narrows to a conical module at the other. The Ag is placed in a quartz tube, of the same diameter and about 9 cm. long, constricted at both ends in such a way that one of the ends fits the nozzle of the other tube. The other end is attached by means of a ground joint to an outlet tube for unreacted S vapor. The S, in a boat, is placed in the first of the two chambers formed by the 18-cm.-long quartz tube. Then the tubes containing the S and Ag are placed inside a larger quartz tube set in an electric furnace. The furnace is heated to 350° C in such a way that sulfur is distilled from the first into the second chamber of the 18-cm.-long tube (purification). The furnace is then set at 250° C and heating is continued in a stream of N₂.

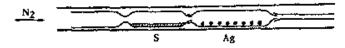


Fig. 278, Preparation of silver (I) sulfide.

Plugging of the outlet tube with excess S is prevented by heating the tube (if necessary, with an additional electric furnace). Depending on the flow rate, the conversion of 10 g, of Ag requires 6 to 8 hours. The excess S remaining in the Ag₂S after completion of the reaction is removed by heating in a stream of N₂. The temperature is maintained below 300°C to prevent sulfur from being driven off from the Ag₂S.

II. Very pure Ag and S are placed at opposite ends of an evacuated, sealed glass tube previously cleaned by the von Wartenberg method (p. 342). An excess of S is used. The tube is heated for 1-2 days at 400°C. It is then pulled (halfway) out of the furnace so that the end containing the sulfur is exposed on the outside. This enables the free sulfur to sublime from the product onto the cold excess sulfur. The reaction is complete within about 12 hours.

Alternate methods: a) Precipitation of an ammoniacal solution of AgNO₃ with H₂S. The precipitate is washed with water and dried at 150°C in a stream of CO₂. Excess S is removed by heating for one hour at 350-400°C in a stream of H₂ [E. von Britzke and A. F. Kapustinski, Z. snorg. allg. Chem. 205, 95 (1932)].

b) Fusion of the calculated amounts of Ag and S in a pressure vessel [A. M. Gaudin and D. W. McGlashan, Econ. Geol. 33, 143 (1932)].

SYNOWTH:

Argentous sulfide.

PROPERTIES:

Black, crystalline. M.p. 845°C; $d_4^{2\circ}$ 7.234, $d_4^{2\circ}$ 7.072. Soluble in KCN solution, insoluble in aqueous ammonia. Transition point β -Ag₂S (rhombic) $\neg \alpha$ -Ag₂S (cubic): 179°C. Heat of formation (α -Ag₂S, 25°C): -7.5 kcal./mole.

REFERENCES:

- I. O. Hönigschmid and R. Sachtleben, Z. anorg. allg. Chem. <u>195</u>, 207 (1931).
- II. C. Wagner. Private communication.

Silver (I) Selenide

Ag₂Se

2 Ag + Se = Ag₂Se 215.8 79.0 294.7

A boat containing selenium and (behind it) a boat containing metallic silver are placed inside a quartz tube. The tube is surrounded by two electrical furnaces, so that the Se is heated to 300° C, while the Ag is at 400° C. A stream of O₂-free nitrogen carries the Se to the silver (see Fig. 278, preparation of Ag₂S). The Se vapor is passed over the metal until large amounts of Se begin to accumulate behind the Ag. The heat is maintained at 400° C for some time after that to remove any Se which may have adhered to the product surface. The conversion of 5 g. of Ag requires 6-8 hours. Dissociation begins above 400° C.

Alternate method: Reaction of soluble Ag saits with CuSe. The reactions with Cu₂Se and Cu₂Se₂ give metallic Ag as a by-product [W. Geilmann and Fr. W. Wrigge, Z. anorg. allg. Chem. <u>210</u>, 378 (1933)].

PROPERTIES:

Black, crystalline, d_4^{24} 8.187, Crystal structure: at 75°C tetragonal with c/a = 0.66; at 80°C tetragonal with c/a = 0.94; at 240°C cubic. Heat of formation (cubic Ag₃Se, 25°C): -6.0 kcal. per mole.

REFERENCE:

O. Hönigschmid and W. Kapfenberger. Z. anorg. alig. Chem. <u>212</u>, 198 (1933).

Silver (I) Telluride

Ag₃Te

 $2 \text{ Ag} + \text{Te} = \text{Ag}_{2}\text{Te}$ 215.8 127.6 343.4

Prepared by passing Te vapor over Ag. Nitrogen serves as the carrier gas and the reaction temperature is 470 °C. The flow rate of the Te vapor should be slow; i.e., the amount of Te entering the reaction chamber should not exceed the reactive capacity of the Ag. The apparatus is identical to that used for Ag₂Se. The conversion of 3 g. of Ag requires 72-96 hours. Excess Te is removed by beating to 500-540 °C in high vacuum. Well-crystallized products are obtained.

Alternate method: Heating Ag in a porcelain crucible in an atmosphere of Te, with exclusion of air [P. Rahlfs, Z. phys. Chem. (B) 31, 157 (1936)].

PROPERTIES:

Gray-black, crystalline. $d_4^{2\circ}$ 8.318. Transition point β -Ag₂Te (rhomble) $\rightarrow \alpha$ -Ag₂Te (cubic): 149.5°C. Heat of formation (β -Ag₂Te, 25°C) -5.0 kcal./mole.

REFERENCE:

O. Hönigschmid, Z. anorg. alig. Chem. 214, 281 (1933).

Silver Sulfate

Ag₂SO₄

 $2 \text{ AgNO}_3 + \text{H}_2 \text{SO}_4 = \text{Ag}_2 \text{SO}_4 + 2 \text{ HNO}_3$ 339.8 98.1 311.8 126.0

A solution of $AgNO_3$ in some H_3O is treated with 1:1 sulfuric scid. The Ag_3SO_4 precipitate is centrifuged, dissolved in hot conc. H_2SO_4 (in a Pt dish if high product purity is required), and boiled for several minutes to expel the nitric acid. The acid sulfate which crystallizes on cooling is centrifuged and treated with water in a Pt dish. The normal sulfate thus crystallizes as a fine powder (evolution of heat). The supernatant is decanted and the crystals washed with pure water until free of acid. The Ag_2SO_4 is centrifuged and dried on an air bath at 110°C. The entire operation must be conducted in a dustproof atmosphere.

Alternate methods: a) Treatment of AgNO₃ solution with MagO₄ solution [O. Hönigschmid and R. Sachtleben, Z. anorg. alig. Chem. 195. 207 (1931)]. b) Solution of Ag metal in sulfuric acid (O. Hönigschmid and R. Sachtleben, loc. cit.).

c) Finely divided Ag₂SO₄ is obtained by precipitation of its aqueous solution with alcohol. The product is dried in vacuum at 100°C [H. Hahn and E. Gilbert, Z. anorg. allg. Chem. <u>258</u>, 91 (1949)].

PROPERTIES:

Colorless crystals. M.p. 657°C, decomposes at 1085°C; d_{15}^{15} 5.460. Sparingly soluble in water; solubility (18°C): 2.57 · 19⁻². g./100 g. H₂O. Slightly decomposed by light, acquiring a light-violet color. Dissociates on melting, acquiring a yellow color which disappears on treatment with gaseous SO₃. Crystal structure: orthorhombic. Heat of formation (25°C): -170.5 kcal./mole.

REFERENCE:

Th. W. Richards and G. Jones. Z. anorg. allg. Chem. 55, 72 (1907).

Silver Sulfite

Ag₂SO₂

 $2 \text{ AgNO}_{3} + \text{ Na}_{3}\text{SO}_{3} = \text{ Ag}_{2}\text{SO}_{3} + 2 \text{ NaNO}_{8}$ 339.8 125.0 295.8 170.0

A solution of $AgNO_3$ is treated at room temperature with the stoichiometric quantity of Na_3SO_3 solution, yielding a precipitate of Ag_2SO_3 , which is filtered, washed with well-boiled water, and dried in vacuum.

Alternate method: Precipitation of aqueous AgNO₃ with sulfurous acid [J. Muspratt, Liebigs Ann. <u>50</u>, 286 (1853)].

PROPERTIES:

Colorless powder. Sparingly soluble in water, soluble in aqueous ammonia. Decomposes in light and on heating, forming the dithionate and sulfate. Insoluble in liquid SO₂.

REFERENCES:

P. Berthier, Ann. Chim. Phys. (3) <u>7</u>, 82 (1817); K. Seubert and M. Elten. Z. anorg. alig. Chem. <u>4</u>, 44 (1894).

Silver Amide

AgNH₁

AgNO₃ + KNH₄ == AgNH₈ + KNO₃ 189.9 55.1 123.9 101.1

Silver amide is formed in the reaction between potassium amide and silver nitrate, both dissolved in liquid ammonia. Good

results are obtained with the two-arm tube shown in Fig. 279, in which KNH₂ solution is allowed to flow into excess $AgNO_3$ solution, causing precipitation of $AgNH_2$.

A) KNH2

First, KNH₂ is prepared in arm β from potassium metal and NH₃. To achieve this, inlet tube c is connected to a source of absolutely dry NH₃ and the entire apparatus is dried by passing through NH_3 and heating. Then a is temporarily closed off with a stopper and oxide-free K, together with a few milligrams of sponge Pt as catalyst, is introduced at b in a stream of NH_3 . Inlet tube b is melt-sealed to a pressure-resistant tip, the pressure gradient required for the glass-blowing operation being achieved by brief alternate closing and opening of inlet a with a finger. The AgNOs is now introduced into arm A and dried in a stream of NH_3 . Arm A is then melt-sealed at a in the same way as b, the pressure gradient being achieved by removing the plug from stopcock h and closing the resultant two openings (when required) with a finger. Arm B is then immersed in ice water and NH3 is allowed to condense in it until it fills 1/4 of the volume. In the presence of Pt, 1 g. of K is converted to KNH2 within 15 minutes. After completion of the reaction, the Ha by-product is allowed to escape via stopcock h.

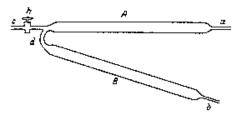


Fig. 279. Preparation of silver amide.

B) AgNH₂

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The AgNO₃ in arm A is dissolved in a manner similar to that presented above, and both arms are then filled to half their volume with liquid NH₃. After the solutions have become homogeneous, they are combined by allowing the KNH₃ solution to flow into the AgNO₃ solution. The resultant precipitate of AgNH₃ ectiles well and is purified by decantation with liquid NH₃. This is carried out by pouring the supernatant liquid NH₃ into arm B and redistilling it into A (B is then in lukewarm water, A in ice unler). The precipitate is vigorously agitated, together with the NH₃ which condenses on it, and is then allowed to settle. The

supernatant liquid NH₃ is again poured off into 3. This operation is repeated several times. Finally a deep layer of liquid NH₃ is condensed onto the precipitate in A. This arm is then immersed in a -35°C bath in order to establish atmospheric pressure inside the apparatus, stopcock h is opened, and the tube is fused at d. The liquid NH₃ is allowed to evaporate slowly through stopcock h and the tube is evacuated to remove residual NH₃.

These reactions may also very conveniently be carried out in the apparatus of Fig. 69, p. 87; this apparatus is an improved version of the one described above.

PROPERTIES:

White, quite voluminous precipitate (when moist). Soluble in ammonium salt solutions, absolute ammonia, and excess KNH₂; insoluble in excess AgNO₃. Blackens on exposure to light. The precipitate shrinks considerably on drying and acquires color. Extraordinarily explosive when dry. Apparently impossible to obtain an absolutely pure state.

REFERENCES:

E. C. Franklin. Z. anorg. allg. Chem. <u>46</u>, 1 (1905); R. Juza, Ź. anorg. allg. Chem. <u>231</u>, 121 (1937).

Silver Azide

AgN₂

 $AgNO_3 + NaN_3 = AgN_3 + NaNO_3$ 169.9 65.0 149.9 85.0

A solution of NaN₃ is treated in the cold with a slight excess of $AgNO_3$ solution. The AgN_3 precipitate is decanted, filtered, washed with water, alcohol and ether, and dried in vacuum over conc. HaSO₄.

Alternate methods: a) Slow addition of a 1% AgNO₃ solution to 1.5% aqueous HN₃, prepared by distillation of a solution of NaN₃ in H₂SO₄. The product is washed free of Ag ion [F. V. Friedländer, J. Amer. Chem. Soc. <u>40</u>, 1945 (1918); T. Curtius, Ber. discharchem. Ges. <u>23</u>, 3027 (1890)].

b) Precipitation of a cold, saturated solution of AgNO's with hydrazine sulfate [A. Angeli, Atti Acad. dei Linc. 2, 569 (1893)].

PROPERTIES:

Colorless crystalline needles. M.p. 252°C. Sparingly soluble in water and nitric acid; readily soluble in aqueous aminenias

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Righly explosive. Sensitive to shock and heat. The white color changes to gray-violet on heating to 170-180°C. Detonation temperature about 300°C. Crystal structure: orthorhombic, Heat of formation: +67.3 kcal./mole.

REFERENCE:

G. Tammann and C. Kröger. Z. anorg. alig. Chem. <u>169</u>, 16 (1928).

Silver Nitride

Ag₃N

Potassium hydroxide pellets are added to a solution of AgCl in conc. ammonia until the effervescence, caused by the evolving NH₃, stops. The mixture is diluted with distilled water, filtered through filter paper, and washed with water until the filtrate is neutral. The moist product is transferred from the filter paper to a porcelain dish, where it may be stored under water for some time.

The product contains small amounts of AgCl and Ag, but is free of Ag_2O_2 .

Alternate methods: a) A solution of Ag_2O in conc. aqueous ammonia is allowed to stand in air or heated on a water bath. The same may be achieved by precipitation with alcohol. The product is impure, with a variable content of Ag_2O and Ag [F. Raschig, Liebigs Ann. 233, 93 (1886)].

b) Solid AgF \cdot 2NH₃ is stored for several days over H₂SO₄ in a desiccator. The product is free of Ag₂O and rich in Ag; the yield is small [L. J. Olmer and Dervin, Bull. Soc. Chim. France (4) <u>35</u>, 152 (1924)].

SYNONYM:

Т

(Berthollet's) fulminating or detonating silver.

PROPERTIES:

Formula weight 337.65. Black flakes, sometimes shining black; crystalline appearance (when prepared according to Raschig, see above). Insoluble in H_2O , soluble in dilute mineral acids, explosive reaction with conc. acids. Both the dry and the moist product may be stored in air at room temperature for a long time. Slowly decomposes at 25°C. Decomposes at room temperature in vacuum. Decomposes explosively in air at about 165°C. Very sensitive (explodes) when touched with objects of great relative hardness, even when moist. Extremely sensitive when dry, but relatively easy to handle when moist. Explodes readily when prepared by Raschig's method, d_{4}^{+2} 9.0. Crystal structure: cubic. Heat of formation (25°C): +61.0 kcal/mole.

REFERENCE:

H. Hahn and E. Gilbert. Z. anorg. Chem. 258, 77 (1949).

Silver Acetylide

Ag₁C₈

 $2 \text{ AgNO}_{3} + \text{ C}_{2}\text{H}_{2} = \text{ Ag}_{2}\text{C}_{2} + 2 \text{ HNO}_{3}$ 339.8 22.41. 239.8 128.0

Pure acetylene is introduced into a solution of $AgNO_3$ which has been treated with a large excess of ammonia. The white precipitate of Ag_2C_2 is filtered, washed with water, then with alcohol and ether, and dried over P_3O_5 in a desiccator.

PROPERTIES:

White powder, light sensitive, very explosive, particularly when dry. Soluble (decomposition) in KCN solution, yielding $C_{B}H_{B}$. Decomposed by HCl into AgCl and $C_{B}H_{B}$. Decomposes hydrolytically in water and alkalis.

REFERENCE:

J. Eggert. Z. Elektrochem. 24, 150 (1918).

Silver Cyanamide

Ag₂CN₂

Careful addition of HNO₃ to commercial CaCN₂ at 0°C and pH 6 yields H_2CN_2 . The solution thus obtained, which contains about 10% H_3CN_2 , is treated with an ammoniacal solution of AgNO₃ (added in small portions). The resultant Ag₃CN₂ is purified by solution in dilute HNO₃ and reprecipitation with dilute NH₃; it is washed and rapidly dried at 130°C.

PROPERTIES:

Formula weight 255.79. Yellowish-white powder containing 99.5% $Ag_{2}CN_{2}$. Soluble in KCN: $Ag_{2}CN_{2} + 4$ KCN = 2K (Ag (CN) i + K₂CN₂. Pyrolysis in vacuum proceeds via the intermediate

e na węs na przedł silver dicyanamide, AgC_2N_3 , which is stable up to 600°C. The decomposition is complete at 750°C. The residue consists of Ag which is free of cyanide and N₂. If the temperature rise is too rapid, the pyrolysis becomes explosive.

REFERENCE:

A. Chrétien and B. Woringer. Compt. Rend. Hebd. Séances Acad. Sci. <u>232</u>, 1114 (1951).

Silver Carbonate

Ag₂CO₁

 $2 \text{ AgNO}_{3} + \text{Na}_{2}\text{CO}_{3} = \text{Ag}_{2}\text{CO}_{3} + 2 \text{ NaNO}_{3}$ 339.8 100.0 275.8 170.0

A solution of $AgNO_3$ is treated with alkali carbonate or bicarbonate. When precipitating with the carbonate, avoid an excess of the reagent, since the Ag_2CO_3 precipitate may then contain oxides. The product is filtered, washed with water, and dried to constant weight over H_2SO_4 and P_2O_5 . It still contains traces of water.

Due to its sensitivity to light, a pure silver carbonate can be obtained only when the preparation is carried out in red light.

Alternate method: Electrolysis of a 0.02M solution of NaHCO₃ using a silver anode and platinum cathode. The crystalline precipitate at the anode is Ag_2CO_3 [P. Demers, Canad. J. Res. (A) <u>17</u>, 77 (1939)].

PROPERTIES:

I.

Light-yellow powder. Very sparingly soluble in water; solubility (25°C): $3.2 \cdot 10^{-3}$ g./100 g. H₃O. Soluble in conc. alkali carbonate solutions, KCN solution, HNO₃ and H₃SO₄. Splits off CO₂ on beating (CO₂ pressure at 218°C = 752 mm.). d_4^{30} 6.077. Heat of formation (25°C): -120.8 kcal./mole.

BEFERENCE:

G. H. G. Jeffrey and A. W. Warnington. Chem. News 132, 373 (1939).

Silver Nitrite

AgNO₂

 $AgNO_{2} + KNO_{2} = AgNO_{2} + KNO_{3}$ 169.9 85.1 153.9 101.1

A solution of 5 parts of KNO_3 is added to a solution of 8 parts of $AgiO_3$. The resultant pale yellow precipitate is usually

contaminated with some Ag_zO , which is removed by recrystallization from water at 70°C. On cooling, $AgNO_2$ crystallizes in the form of hair-thin, almost colorless needles. It is best to work under red light to prevent decomposition.

PROPERTIES:

Colorless to yellow needles. Somewhat soluble in water; the solubility increases markedly with temperature: $(15^{\circ}C)$ 0.28, $(60^{\circ}C)$ 1.38 g./100 g. H₂O. Soluble in excess nitrites, with formation of complex salts. Blackens in light. Decomposes at 140°C; dissociates into Ag and NO₂ on dry heating. In aqueous solution, gradually decomposes into Ag, AgNO₃ and NO. d_4^{26} 4.453. Crystal structure: orthorhombic. Heat of formation: -11.6 kcal./mole.

REFERENCE:

J. A. A. Ketelaar. Z. Kristallogr. (A) 95, 383 (1936).

Silver Tartrate

Ag₂C₄H₄O₄

| 2 AgNO ₃ | + | KNaC ₄ H ₄ O ₅ | Ag _t C _i H _i O _t | + | KNO ₅ | + | NaNO ₅ |
|---------------------|---|---|--|---|------------------|---|-------------------|
| | | (4 H ₂ O) | | | | | |
| 339.8 | | 282.2 | 363.8 | | 101.1 | | 85.0 |

Stoichiometric quantities of $AgNO_3$ and potassium sodium tartrate (Rochelle salt) are dissolved in water and the solutions combined. On addition of alcohol (in which silver tartrate is insoluble), the product precipitates as a white, cheeselike deposit which is immediately filtered through a suction or Büchner filter. The precipitate is washed with aqueous alcohol until no further Ag^+ ion is detectable. Further purification may be achieved by crystallization from 80°C water, a small quantity of Ag_2O being formed in the process. The aqueous solution is filtered and alcohol is again added. The precipitate is filtered, washed first with aqueous, then with absolute alcohol or acetone, and dried in vacuum over H_2SO_4 .

Due to the light sensitivity of the compound, it is best to work in the dark.

Alternate method: A hot, moderately conc. solution of Rochelle salt is added to an 80°C dilute solution of AgNO₃; the reaction (addition) is complete when the continually forming precipitate no longer dissolves. The silver tartrate crystallizes on cooling in the form of fine flakes which acquire a white, metallic sheen on washing. PROPERTIES:

White powder or crystalline flakes, not entirely stable in daylight. Soluble in dilute nitric acid, sparingly soluble in H_{2O} (solubility at 25°C:0.20 g./100 g. H_{2O}); insoluble in alcohol, acetone and other. Decomposes in ammonia and NaOH, yielding Ag₂O. Evolves CO₂ on dry heating, leaving pyrotartaric acid and Ag as residue, $d_{2}^{\pm 5}$ 3.432.

REFERENCES:

L. Reckenbacher. Liebigs Ann. 38, 132 (1841); H. Sauer. Unpublished.

o-Phenanthrolinesilver (II) Persulfate

[Ag phen_] S₁O₈

$$2 \text{ AgNO}_{3} + 4 \text{ C}_{12}\text{H}_{8}\text{N}_{2} + 3 (\text{NH}_{4})_{2}\text{S}_{2}\text{O}_{8}$$

$$339.8 \quad 720.8 \quad 684.9$$

$$= 2 [\text{Ag}(\text{C}_{12}\text{H}_{8}\text{N}_{2})_{2}]\text{S}_{2}\text{O}_{8} + 2 (\text{NH}_{4})_{2}\text{SO}_{4} + 2 \text{ NH}_{8}\text{NO}_{3}$$

$$1320.9 \quad 284.3 \quad 160.1$$

Two equivalents of an aqueous solution of o-phenanthroline are added to a solution of $AgNO_3$. A colorless, gelatinous precipitate is formed; it rapidly turns red-brown on addition of a conc. solution of $(NH_4)_3S_3O_6$, and settles on standing as fine crystals. The product is suction-filtered, washed with cold water, and dried, first with alcohol and ether and then in a desiccator. The yield is quantitative.

PROPERTIES:

Formula weight 660.44. Chocolate brown, very stable crystalline powder. Insoluble in water. Readily soluble (without decomposition) in cold conc. nitric acid, yielding a dark brown solution from which the perchlorate may be precipitated by addition of an excess of conc. NaClO₄ solution. Forms AgO in alkali hydroxides.

REFERENCE:

W. Hieber. Ber. dtsch. chem. Ges. 61, 2149 (1928).

Tris-α,α'-dipyridylsilver (II) Perchlorate [Ag(dipyr),](ClO.).

The reaction between silver nitrate and α, α' -dipyridyl yields bis- α, α' -dipyridylsilver nitrate [Ag(dipyr)₂]NO₃, which is converted into bis- α, α' -dipyridylsilver(II) persulfate [Ag(dipyr)₂]S₂O₈ with $K_2S_pO_6$. Treatment of this compound with nitric acid yields tris- α, α' -dipyridylsilver (II) nitrate $[Ag(dipyr)_3](NO_3)_2$; addition of NaClO₄ to an aqueous solution of this nitrate yields a precipitate of the corresponding perchlorate.

A) BIS-α, α'-DIPYRIDYLSILVER NITRATE [Ag(dipyr)2] NO3

A hot solution of 16.9 g. of AgNO₃ in aqueous ethanol is added to a hot solution of 31.2 g. of α, α' -dipyridyl in ethanol, yielding a precipitate of $[Ag(dipyr)_2]NO_3$. Additional product is recovered upon concentration of the mother liquor. The compound is recrystallized from hot dilute ethanol.

PROPERTIES:

Formula weight 482.27. Yellow needles. Decomposes at 155°C. Decomposes slowly in light. Sparingly soluble in cold and hot water and in common organic solvents (except alcohols).

B) BIS-α, α'-DIPYRIDYLSILVER (II) PERSULFATE [Ag (dipyc)2] S20g

The yellow needles of $[Ag(dipyr)_2]NO_3$ are stirred into an excess of cold, saturated aqueous $K_2S_2O_8$; a deep red-brown precipitate of the complex persulfate is produced. The reaction is complete after two hours of constant stirring. The precipitate is washed with cold water.

PROPERTIES:

Formula weight 612.39. Red-brown precipitate. Decomposes at 137°C. Very sparingly soluble in water, insoluble in the common organic solvents. In air, converts to the corresponding hydrogen sulfate.

C) TRIS- a, a'-DIPYRIDYLSILVER (II) NITRATE [Ag (dipyr)3] (NO3)2

Product (B) is triturated in a mortar with cold nitric acid (d 1.4). The excess acid is removed and the residue extracted with warm water. The brown aqueous extract is treated with an excess of aqueous NH_4NO_3 and cooled with ice, thus precipitating small, dark-brown needles of the dinitrate. The precipitate is purified by solution in warm water and reprecipitation with aqueous NH_4NO_3 .

PROPERTIES:

Formula weight 700.47. Dark-brown needles. Decomposes at 176°C. Soluble in water; the aqueous solution decomposes slowing, evolving O₂. Powerful oxident. B) THIS O, C DIPYRIDYUSILVER (II) PERCHLORATE [Ag(dipyr)3] (CIO4)2

This compound is precipitated when $NaClO_4$ is added to an aqueous solution of $[Ag(dipyr)_3](NO_3)_2$. The precipitate is washed with warm water.

PROPERTIES:

Formula weight 775.36. Orange-brown crystals. Detonates on heating. Very sparingly soluble in water.

ANALYSIS:

Determination of the Ag (II) in compounds B-D: the complex salts are treated with cold aqueous KI, yielding iodine: $AgX_2 + 2 KI \rightarrow 2 KX + AgI + \frac{1}{2} I_2$. The iodine is titrated with Na₂S₂O₃ solution.

REFERENCES:

G. T. Morgan and F. H. Burstall, J. Chem. Soc. (London) <u>1930</u>, 2594; H. Kainer. Thesis, Heidelberg, 1952.

Very Pure Gold

Gold (20 g.) is dissolved in aqua regia in an 800-ml. beaker, and the solution is concentrated to a thick sirup. The nitric acid is expelled by evaporating the solution five times on a steam bath, each time with 20 ml. of hydrochloric acid (4:1). The residue is taken up in 650 ml. of hot water and digested until all soluble material is dissolved. It is then allowed to settle for eight days in a dust-free atmosphere. The precipitate consists of AgCl containing small amounts of Au, Pd, SiO_2 , etc. The gold solution is filtered through a double layer of thick filter paper, without disturbing the precipitate. This and all later precipitates are not worked up further to obtain gold.

Experience indicates that the gold refined by use of SO_2 still contains some Pd, while that precipitated with oxalic acid contains Cu. Pb and other metals. Therefore both of these procedures must be used to obtain gold of the desired purity. Sulfur dioxide is passed through the warm gold solution (80°C) obtained above; the gold precipitates quantitatively on careful neutralization with ammonis (1:1). The product is allowed to settle overnight and the deposit of spongy gold is washed by decantation with hot water; it is then heated for four hours on a steam bath with conc. hydrochloric acid and washed free of acid with hot water. Then it is redissolved

in a beaker. The entire procedure is repeated eight times in order to remove Ag, Cu, Ni, Zn and Pb. The product is then digested for 12 hours with ammonia (1:1), washed free of ammonia with water, heated for four hours on a steam bath with hot cone. nitrio acid, and decanted. Ammonia (1:1) is again added and later removed by washing with water. The gold sponge is dissolved in dilute aqua regia; after addition of HCl, the solution is concentrated by evaporation, diluted with H2O, decanted and filtered. The gold is precipitated by careful addition (there is a danger of foaming over) of small portions of powdered, crystalline oxalic acid. If the solution retains a yellow color, it is carefully neutralized with ammonia and more oxalic acid is added; the addition of the acid is continued until the solution remains colorless. The resultant gold sponge is dissolved and reprecipitated with oxalic acid. It is then Pd-free. Finally the gold is redissolved, precipitated with SO2, digested with conc. hydrochloric acid, and washed with water. The last traces of HCl are removed with ammonia. The product is transferred to a glazed porcelain dish and dried at 110°C. Yield 75-80%. The gold prepared in this manner is spectroscopically pure (free of metallic Cu, Ag, Ni, Zn and Pt).

Alternate methods: a) Preparation of pure gold by the method of G. Krüss. The product is probably not as pure as that prepared by the method described above [G. Krüss, Liebigs Ann. 238, 43 (1887)].

b) Extraction of AuCl₃ with ether. Total impurities in the product, about 0.001% [F. Mylius, Z. anorg. allg. Chem. <u>70</u>, 203 (1911)].

PROPERTIES:

Atomic weight 197.0. M.p. 1063°C, b.p. 2960°C; d^{17.5} 19.29. Crystal structure: type A1.

REFERENCE:

T. A. Wright. Metals and Alloys 3, 146 (1932).

Colloidal Gold

A mixture of 120 ml. of very pure, twice-distilled water (silver) condenser) and 2.5 ml, of a solution of 6 g, of $HAuCI_4 \cdot 4 H_2O$ in one liter of water is prepared and brought to a boil as rapidly as possible. Shortly before the boiling point is reached, 3 ml, of 0.18N solution of very pure potassium carbonato is added. As soon as the solution begins to boil, it is rapidly swirled around (or stirred with a Pyrex glass rod), while 3-5 ml. of a dilute solution of formaldehyde (1.3 ml. of 40% formaldehyde in 100 ml. of water) is added. Stirring is continued until a reaction is evident (this usually occurs within a few seconds—one minute at most), (this usually occurs

Alternale methods: a) Reduction with ethereal solution of phosphorus (R. Zsigmondy and P. A. Thiessen, Das kolloide Gold [Colkoidal Gold], Leipzig, 1925, p. 487).

b) Reduction with hydrazine hydrate or phenylhydrazonium chioride [A. Gutbier and F. Resenscheck, Z. anorg. alig. Chem. 39, 112 (1904)].

c) Reduction with sodium anhydro methylene citrate (citramin) [L. Vanino, Kolloid-Z, 20, 122 (1917)].

d) Reduction with alkaline formaldehyde solution [P. P. von Weimarn, Kolloid-Z. 33, 75 (1923)].

e) Sol of gold by pulverization in an electric arc [Th. Svedberg, Ber. dtsch. chem. Ges. <u>39</u>, 1705 (1906); G. Bredig, Angew. Chem. 950 (1898); E. F. Burton, Phil. Mag. <u>11</u>, 425 (1906)].

PROPERTIES:

Bright red sol, particle size about $1-6 \cdot 10^{-7}$ cm. Highly sensitive to electrolytes. Concentrated solutions (up to 0.12% gold) may be obtained by dialysis.

REFERENCE:

R. Zsigmody and P. A. Thiessen. Das kolloide Gold [Colloidal Gold], Leipzig, 1925, p. 33.

Gold from Residues

L FROM PLATING BATHS

A clay cell filled with NaCl solution and provided with a zinc electrode is placed in the gold solution. An electrode made of a piece of brass sheet is immersed in the gold solution and the two electrodes are connected into a circuit. The gold is deposited quantitatively on the brass electrode over a period of a few weeks, during which the brass electrode is replaced once or twice and the Zn electrode is pickled several times.

IL FROM WASTE CONTAINING GOLD AND SILVER

The particles are calcined and the resultant powder is boiled with conc. nitric acid to remove Ag and other metals. The diluted solution is filtered and the residue is heated with aqua regia on a steam bath for 24 hours. The gold is precipitated from the filtrate with FeSO₄ and worked up.

HI. FROM INDUSTRIAL ALLOYS

The gold alloy is ground as finely as possible and heated with conc. hydrochloric acid on a sand bath, conc. nitric acid being added in drops from time to time. When solution is complete, the mixture is evaporated in a porcelain dish placed on a steam bath (dust-free atmosphere) until the liquid solidifies on cooling. The residue is taken up in a large quantity of water and allowed to stand for some time; the precipitated AgCl is then filtered off. The solution is heated and the gold is precipitated with excess aqueous FeCl₂. The supernatant is decanted and the residue boiled with dilute hydrochloric acid until the HCl ceases to yellow. The solution is then filtered, dried and fused with borax in a porcelain crucible. If higher purity is desired, the procedure is repeated. If present, Pt, Pd and Tl may be removed from the filtrate with Fe or Zn.

Alternate methods: a) Reduction with alkaline H₂O₃ [L. Vanino and L. Seemann, Ber. dtsch. chem. Ges. <u>32</u>, 1968 (1899)].

b) The gold solution is added at 100°C to a solution of Hg $_2$ (NO $_3$) $_{3*}$ yielding very finely divided gold (L. Vanino, Handbuch der präp. Chemie [Handbock of Prep. Chemistry], Stuttgart, 1921, Vol. I, p. 520).

c) Electrolysis of Ag- and Pt-containing alloys [W. Möbius, Berg- und hüttenm. Ztg. <u>44</u>, 447 (1885); <u>47</u>, 324 (1888); Chemiker-Ztg. <u>15</u>, Rep. 18 (1891); E. Wohlwill, Z. Elektrochem. <u>4</u>, 379 (1897)].

REFERENCES:

I. Plage, Industr.-Bl. 190 (1878).

- II. W. Adolphi. Chemiker-Ztg. 52, 109 (1928).
- III. A. Bender, Anleitung z. Darstellung anorg. Preparate [Introduction to the Preparation of Inorganic Compounds], Stuttgart, 1893.

Gold (I) Chloride

AuCl

Prepared by thermal decomposition of an auric chloride obtained from hydrogen tetrachloroaurate (III).

| HAuCl ₄ | = | AuCl | ł | HCl | Ŧ | Cla | |
|--------------------|---|-------|---|------|---|------|--|
| $(4 H_1 O)$ | | | | | | | |
| 411.9 | | 232.5 | | 36.5 | | 70.9 | |

Gold (5-10 g.) is dissolved in aqua regia and the solvents are, removed by vacuum distillation (aspirator) at water bath temperature.

The solution is protected by a blanket of CO_3 introduced through a capillary. The nitric acid is expelled by double evaporation with conc. hydrochloric acid, and the resultant dark red-brown melt is poured into a dish where it congeals to a crystalline mass. This is heated to 100°C in high vacuum, until no vapor pressure is evident. Since the HAuCl₄ liquefies again during this operation, care should be exercised to avoid spattering. After all water is expelled, the residue is heated to 156°C (boiling bromobenzene bath). At higher temperatures (170-205°C) the decomposition is complete within a few hours.

Alternate methods: a) Thermal decomposition of AuCl₃ in air at 185°C [J. Thomsen, J. prakt. Chem. 13, 337 (1876)].

b) Decomposition of AuCl₃ in a stream of dry HCl at 175°C [M. E. Diemer, J. Amer. Chem. Soc. <u>35</u>, 552 (1913)].

c) Decomposition of AuCl₃ in a stream of dry air [F. H. Campbell, Chem. News 96, 17 (1907)].

The products prepared by methods a-c are not completely pure.

SYNONYMS:

Aurous chloride, gold monochloride.

PROPERTIES:

Light yellow crystals, not deliquescent. M.p. (dec.) 289°C; d_4^{25} 7.4. Soluble in alkali chloride solutions. Decomposes on solution in water. Heat of formation (25°C): -8.4 kcal/mole.

REFERENCE:

W. Biltz and W. Wein. Z. anorg. allg. Chem. 148, 192 (1925).

Gold (III) Chloride

ApCl₂

L

 $2 \text{Au} + 3 \text{Cl}_3 = 2 \text{Au}\text{Cl}_3$ 394.0 67.21. 600.7

Finely divided gold is treated at $225-250^{\circ}$ C (but not higher) with gaseons Cl_2 at a pressure of 900-950 mm. (The gold powder is obtained by precipitating a solution of a gold salt with sulfurous acid, washing and drying at 180°C.) The powder is in a porcelain beat which is placed in a glass tube. At the point immediately adjoining the boat, the tube widens into a sphere with outlets at top and bottom. Excess Cl_2 escapes through the upper outlet; this outlet also carries a rod, which can be used to push the AuCl₃ (which condenses in the sphere) into a storage flask via the lower outlet. The yield is 0.1-0.2 g. per hour of large (up to 10 mm. long) crystals.

II. About 0.2-0.6 g, of freshly precipitated gold is placed in a 50-ml. flask connected to the atmosphere via a reflux condenser and a drying tower. Molten iodine monochloride is added in drops through a side tube. The reaction starts when the flask is heated. When the reaction subsides, an excess of ICl is added and the mixture is heated for a short time until boiling just begins. The solution is cooled and extracted several times with CCl₄ (distilled over P_2O_5). The suspension is then filtered (suction) in a stream of N₂ through a sintered glass funnel; the residue is washed with CCl₄ and freed of CCl₄ in vacuum. The yield is quantitative.

Alternate method: $HAuCl_{\bullet} \cdot 4 H_{B}O$ is carefully heated in a stream of Cl_{2} ; final heating for half an hour at 200°C [M. E. Diemer, J. Amer. Chem. Soc. <u>35</u>, 553 (1913)].

SYNONYMS:

Auric chloride, gold trichloride.

REFERENCES:

Formula weight 303.37. Ruby-red crystals (when sublimed) or red-brown to dark ruby-red crystalline mass. M.p. 229°C, b.p. (dec.) 254°C; $d_{4}^{2\circ}$ 3.9. Melts at 288°C under a Cl₂ pressure of 2 atm. Sublimes at 180°C. Hygroscopic; soluble in H₂O with formation of H₂[AuCl₃O]. The neutral aqueous solution decomposes gradually with separation of metallic gold; acidic solutions are more stable. Soluble in alcohol and ether. Heat of formation (25°C): -28.3 kcal./mole.

REFERENCES:

M. Petit. Bull. Soc. Chim. France, Mém. <u>37/38</u>, 1141 (1925);
 W. Fischer and W. Biltz. Z. anorg. alig. Chem. <u>176</u>, 81 (1928).

II. V. Gutmann, Z. anorg. alig. Chem. 264, 169 (1951).

Hydrogen Tetrachlorocurate (81)

HABCL · 4 HtO

 $2 A_{u} + 3 Cl_{e} + 2 HCl = 2 HA_{u}Cl_{s}$ (4 H_sO) 394.0 212.7 72.9 823.8

Precipitated gold is dissolved in aqua regia and the solvent is evaporated at steam bath temperature (aspirated vapor). The nitric

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acki is expelled by repeating the procedure twice with conc. **bythochloric acid**, which is itself removed by evaporation. The **resultant melt** is poured into a dish, where it congeals to a **crystalline mass**. The residual mother liquor is decanted, and the **crystals are crushed** to allow rapid drying in a drying closet. The **mass is pulverized** several times during the drying operation until **it is completely** dry.

PROPERTIES:

Formula weight 411.90. Elongated, light-yellow needles, deliquescent in moist air. Soluble in water, alcohol and ether. The aphydrous compound crystallizes from alcohol. One molecule of H_2O is given off on prolonged standing in dry air. Crystal structure: monoclinic. Heat of formation: -4.5 kcal./mole.

STNONTHS:

Gold trichloride acid; chloroauric acid; aurochlorohydric acid; bydrochloroauric acid.

REFERENCES:

W. Biltz and W. Wein. Z. anorg. allg. Chem. <u>148</u>, 192 (1925); J. Thomsen, Ber. disch. chem. Ges. <u>16</u>, 1585 (1883).

Potassium Tetrachloroaurate (III)

KAuChe 1/2 HaO

 $2 \text{AuCl}_{3} + 2 \text{KCl} + \text{H}_{2}\text{O} = 2 \text{KAuCl}_{4} \cdot \frac{1}{2} \text{H}_{2}\text{O}$ 606.7 149.1 18.0 773.9

An aqueous solution of $AuCl_3$ or $HAuCl_4$, strongly acidified with HCl, is treated with an equimolar quantity of conc. aqueous KCl, and the mixture is evaporated over H_3SO_4 or at a moderately high temperature.

PROPERTIES:

Formula weight 386.94. Light-yellow needles, stable in air. Soluble in water and alcohol, insoluble in ether. Loses water of crystallization at 100°C. Crystal structure: monoclinic.

STRONTLE:

Anrie potassium chloride,

REFERENCE:

H. Topsöe. Ber. Wien. Akad. II, 69, 261 (1874).

Gold (III) Oxide

Au₁O₃

 $2 \operatorname{Au}(OH)_{3} = \operatorname{Au}_{2}O_{3} + 3 \operatorname{H}_{2}O$ 496.0 442.0 54.0

Gold hydroxide is made according to the procedure outlined in the next preparation and heated to constant weight at 140-150°C.

It is best to start from Au metal if the product must be entirely free of nitrogen oxides. The gold is dissolved in aqua regia and the nitric acid is removed completely by evaporation with hydrochloric acid, repeated five times. The hydroxide is precipitated with a small excess of Na₂CO₃ (very slight blue color on litmus paper), washed several times with water, centrifuged and purified by electrodialysis for 14 days. The product is dried and converted to Au₂O₃ at 140-150°C.

Crystalline Au₂O₃ cannot be obtained by dehydration of Au(OH)₃. Alternate methods: a) By atomization of gold by means of a high-frequency spark in ozonized O₃. The oxidation product contains about 40% Au₂O₃, the rest being elemental Au (see Thiessen and Schütza, as well as Schütza and Schütza, in references below).

b) Precipitation of Au(OH)₃ from AuCl₃ solution with potassium hydroxide by Fremy's method [W. E. Roseveare and T. F. Buehrer, J. Amer. Chem. Soc. <u>49</u>, 1221 (1927)].

DETERMINATION OF ACTIVE OXYCEN

The solution is boiled in 0.1N oxalic acid and back-titrated with KMnO₄ solution.

SYNONYMS:

Gold trioxide; gold sesquioxide; suric oxide.

PROPERTIES:

Black to brownish black. Soluble in conc. acids, markedly, soluble in glacial acetic acid. Decomposes above 160°C interfact and O_2 , Heat of formation (25°C): +19.3 kcal./male.

REFERENCES:

P. A. Thiessen and H. Schütza, Z. anorg. alig. Chem. <u>243</u>, 32 (1939); H. Schütza and I. Schütza, Z. anorg. alig. Chem. <u>245</u>, 59 (1940); G. Lunde, Z. anorg. alig. Chem. <u>163</u>, 345 (1997).

Gold (III) Hydroxide

Au(OH);

 $2 \text{ KAuCl}_{4} + 3 \text{ Na}_{2}\text{CO}_{3} + 3 \text{ H}_{2}\text{O}$ $(^{1}/_{4} \text{ H}_{3}\text{O})$ $773.9 \quad 318.0 \quad 54.0$ $= 2 \text{ Au}(\text{OH})_{3} + 6 \text{ NaCl} + 2 \text{ KCl} + 3 \text{ CO}_{2}$ $496.0 \quad 350.7 \quad 149.1 \quad 132.0$

A solution of KAuCl₄ is heated for several hours on a water bath with an excess of Na_2CO_3 . The resultant precipitate is filtered, thoroughly washed, digested with warm, dilute sulfuric acid, and carefully washed in a glass filter crucible until the filtrate is free of H_2SO_4 . The product is dried at room temperature over H_2SO_4 .

Alternate methods: a) Precipitation of AuCl₃ solution with MgCO₃ [G. Krüss, Liebigs Ann. <u>237</u>, 290 (1887)].

b) Hydrolysis of gold sulfate or nitrate [P. Schottländer, Liebigs Ann. 217, 312 (1883)].

c) Fusion of gold with Na_2O_2 and decomposition of the resultant sodium aurate with dilute sulfuric acid [F. Meyer, Compt. Rend. Hebd. Séances Acad. Sci. <u>145</u>, 805 (1907)].

d) Anodic oxidation of gold in 1N sulfuric acid (F. Jirsa and O. Buryànek, Z. Elektrochem. 29, 126 (1923); W. G. Mixter, J. Amer. Chem. Soc. 33, 688 (191)].

STNONTM:

Auric hydroxide.

PROPERTIES:

Formula weight 248.02. Brown powder. Insoluble in H_aO , **which is a conc.** acids and hot KOH. When dried over P_aO_5 in **vacuum**, the compound is converted to AuO(OH) (slowly at room temperature, rapidly at 100°C), whereby the color changes, the final one ranging from yellowish red to ocher-brown. Converts to Au₂O₃ at 140-150°C.

REFERENCE:

R. Lydén, Z. anorg. allg. Chem. 240, 157 (1939).

Potassium Aurate

KAuO₂ · 3 H₁O

 $2 \operatorname{Au}(OH)_3 + 2 \operatorname{KOH} + 2 \operatorname{H}_2 O = 2 \operatorname{KAuO}_2 \cdot 3 \operatorname{H}_2 O$ 496.0 112.2 38.0 644.8

Auric hydroxide is reacted with warm conc. KOH in the absence of atmospheric CO_2 . After filtration the solution is allowed to evaporate in the dark. The precipitated crystals are dried in vacuum over H_2SO_4 .

PROPERTIES:

Formula weight 322.15. Light-yellow needles, soluble in water, giving a highly alkaline reaction. Decomposes on gentle heating, giving off water and oxygen. The residue consists of Au, KOH and KO_2 .

REFERENCES:

F. Meyer, Compt. Rend. Séances Acad. Sci. <u>145</u>, 805 (1907); E. Frémy. Ann. Chim. Phys. <u>31</u>, 483 (1853).

Gold (I) Sulfide

Au₁S

| 2 K[Au(CN) _z] | + | H ₂ S - | - 2 HCl | - | Au _# S | Ŧ | 2 KCl | ÷ | 4 HCN | |
|---------------------------|---|--------------------|---------|---|-------------------|---|-------|---|-------|--|
| 576.9 | | 22.41. | 72,9 | | 428.1 | | 149.1 | | 108.1 | |

A conc. solution of $K[Au(CN)_2]$, obtained by treatment of a solution of $AuCl_3$ with excess KCN, is saturated with H_2S . Hydron chloric acid is added to the clear solution and the mixture ds heated, resulting in the appearance of a brown color. A heavy, rapidly settling precipitate is formed on boiling. This is filtered with water, and then successively with alcohol, ether, CS_3 and finally again with ether. The product is dried to constant weight over P_2O_8 .

The product usually contains sulfur and some moisture, which are difficult to remove. It may be freed of S by dissolving in MCM. filtering and reprecipitating with boiling hydrochloric abids that is

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PROPERTIES:

Brown-black powder when dry, steel-gray when moist. The frashly precipitated compound is readily soluble in water, forming a colloid, particularly in the presence of H_2S . Easily recoagulated by hydrochloric acid and salts. Insoluble after drying over P_2O_5 . Resistant to conc. hydrochloric acid and H_2SO_4 , as well as to KOH. Oxidized by aqua regia and strong oxidants. Soluble in solutions of KCN and alkali polysulfides. Decomposes at 240°C into Au and S.

REFERENCE:

L. Hoffmann and G. Krüss. Ber. dtsch. chem. Ges. <u>20</u>, 2361 (1887).

Gold (II) Sulfide

AuS

 $8 \operatorname{AuCl}_{s} + 9 \operatorname{H}_{s}S + 4 \operatorname{H}_{s}O = 8 \operatorname{AuS} + 24 \operatorname{HCl} + \operatorname{H}_{s}SO_{4}$ $\bigcup_{s} 242.7 \quad 20.21, \quad 7.2 \quad 183.3 \quad 87.5 \quad 8.8$

A neutral 1-3% solution of AuCl₃ is precipitated in the cold (the temperature must not exceed 40°C) with H_3S or an alkali sulfide. The precipitate is filtered, thoroughly washed with water, and treated with alcohol, anhydrous ether, CS_3 and again with ether. The product is dried at 130°C over P_3O_5 .

Alternate method: A solution of $AuCl_3$ is added in drops to an aqueous solution of sodium dithiosulfatoaurate (I) (for preparation, see under Au_3C_3) (Antony and Lucchesi, see references below).

PROPERTIES:

Formula weight 229.07. Deep black. Insoluble in water and acids; soluble in aqua regia and solutions of potassium cyanide and alkali polysulfides. Resistant to KOH in the cold, decomposes after prolonged boiling, liberating gold. Thermal decomposition begins at 140°C.

REFERENCES:

U. Antony and A. Lucchesi. Gazz. Chim. Ital. <u>19</u>, 552 (1889); <u>20</u>,
 61 (1890); L. Hoffmann and G. Krüss. Ber. dtsch. chem.
 Ges. <u>20</u>, 2704 (1887).

Gold (III) Sulfide

Au_tS₂

 $\begin{array}{rcl} 2 \ \text{HAuCl}_{4} &+ \ 3 \ \text{H}_{2}\text{S} &= \ \text{Au}_{2}\text{S}_{4} &+ \ 8 \ \text{HCl} \\ (4 \ \text{H}_{2}\text{O}) \\ & \\ 823.8 & 67.2 \ l , & 490.2 & 291.7 \end{array}$

A fast stream of $H_{2}S$ is introduced into 1N hydrochloric acid at -2 to -4°C; simultaneously, a cooled solution of HAuCl₄ · 4 H₂O is allowed to flow in. The black precipitate is digested with water, washed free of acid, treated with alcohol and ether, extracted with CS₂ in a Soxhlet extractor, washed with ether, and dried in vacuum over $P_{2}O_{5}$.

Alternate methods: a) A solution of AuCl₃ in absolute ether is saturated with H_2S . The product is washed with CS_2 and alcohol [K. A. Hofmann and F. Höchtlen, Ber. dtsch. chem. Ges. <u>37</u>, 245 (1904)].

b) Completely dry LiAuCl₄ \cdot 2 H₂O is treated with H₂S at --10°C. The product is extracted with alcohol, CS₂, and again with alcohol and ether, and dried at 70°C in pure N₂ [U. Antony and A. Lucchesi, Gazz. Chim. Ital. <u>19</u>, 552 (1889)].

PROPERTIES:

Deep black. Insoluble in water. Resistant to hydrochloric and sulfuric acids and dilute nitric acid. Vigorous reaction with conc. nitric acid. Soluble in conc. Na₂S solution, alkali polysulfides and KCN. $d_4^{2\circ}$ 8.754.

REFERENCE:

Gold (I) Acetylide

Au₁C₂

Prepared by precipitating a solution of sodium dithiosulfatoaurate (I), Na₃[Au(S₂O₃)₂] \cdot 2 H₂O, with acetylene.

A) SODIUM DITHIOSULFATOAURATE (I)

A solution of 3 parts of $Na_3S_3O_3 \cdot 5 H_3O$ in 50 parts of waten is reacted (stirring) with a solution of 1 part of AuCl₃ in 50 parts

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A. Gutbier and E. Dürrwächter. Z. anorg. alig. Chem. 121, 266 (1922).

of water. The gold solution is added in portions, each portion being added only after the red color resulting from the previous addition has disappeared. The compound is precipitated from this solution with 96% alcohol and purified by repeated solution in water and reprecipitation with alcohol.

B) GOLD (I) ACETYLIDE

A solution of $Na_3[Au(S_3O_3)_3]$ is reacted with an excess of strong aqueous ammonia and then slowly saturated with C_2H_2 . The solution becomes yellow, and a yellow precipitate deposits after some time. It is washed by decantation with water and alcohol, filtered and dried over H_2SO_4 .

PROPERTIES:

Formula weight 418.02. Yellow powder. Insoluble in water; decomposes in boiling water without evolution of C_2H_2 ; decomposes slightly in hydrochloric acid with evolution of C_2H_2 . Extremely explosive when dry. Detonates at 83°C if rapidly heated.

REFERENCE:

A. Mathews and L. L. Watters. J. Amer. Chem. Soc. <u>22</u>, 108 (1900).

Gold (I) Cyanide

AuCN

 $\frac{\text{K}[\text{Au}(\text{CN})_{2}] + \text{HC}!}{288.1} = \frac{\text{Au}\text{CN} + \text{HCN} + \text{KC}!}{223.0} + \frac{1}{27.0} + \frac{1}{74.6}$

An aqueous solution of $K[Au(CN)_3]$ is mixed in the cold with hydrochloric acid and warmed to 50°C. Most of the AuCN precipitates. The mixture is evaporated to dryness on a steam bath, resulting in removal of HCN. The residue is taken up in water, filtered, thoroughly washed (in the absence of sunlight) to remove KC1, and dried over H_3SO_4 or P_3O_5 .

Alternate methods: a) Precipitation of a solution of AuCl₃ with KCN [P. O. Figuier, J. Pharm. Chim. <u>22</u>, 329 (1836)].

b) Decomposition of Na[Au(CN)₂] with HCI [A. Wogriaz, Metalloberfläche 8, 11, 162 (1954)].

PROPERTIES:

Leanon-yellow crystalline powder. Stable in air. Sparingly soluble in water and dilute acids. Soluble in solutions of alkali

cyanides, KOH, ammonia, Na₂S₃O₃ and (NH $_{4}$)₃S. Decomposes with separation of Au on dry heating. Unstable in light when moist, d_{4}^{20} 7.12. Crystal structure: hexagonal.

REFERENCE:

K. Himly. Liebigs Ann. 42, 157 (1842).

Potassium Dicyanoaurate (I)

K[Au(CN)_z]

Formed when "fulminating gold" is dissolved.

Pure gold (10 g.) is dissolved in 50 ml. of aqua regia (34 ml. of conc. hydrochloric acid and 16 ml. of nitric acid, d 1.33) on a steam bath. When solution is complete (after about two hours), "fulminating gold" is precipitated by addition of an excess of ammonia. It is washed until Cl-free, dissolved while still moist in a slight excess of KCN solution, concentrated on a steam bath, and allowed to crystallize overnight. Additional salt may be recovered from the mother liquor. The product is recrystallized from an equal amount of boiling water, and dried over P_3O_5 or conc. H_2SO_4 .

Alternate methods: a) Electrolytic solution of Au in warm aqueous KCN [J. Glassford and J. Napier, Phil. Mag. 25, 61 (1844)].

b) To prepare solutions of $K[Au(CN)_3]$ or $Na[Au(CN)_3]$ for use in gold-plating baths and still avoid using gold sponge or evolution of HCN, HAuCl₄, in an amount corresponding to 3 parts by weight of Au, is dissolved in 50 parts by weight of water. The flask contents are swirled around while Na_3CO_3 or K_3CO_3 is added until a test with Congo paper no longer yields a blue color. The gold solution is then poured into a porcelain dish and allowed to react (stirring) with 5.2 parts by weight of NaCN or 6.8 parts of KCN; the solution becomes warm and colorless. Six parts of annealed 0.02-mm,-thick gold foil, cut into small chips, are added, and the mixture is heated for several hours on a water bath with stirring and replenishing of the evaporating water. Residual unreacted gold is removed and the solution is evaporated to dryness [A, Wogrinz, Prakt. Chem. (Vienna) 3, 216 (1952)].

SYNONYM:

Gold potassium cyanide.

PROPERTIES:

Formula weight 288.14. Colorless crystals. Readily soluble in H_{gO} , sparingly soluble in alcohol, insoluble in ether and accione.

Precipitated from saturated aqueous solution by sulfuric acid, hydrochloric acid, nitric acid and alcohol. Decomposes on boiling with acids. Stable in air and light. $d_{1}^{2\circ} 3.45$.

REFERENCE:

F. Chemnetius, Chemiker-Ztg. 51, 823 (1927).

SECTION 20

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Zinc, Cadmium, Mercury F. WAGENKNECHT AND R. JUZA*

Zinc

Zn

VERY PURE ZINC

Certain grades of commercial zinc are quite pure. The highest purity may be achieved by distillation (Procedure I) or, starting from $ZnSO_4$, by purification of the salt and electrolytic isolation of the metal (Procedures I and II). Extreme purity of zinc salts is particularly important in the preparation of scintillators.

I. PURIFICATION OF ZINC SULFATE IN SOLUTION

Alumina, standardized by the method of Brockmann, is introduced in portions into a glass tube (30 cm. long, 4 cm. diameter) provided with a fritted glass disk at one end. After each addition the adsorbent is compacted with a glass pestle or by applying a vacuum. The material is allowed to fill 2/3 to 4/5 of the tube length. The material is prevented from fluidizing by placing a piece of filter paper on top. The flask containing the solution is above the column; the liquid flows into the column through an inlet tube bent at an acute angle. The bottom end of the column is placed in a suction flask. Continuous operation of the system is achieved by applying a slight vacuum. The adsorbent removes As, Sb, Bi, Cr, Fe, Hg, U, Pb, Cu and Ag.

To remove Ni or Co, the ZnSO₄ solution is made alkaline with ammonia and filtered through alumina that has been pretreated with an alcoholic solution of, respectively, diacetyldioxime or \hat{a} nitroso- β -naphthol.

Manganese may be removed by adding to the ZnSO₄ solution 0.5 g. of $(NH_4)_2PbCl_6$ hydrolyzed in one liter of redistilled (!) H₃O, heating the mixture for a short time to the boiling point,

^{*}The second edition was revised by Dr. H. U. Schuster of

and filtering off the deposit of PbO₂ flakes after 24 hours. Traces of the Pb are removed by passing the solution through an Al_2O_3 column and concentrating the product. Solutions purified with Al_2O_3 as above satisfy the most stringent requirements.

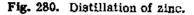
II. ELECTROLYTIC SEPARATION

The electrolyte should contain 40-60 g./liter of Zn (calculated as the sulfate). A piece of silk taffeta serves as the membrane. Pure ZnO is suspended by stirring in the anode chamber. The cathode is Al or Pt, the anode is Pt. The current density is 0.01-0.03 amp./cm.² The Zn deposit may be peeled off cleanly from the aluminum sheet by cutting off its edges. Inclusions are removed by fusing with a small quantity of NH4Cl in a porcelain crucible. The ingot is pickled clean with HCl and thoroughly washed with distilled water.

III. DISTILLATION OF METALLIC ZINC

The last step in the purification of the Zn metal is a double vacuum distillation. The operation is carried out in a Vycor tube shaped as in Fig. 280. After the distillation (650 $^{\circ}$ C), a





slight gray deposit, which is separate from the main body of the distillate, may be observed at b. It contains Cd. Traces of a black, very fluffy impurity are left at a. No impurity deposit is formed at b during the subsequent second distillation. To prevent contamination of the final product

with some heavy, low-volatility components still present, the second distillation is stopped before the material at a is depleted. The resultant Zn product is spectroscopically pure. If a quartz tube is used and larger amounts of Zn (e.g., 30 g.) are distilled, the distillate adheres very strongly to the tube wall.

PROPERTIES:

Atomic weight 65.38. Bluish white. Solubility in Hg (18°C) 2.2 g. Zn/100 g. Hg. M.p. 419.4°C, h.p. 905.7°C; d 7.133. Hardness 2.5. Crystal structure: type A3 (Mg type). Electrochemical equivalent 1.220 g. (amp. hr.)⁻¹.

SEPERENCES:

L. E. Tiede and W. Schikore. Ber. dtsch. chem. Ges. <u>75</u>, 586 (1942); W. Schikore and E. G. Müller. Z. anorg. Chem. <u>255</u>,

327 (1948); W. Schikore and T. Pankow. Ibid. 258, 15 (1949).

- II. F. Mylius and O. Fromm. Z. anorg. allg. Chem. 9, 144 (1895).
- III. R. Petermann. Thesis, Bern, 1946; O. Hönigschmid and M. von Mack. Z. anorg. allg. Chem. 246, 363 (1941).

Zinc Hydride

ZnH,

L

 $ZnI_2 + 2LiAlH_4 = ZnH_2 + 2AiH_3 + 2LiH_4$ 319.2 75.8 67.4 59.9 267.7

Ether solutions of ZnI3 and LiAlH4 (mole ratio 1:2) are mixed at -40°C or below; a white precipitate forms. The product must be separated immediately by centrifugation to prevent contamination by polymeric $(AIH_3)_x$, which begins to form after some time. The Lil remains in the supernatant solution.

| п. | Zo(CH ₃) ₂ + | 2 LiAih | ≠ ZnH₁ | + 2 LiAlH ₃ CH ₃ |
|----|-------------------------------------|---------|--------|--|
| | 95.4 | 75.9 | 67.4 | 103.9 |

Dimethylzinc (0.57 g., ~ 6 mmoles) is distilled in a completely dry atmosphere into an ice-cold solution of 0.59 g. (~15.6 mmoles) of LiAlH₄ in 10 g. of absolute ether (predried over LiAlH₄). The white precipitate obtained on heating the mixture to room temperature is filtered, washed several times with absolute ether, and freed of adhering ether by heating to 50°C in vacuum.

The dimethylzinc needed for this preparation is obtained by heating $Hg(CH_3)_3$ (p. 1119) with a large excess of zinc shot in a closed tube. At 120°C the yield is quantitative after 64 hours. The dimethylzinc may be distilled at atmospheric pressure in a stream of N₂. B.p. 46°C.

PROPERTIES:

Solid, white, nonvolatile when pure. Readily oxidized; reacts with H₂O or humid air, evolving H₂. This reaction is very vigorous in the case of old preparations, which often ignite spontaneously. Stable for some time at room temperature in dry air; in high vacuum at 90°C, gradually decomposes to the elements.

REFERENCES:

- L. W. Wiberg, W. Henle and R. Bauer. Z. Naturforschg. 6b, 393 (1951).
- IL G. D. Barbaras, A. E. Finholt, H. J. Schlesinger et al., J. Amer. Chem. Soc. 73, 4585 (1951). 0

Zinc Chloride

ZnClr

| 7 .n | + | 2 HCl | 7 | ZnCl ₂ | ÷ | H2 | |
|-------------|---|-------|---|-------------------|---|-----|--|
| 65.4 | | 72.9 | | 136.3 | | 2.0 | |

L Very pure, anhydrous $ZnCl_2$ is prepared by treating Zn with dry HCl at 700°C in a quartz boat placed in a tube of high-melting glass. At this temperature, the formation and sublimation of ZnCl_ proceed at sufficiently high rates. The sublimed chloride is collected in a section of the tube which is kept cool for this purpose. Temperatures above 700°C should be avoided, since entrainment of zinc vapor with the chloride may result, a phenomenon recognizable by the appearance of a color in the otherwise colorless sublimate. For additional purification, the chloride may be resublimed in a stream of HCl.

II. The same reaction can be carried out in anhydrous ether. Ether and excess HCl are removed on a steam bath (vacuum).

III. $2n + 2 CuCl = ZnCl_s + 2 Cu$ 65.4 198.0 136.3 127.1

A 6.7% solution of CuCl in pure, dry acetonitrile (distilled several times over P_3O_5) is electrolyzed at room temperature with a Pt cathode and a Zn anode (voltage across the terminals is 12 v.). The electrolysis proceeds under a blanket of absolutely dry N₂. The reaction is complete when a gray coating of Zn is observed on the Cu deposited at the cathode. The solvent is evaporated in vacuo, and the acetonitrile solvate of ZnCl₂ is converted into the unsolvated salt by careful heating. Yield 96-98\%.

If the appropriate copper salts are used, the process may also be employed for the preparation of $2nBr_3$ and $2nI_2$, and by substituting a cadmium anode for the zinc electrode, $CdBr_3$ and CdI_3 may be prepared.

Zinc chloride exists in three different crystal modifications. Details on the preparation and the structure of the pure individual modifications are given by H. R. Oswald and H. Jaggi [Helv. Chim. Acta 43, 72 (1960)].

PROPERTIES;

Coloriess, highly hygroscopic, small crystals. M.p. 313°C, hp. 732°C; d (pycn.) 2.93. Solubility per 100 ml. of H_2O : (0°C) 200 c. (20°C) 367 g. (d 2.08), (100°C) 614 g. Crystallizes in the anhydrous form only above 28°C. Soluble in methanol, ethanol, ethanol, ethanol, ethanol,

REFERENCES:

- I. O. Hönigschmid and M. von Mack. Z. anorg. allg. Chem. 249, 366 (1941); for apparatus, see O. Hönigschmid and F. Wittner. Ibid. 226, 295 (1936).
- II. R. T. Hamilton and J. A. V. Butler, J. Chem. Soc. (London) 1932, 2283.
- III. H. Schmidt. Z. anorg. allg. Chem. 271, 305 (1953).

Zinc Hydroxychloride

Zn(OH)Ct

 $Z_{RO} + Z_{RC}l_{2} + H_{2}O = 2 Z_{R}(OH)Cl$ 81.4 136.3 18.0 235.7

Zinc hydroxychloride is one of the basic zinc halides which can be prepared as well-defined crystalline compounds by several methods, for example, by dissolving ZnO in zinc halide solutions of definite concentration.

The compound is prepared by adding 6-7 g, of ZnO to 100 ml. of a 70% solution of ZnCl₂ and heating to about 150°C until solution is complete. (If seeding crystals are present, the solution becomes turbid and crystallization begins at 133°C.) A coarsely crystalline product is obtained by cooling the solution to 50°C (where the first crystals separate), then heating to 135°C and allowing the mixture to cool slowly to room temperature over a period of 24 hours. Most of the crystals deposit between 130 and 100°C. The mass is carefully crushed and washed with acetone until the filtrate exhibits only a weak opalescence on addition of AgNO₃. The product is dried in vacuum over CaCl₂.

SYNONYM:

Zinc chloride hydroxide.

PROPERTIES:

Formula weight 117.85. Colorless hexagonal leaflets. The chloride content is removed by water.

REFERENCES:

Driot. Comptes Rendus Hebd. Séances Acad. Soi. <u>150</u>, 1426 (1910); W. Feitknecht. Helv. Chim. Acta <u>13</u>, 22 (1930).

. . .

Ammonium Tetrachlorozincate

(NH4),ZnCl4

| ZnCl. | + | $2 NH_{1}Cl$ | 5 | (NH ₄) ₂ ZnCl ₄ |
|-------|---|--------------|---|---|
| 136 8 | | 107.0 | | 243.3 |

A solution of 70 g. of $ZnCl_3$ and 30 g. of NH_4Cl is prepared by besting with 29 (!) ml. of hot H_2O . It is advisable to measure the water with a balance. The homogeneous diammonium salt crystallizes on cooling. Yield 45 g.

The three-component system $ZnCl_2-NH_4Cl-H_2O$ has been investigated by Meerburg. It was found that $(NH_4)_2ZnCl_4$ can be precipitated only from solutions which have higher concentrations of $ZnCl_2$ than the desired salt. A solution containing $ZnCl_2$ and NH_4Cl in a 1:2 ratio usually yields the salt $ZnCl_2 \cdot 3NH_4Cl$.

PROPERTIES:

Shiny, orthorhombic leaflets, crystallizable only from $2nCl_2$ solutions. M.p. ~ 150°C; d 1.88. Crystal class D_{2b} .

REFERENCE:

P. A. Meerburg, Z. anorg. alig. Chem. 37, 199 (1903).

Zinc Bromide

ZnBr:

 $Zn + HBr + \frac{1}{2}Br_2 = ZnBr_2 + \frac{1}{2}H_2$ 65.4 80.9 79.9 225.2

The purest material is obtained by electrolytically dissolving purified Zn in a mixture of aqueous HBr and Br_2 in a quartz dish. The solution is digested with an excess of Zn, filtered and crystallized by evaporation. The crystals are recrystallized from dilute hydrobromic acid and separated from the mother liquor by centrifugation. The product is then sublimed in a stream of HBF-N₂.

Alternate method: See under zinc chloride, p. 1070.

PROPERTIES:

Coloriess, highly hygroscopic crystals. Sublimes, producing instrous meedles. M.p. 394°C, b.p. 650°C; d 4.201. Solubility (0°C) 388 g. (2 H_2O); (100°C) 675 g. (anhydrous $ZnBr_3$)/100 ml. H_2O . Anhydrous when crystallized above 37°C. Soluble in alcohol and ether. Crystal structure: tetragonal; space group 14_1 /acd.

REFERENCES:

G. P. Baxter and M. R. Grose, J. Amer. Chem. Soc. <u>38</u>, 868 (1916);
 G. P. Baxter and J. R. Hodges. Ibid. <u>43</u>, 1242 (1921).

Zinc lodide

Zol,

 $Z_n + I_2 = Z_n I_2$ 65.4 253.8 319.2

I. One part of zinc dust is digested with three parts of iodine and 10 parts of H_2O until disappearance of the I_3 . The mixture is filtered and concentrated over H_3SO_4 and NaOH in a vacuum desiccator (N₂ atmosphere). The ZnI₃ which crystallizes out is vacuumdistilled at about 400 °C.

Well-dried ZnI_2 , prepared by the wet method, is sublimed in an oil-pump vacuum. The evolving iodine is expelled from the apparatus. The compound is obtained as a pure white sublimate.

II. One part of zinc dust is refluxed with two to four parts (depending on the quality of the Zn dust) of iodine and 10 parts of absolutely anhydrous ether until the initial coloration of the liquid disappears completely. The residual Zn-ZnO slurry is removed from the ether solution by filtration through a fritted glass filter. Most of the ether is distilled off, leaving a product containing about 0.5 mole of ether per mole; the ether is driven off in vacuum (fanning of the flask with a flame will help).

Alternate method: See under zine chloride, p. 1070.

PROPERTIES:

Colorless, highly hygroscopic crystals. M.p. 446°C, b.p. 624°C; d 4.736. Solubility (18°C) 432 g.; (100°C) 510 g. (anhydrous salt)/100 ml. H_2O . Below 0°C, $ZnI_2 - 2H_2O$ crystallizes out of solution. Soluble in ethanol, ether, acetone and dioxane. Sublimes in vacuum (crystal needles). Decomposes on heating in air. Crystal structure: tetragonal; space group 14, /acd.

REFERENCES:

- I. T. J. Webb, J. Phys. Chem. <u>27</u>, 450 (1923); W. Biltz and C. Messerknecht, Z. anorg. allg. Chem. <u>129</u>, 161 (1923).
- IL Unpublished experiments of P. Laurer and R. Platz, Heidelberg.

Zinc Hydroxide

(crystalline)

r-Zn(OH)2

L $ZnO - NaOH + H_2O = NaZn(OH)_3 = Zn(OH)_2 + NaOH$ sl.4 40.0 18.0 139.4 99.4 40.0

Analytical grade ZnO (160 g.) is refluxed in a round-bottom flask containing a solution of 600 g. of NaOH in 300 ml. of H_2O . After the ZnO is dissolved, the solution is diluted with 300 ml. of H_2O and cooled to 60°C. At this point, the volume of the solution is about 900 ml. It is filtered and diluted 10 times with water. Crystalline Zn(OH)₂ separates out after 2-3 weeks. This is filtered, washed first with cold water, then several times with warm water, and dried over conc. H_2SO_4 .

Small needles are formed during the initial stages of crystallization; however, standing converts them into the other crystal form.

II. Amorphous $Zn(OH)_2$ is prepared by adding the stoichiometric quantity of ammonia to a solution containing a known quantity of $ZnSO_4$. The precipitate is filtered and washed thoroughly to remove as much of the adsorbed sulfate as possible (if the $Zn(OH)_2$ is worked up without preliminary washing, the product consists of basic sulfates]. The moist, washed precipitate is dissolved in the required amount of conc. ammonia. Then NH_3 is slowly separated from the solution by placing the beaker with the ammonia solution together with a beaker with H_2SO_4 under a bell jar. A large quantity of crystals is obtained within a week. It is important that the initial removal of NH_3 be slow; then the resultant crystals are 0.5 cm. long, on the average.

PROPERTIES:

Colorless crystals. In equilibrium with water, stable up to **29***C; decomposes at higher temperature. d 3.053. Crystal structure: type C31 [ϵ -Za(OH)₂ type].

In addition to the stable ϵ -Zn(OH)₂, there are five additional crystalline forms of the compound, which are unstable and convert spontaneously to ϵ -Zn(OH)₂.

REFERENCES:

- J. R. Scholder and G. Hendrich, Z. anorg, allg. Chem. <u>241</u>, 76 (1939).
- II. H. G. Dietrich and J. Johnston. J. Amer. Chem. Soc. 49, 1419 (1927).

Zinc Sulfide

ZaS

 $ZnSO_4 + H_2S = ZnS + H_2SO_4$ (7 H₂O) 287.6 22.4 l. 97.4 98.1

I. Zinc sulfide is preferably precipitated from a slightly acidic buffered aqueous solution: an aqueous solution of $ZnSO_4$ is treated with ammonium acetate; it is then saturated with H_3S with heating and frequent stirring (optimum pH for precipitation: 2-3). The precipitate is allowed to settle and the supernatant is decanted. The precipitate is shaken with 2% acetic acid saturated with H_2S ; the solid is allowed to settle and the washing is repeated. To obtain an oxide-free product, the filtration and drying should be carried out in the absence of air.

II. Well-crystallized zincblende is obtained from pure, dry precipitated zinc sulfide by heating the sulfide in a stream of nitrogen for eight hours at 600-650 °C. The reactor is a ceramic tube.

Pure wurtzite may be prepared from the same ZnS precipitate by heating in a stream of N_3 for one hour at 1150 °C.

PROPERTIES:

White powder. M.p. ~ 1650°C (appreciable volatilization); distills without decomposition at high vacuum $(5 \cdot 10^{-4} \text{ mm.})$. d 4.14, Solubility (18°C) 0.688 mg. (freshly precipitated)/100 mi. H₂O. Soluble in dilute mineral acids. Hardness 3.6-4 (both modifications). The low-temperature modification (sphalerite) crystallizes in the cubic B3 system (zincblende), the high-temperature modification (wurtzite) in the hexagonal B4 system. Transition point: about 900°C. Grinding at room temperature converts the metastable wurtzite to zincblende. REFERENCE:

H. Piats and P. W. Schenk. Angew. Chem. 49, 822 (1936).

Zinc Formaidehydesulfoxylate

Zn(SO, CH,OH);

 $\frac{2 Z_n S_2 O_4}{SS7.0} + \frac{4 CH_2 O}{120.1} + \frac{2 H_2 O}{36.0} = \frac{Z_n (SO_2 \cdot CH_2 OH)_2}{255.6} + \frac{Z_n (SO_3 \cdot CH_2 OH)_2}{287.0}$

A 33% solution of ZnS_2O_4 (1300 g.) is added to 600 g. of a 30% formaldehyde solution; the addition is accompanied by a temperature rise to 50°C. The liquid is stirred and the temperature maintained at 60-65°C for some time. The mixture is filtered and set aside for 2-3 days. The clear solution is again filtered and concentrated in vacuum while SO_2 is aspirated in through a boiling capillary. The zinc formaldehydesulfoxylate is the first to precipitate. The crystals are separated from the mother liquor by centrifugation and dried by heating in vacuum.

The tribydrate is obtained at 60°C from a solution of 100 g, of the anhydrous salt in 100 ml. of H_2O , the tetrahydrate by allowing a solution saturated at 20°C to stand for some time.

The ZnS_2O_4 solution required in the preparation cannot be prepared according to the directions given on p. 394, since the latter procedure yields aqueous solutions containing only about 10% ZnS_2O_4 . In this case it is better to react a mixture of the purest possible Zn dust (200 g.) and H_3O (400 ml.) with SO_2 , which should be prewashed with an alkaline solution of $Na_3S_2O_4$. The reaction proceeds according to:

$$Zn + 2SO_2 = ZnS_2O_4$$

65.4 128.1 193.5

and is carried out in a wide-neck Erlenmeyer flask at 35-40 °C (stirring). Initially, the mixture must be cooled; later it should be warmed. After several hours the reaction siurry is allowed to settle and the product is filtered through a Buchner funnel. The concentration of the viscous, unstable solution is determined by titration with a 0.01 M solution of indigo carmine [1 mole of indigo is equivalent to 1 mole of $S_3O_4^{3-}$; for additional analytical methods see G. Panizzon, Melliand Textilber. 12, 119 (1931)].

A method for the preparation of secondary zinc formaldehydemethodylate is described in M. Bazlen, Ber. Dtsch. chem. Ges. 29, 1470 (1927); cf. also K. Jellinek, Das Hydrosulfit [Hydroxysuline], Part II, Stuttgart, 1912.

SYNONYMS:

Primary zinc oxymethanesulfinate; monozinc formaldehydesulfoxylate.

A technical-grade product containing over 90% of the anhydrous compound is available under the names Dekrolin soluble conc. (BASF), water-soluble Hydrosulfit BZ (Ciba), Sulforite S conc. (Du Pont), etc.

PROPERTIES:

Colorless crystal needles. The anhydrous salt is stable in air. The trihydrate (flakes with a nacreous luster) and the tetrahydrate (rhombohedral leaflets) are more labile. Soluble in H_3O . The solution acts as a bleaching agent and is quite resistant to acids. The reducing activity increases markedly with temperature; the rH values of a formic acid solution at pH 3 are: (25°C) 15; (50°C) 2; (90°C) a maximum of 0.5. Decomposes on prolonged boiling. The warm solution turns alkaline indanthrene yellow G paper blue and decolorizes an alcoholic solution of neutral red.

REFERENCES:

K. Winnacker and E. Weingaertner, Chem. Technologie, Vol. 2, p. 80, Munich, 1950; BIOS Final Report No. 422, London, 1945; H. von Fehling, Neues Handwörterb, d. Chemie [New Handbook of Chemistry], Vol. X, p. 291, Braunschweig, 1930; A. Schaeffer, Melliand Textilber, 30, 111 (1949).

Ammonium Zinc Sulfate

(NH4),Zn(SO4), 6 H4O

| $(NH_4)_2SO_4$ | + $Z_n SO_4 \cdot 7 H_t O =$ | $(NH_4)_2 Zn(SO_4)_2 \cdot 6 H_2O$ | + H _t O |
|----------------|------------------------------|------------------------------------|--------------------|
| 132.1 | 287.6 | 401.7 | 18.0 |

A solution of 45.2 g. of $2nSO_4 \cdot 7H_2O$ and 20.8 g. of $(NH_4)_2SO_4$ is prepared in 75 ml. of boiling H_2O . The solution is filtered through a jacketed funnel heated with hot water. The crystalls precipitating from the filtrate are separated from the mother liquor and dried in vacuum over anhydrous ammonium zinc sulfate or H_2SO_4 . Yield 50 g.

PROPERTIES:

Water-clear, efflorescent, monoclinic crystals, Solubility of the anhydrous salt (0°C) 7.3 g.; (20°C) 12.6 g.; (85°C) 46.2 g. per 100 mi. H₂O. d 1.93. Space group C_{Sb}^{S} .

Zinc Selenide ZnSe ZnSO₄ + H₁Se = ZnSe + H₂SO₄ (7 H₂O) 287.6 22.41. 144.3 98.1

L A dilute solution of $ZnSO_4$, buffered with ammonium acetate, is added dropwise to a saturated aqueous solution of H_2Se , while a stream of H_2Se (from Al_2Se_3 and dilute HCl), diluted with oxygenfree N_2 or H_3 , is passed through the liquid. The precipitation vessel is heated on a steam bath. The excess H_2Se bubbling out of the solution is absorbed in a wash bottle filled with conc. nitric acid. If the Zn salt solution is introduced too rapidly or in too high a concentration, a white precipitate is formed; it requires a very long time to convert to the yellow ZnSe. Since the yellow ZnSe precipitate is difficult to filter, it is centrifuged and then washed (by centrifugation) first with boiled, weakly ammoniacal H_2O and then with methanol. It is dried in a vacuum desiccator over CaCl₂, then at 120°C in a drying pistol over P_2O_5 .

When moist, zinc selenide is very sensitive to air. Therefore, to remove oxidation products the dry product is placed in a tube and heated for 2-4 hours at 600°C in a stream of H_2 or H_2 Se. A boat containing a small amount of Se is placed ahead of the product. The heating is continued until all the Se in the boat evaporates. The cubic modification is thus obtained.

The hexagonal modification is obtained by treating $ZnCl_2$ vapor with H₂Se.

II. ZnSe may be prepared by a dry method from a mixture of 4 g. of ZnO, 2.5 g. of ZnS, and 6 g. of Se according to:

 $2 ZnO + ZnS + 3 Se = 3 ZnSe + SO_{2}$ 162.7 97.4 236.9 433.0 64.1

The mixture is heated for 15 minutes at 800°C in a covered quartz crucible.

It is also possible to start from 5 g. of ZnS and 6.5 g, of H_3 SeO₃, and then proceed as above. The reaction is formulated as:

$$ZnS + SeO_{4} = ZnSe + SO_{4}$$

97.4 111.0 144.3 64.1

PROPERTIES:

Lemon-yellow powder. Soluble in fuming hydrochloric acid with evolution of H₂Se. d (pycn.) 5.30. Crystal structure: type B3 (zincblende type) or B4 (wurtzite type). REFERENCES:

- I. R. Juza, A. Rabenau and G. Pascher. Z. anorg. alig. Chem. <u>285</u>, 61 (1956); Fonzes-Diacon. Comptes Rendus Hebd. Séances Acad. Sci. <u>130</u>, 832 (1900).
- II. A. Schleede and J. Glassner. German Patent 699,320 (1938), issued to Telefunken Co.

Zinc Amide

Zn(NH_t)_r

 $\begin{array}{rrrr} Zn(C_2H_5)_2 &+& 2NH_3 &=& Zn(NH_3)_2 &+& 2C_2H_6 \\ 123.5 & 34.1 & 97.4 & 60.1 \end{array}$

The preparation is carried out in the apparatus of Fig. 281. Diethylzinc is introduced into the storage vessel through the side tube, a blanket of CO₂ being provided; the side tube is then sealed. For each run, about 3 g, of Zn(CaH5)a is vacuum-distilled from a to b. The apparatus is then filled through stopcock c with very pure N2. The tube connecting the two vessels is broken at d, and 50 ml. of absolute ether, carefully dried with Na wire, is added through e. During these manipulations, the system is flushed with a fast stream of N_2 , which is introduced at c and leaves the apparatus through a CaCl₂ tube attached at d. The $Zn(NH_3)_2$ is precipitated from the ether solution by a stream of carefully purified NH3. Simultaneously, the ether in b is evaporated, an operation which requires about two hours. The product is comminuted by shaking (glass slug f is already present in b). Ammonia is then passed over the product for five hours at 160°C and for 12 hours at room temperature.

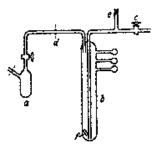


Fig. 281. Preparation of zinc amide. a storage vessel for diethylzinc; f glass slug.

1. 1995 (Mar) 1995 (Mar)

NOPERTES:

Colorisss, amorphous; decomposes slowly in air. d 2.13.

REFERENCE:

R. Juss, K. Fasold and W. Kuhn, Z. anorg, allg. Chem. 234, 86 (1937).

Zinc Nitride

Zn₂N₂

 $3 Z_n + 2 NH_s = Z_{n_s}N_r + 3 H_r$ 196.1 34.1 224.2 6.1

A porcelain boat containing ~7 g. of zinc dust is placed in a Vycor tube. The material is heated in a rapid stream of NH₃ for 17 hours at 500°C, for eight hours at 550°C, and finally for 16 hours at 600°C. In the process, about 3 g. of Zn is lost by distillation. The remainder is converted to Zn_3N_3 . This procedure assumes that the zinc does not fuse into a solid mass, even though it requires temperatures above the melting point for complete conversion to the nitride.

PROPERTIES:

Gray-black; quite stable in air. d (x-ray) 6.40. Crystal structure: type $D5_3$ (Mn₂O₃ type).

REFERENCE:

B. Juza, A Neuber and H. Hahn. Z. anorg. allg. Chem. 239, 273 (1938).

Zinc Phosphides

Zu,P., ZnP.

| 3 Zn | + 2P | = Zn,P, | Zn | + | 2P | = | ZnP, |
|-------|------|---------|----|---|----|---|-------|
| 198.1 | 62.0 | 258.1 | | | | | 127.3 |

L. Weighed quantities of zinc and a very slight excess of red photoborus (total about 12 g.) are slowly heated to 700°C in an concented quartz tube, about 12 cm. long and 10-12 mm. L.D.,

placed in an electric furnace. One end of the tube is allowed to project from the furnace to condense the volatilized phosphorus, which when liquid reacts very rapidly with the zinc. The Zi_3P_4 is then heated to 850°C, sublimed to the other end of the tube, which is maintained at 760°C, and kept at this temperature for about one day. A dense, homogeneous sublimate is obtained.

II. A mixture of Zn_3P_2 and ZnP_2 is obtained by passing phosphorus vapor over hot zinc (the procedure is outlined in the case of Zn_3As_2 , method I; see p. 1083).

PROPERTIES:

 Zn_3P_3 : Gray. d (x-ray) 4.54. Evolves PH₃ with acids. Crystal structure: tetragonal, type D5₉ (Zn_3P_3 type).

 ZnP_2 : Orange to red needles. d (x-ray) 3.51. Sublimes without decomposition in an atmosphere containing phosphorus vapor; insoluble in nonoxidizing acids. Crystal structure: tetragonal; space group D_4^4 or D_4^8 .

REFERENCES:

I. R. Juza and K. Bär. Z. anorg. allg. Chem. <u>283</u>, 230 (1956).
 II. M. von Stackelberg and R. Paulus. Z. phys. Chem. (B) <u>28</u>, 427 (1935).

Zinc Phosphate

Zn_s(PO₄)₂ · 4 H₂O

S ZnSO₄ · 7 H₂O + 2 N₃₂HPO₄ · 2 H₂O 862.7 358.0

 $= 2 H_{3}(PO_{4})_{2} \cdot 4 H_{4}O + 2 Na_{2}SO_{4} + H_{4}SO_{4} + 21 H_{4}O$ 458.2 284.1 98.1

A solution of 5.8 g. of $ZnSO_4 \circ 7H_2O$ in 400 ml. of H_2O is stirred at the boiling point with a solution of 2.5 g. of $Na_2HPO_4 \circ 2H_2O$ in 100 ml. of H_2O . The crystalline precipitate which forms in mediately is analytically pure.

II. $3 Z_{II}O + 2 H_{s}PO_{4} + H_{s}O = Z_{Pa}(PO_{4})_{s} \cdot 4 H_{s}O^{2}$ 244.1 196.0 18.0 458.2

A 69% solution of H_0 PO₄ (d 1.52, 100 g.) is saturated at the boiling point (121°C) with ZnO (about 42 g.), taking care to solution is then cooled to cooled to

ľ,

temperature and finally placed in ice. Ten parts (by volume) of ice-cold water is added with vigorous stirring and the solution is filtered into a porcelain dish, in which it is heated (with stirring) on a steam bath. The transparent lamellae of the tetrahydrate precipitate after a short time; they are suction-filtered, washed with bolling water, and dried on a clay plate. Yield 16 g.

PROPERTIES:

Colorless crystals, needle-shaped and tabular. Solubility in H₂O decreases with increasing temperature; can be recrystallised only from solutions containing phosphoric acid. Soluble in dilute acids and dilute ammonia. Loses two moles of H_2O at 100°C, a third mole at 190°C; the anhydrous salt is obtained at about 250°C. d 3.109. Hardness 2-3. Crystal structure; orthorhombic.

SYNONYM:

Zinc orthophosphate.

REFERENCES:

- L. E. Thilo and J. Schulz, Z. anorg. allg. Chem. 265, 201 (1951).
- IL. N. E. Eberly, C. V. Gross and W. S. Crowell. J. Amer. Chem. Soc. 42, 1432 (1920).

Zinc Hydroxyphosphate

Zn₄(OH)PO₄

| $Zn_{i}(PO_{i})_{r}$ | + | ZnQ | + | H _f O | 2 Zn ₂ (OH)PO ₄ |
|-----------------------------|---|------|---|------------------|---|
| 4 H ₁ O 458.2 | | 81.4 | | 18.0 | 485.5 |

An intimate mixture of 1.146 g. (0.0025 mole) of $Zn_3(PO_4)_2 \cdot 4H_2O$ (cf. p. 1081) and 1.63 g. (0.02 mole) of ZnO is placed in a porcelain crucible and covered with water; the crucible is half full at this point. The crucible is heated in an autoclave for seven bours at 190°C and 12 atm. The product is digested with 8% methanolic acetic acid on a fritted glass filter and is then washed until the filtrate is free of Zn. After drying at 100°C, the product is analytically pure.

PHOPE BTIES:

Formula weight 242.75. The colorless crystals are identical with the miseral tarbutite. The water of hydration is given off above 456°C. Crystal structure: triolinic.

REFERENCE:

E. Thilo and I. Schulz, Z. anorg. allg. Chem. 265, 201 (1951).

Zinc Arsenides

ZasAss, ZaAss

 $3 Zn + 2 As = Zn_3As_2$ $Zn + 2 As = ZnAs_2$ 196.1 149.8 348.0 55.4 149.8 215.2

I. A Vycor tube containing a porcelain boat with pure zinc is heated to 700°C in an electrical furnace; the atmosphere in the tube consists of dry, pure N_{σ} or H_{σ} . The As, in a second porcelain boat, is placed at the end of the tube which projects out of the furnace and is heated with a gas flame. The As vapor thus produced is carried over the metal by the stream of N_{σ} or H_{σ} . Since the metal has already an appreciable vapor pressure at 700°C, crystals of Zn_3As_{σ} form on the boat rim and on the tube wall, while the unevaporated metal in the boat is converted to a grayblack mass of arsenide.

II. Heating stoichiometric quantities of Zn and As in an evacuated, sealed Vycor bomb at 780° C yields Zn_3As_3 . The same conditions will produce $ZnAs_3$, provided an excess of As is used, since the vapor pressure of As in $ZnAs_2$, which results in decomposition of the latter, is quite high at the above temperature.

PROPERTIES:

 Zn_3As_3 : Gray. Gives off AsH₃ with acids. M.p. 1015°C; d (x-ray) 5.62. Sublimes at the m.p. to give needles or iamellae. Possesses metal-type conductivity. Hardness 3. Crystal structure: type $D5_9$ (Zn_3P_3 type).

ZnAs₂: Gray black. Orthorhombic crystals. M.p. 771°C. Sublimes at the m.p. Hardness 3. d (x-ray) 5.08.

REFERENCES:

M. von Stackelberg and R. Paulus. Z. phys. Chem. (B) 28, 427 (1935); W. Heike. Z. anorg. allg. Chem. <u>118</u>, 264 (1921).

Zinc Thioantimonote

Zn_a(SbS₄)₁

 $3 Z_n Cl_2 + 2 N_{B_0} SbS_4 \cdot 9 H_4 O = Z_{D_3} (SbS_4)_2 + 6 N_2 Cl + 18 H_4 O$ 408.9 962.3 696.1 350.7 324.3

A solution of 25 g. of Schlippe's salt (see p. 619) in 75 mH of H_2O is treated with a solution of 10.6 g. of $ZnCl_2$ (or 22.5 g. of

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EnSO₄ • **TH**₂O) in 50 ml. of H₂O. The chrome yellow precipitate is washed several times by centrifugation with hot water. It is dried at 80°C, then at 100°C; the orange product is ground. It contains about 6% free S, which is extracted in a Soxhiet apparatus with CS_{2n}

PROPERTIES:

Orange powder. Decomposed by HCl. Discolors at 160°C; loses S at 200°C, forming Sb_2S_3 . The corresponding Cd salt is orange-red, the mercury (II) salt ocher yellow. d (pycn.) 3.76.

REFERENCE:

F. Kirchhof, Z. anorg. allg. Chem. 112, 67 (1920).

Diethyizinc

Zn(C:Hi):

| Zo + | - C ₂ H ₂ I | - C,H,ZnI | $2C_{2}H_{3}ZnI =$ | $\operatorname{Zn}(C_2H_5)_2$ | $+ ZnI_2$ |
|------|-----------------------------------|-----------|--------------------|-------------------------------|-----------|
| 65.4 | 156.0 | 221.4 | 442.7 | 123.5 | 319.2 |

I. The 500-ml. flask a of Fig. 282 is charged with 200 g, of dry C_2H_5I (prepared by heating C_2H_5I with Na chips, and siphoning off and distilling the liquid) and 200 g, of zinc dust, previously cleaned with acid and dried at 160-180°C in a

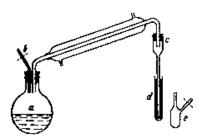


Fig. 282. Preparation of diethylzinc. d mercury seal; e ampoule for product storage. stream of CO₃. Dry zinc turnings are then added until the pile of metal projects above the surface of the liquid. A stream of dry, air-free CO₂ or N₂ is introduced through b, expelling the air in the system. When the apparatus is filled with inert gas, the tip of tube c is dipped slightly into the mercury in cylinder dand capillary b is rapidly flame-sealed. The flask is then heated in an 80°C water bath. The temperature of the

both is gradually raised to 96° C, while the tip of c is lowered into the mercury until it reaches about 20 cm. below the level of the metal. If all necessary precautions to exclude moisture have been taken, the reaction starts after about 1-1.5 hours of refluxing.

The reaction is complete after an additional 1.5-2 hours, when no further droplets of C_2H_6I condense in the flask (solid C_2H_8Znf). The sealed capillary b is cut open, d is removed and replaced by vessel e, and a slow stream of the inert gas is passed through the system. The flask is then tilted so that the condenser points downward, and the $Zn(C_3H_6)_2$ is distilled on an oil bath (about 200°C) into e, which is then sealed in the usual way. Yield about 92%.

H. In Dennis's procedure, the starting material is a zinc-copper compound prepared by reducing a mixture of 200 g. of Zn dust and 25 g. of finely powdered CuO for 20 minutes at 400°C in a stream of H_2 ; the product must be used immediately. Sufficient contact area between the metal and the C_2H_6I is achieved by mixing the finely ground metal with an equal amount of dry sand.

III. Larger quantities of $Zn(C_2H_5)_2$ may be prepared starting from a zinc alloy containing 5-8% Cu, which is prepared by fusing Zn with brass, casting into rods and cutting into chips. When this alloy is used, one half the necessary quantity of the quite expensive C_2H_5I may be replaced by C_2H_5Br . The reaction is then less vigorous.

The product $Zn(C_{2}H_{5})_{2}$ is freed of ethane and $C_{2}H_{5}I$ by lowpressure fractional distillation. It is stored in sealed ampoules or in a flask provided with a well-greased stopcock.

The same procedure may be used for the preparation of: di-n-propylzinc, b.p. (9 mm.) 40°C; di-n-butylzinc, b.p. (9 mm.), 81°C; and disopentylzinc, b.p. (12 mm.) 100-103°C.

PROPERTIES:

Colorless liquid. M.p. -30° C, b.p. (760 mm.) 117.6°C, (30 mm.) 27°C, (4 mm.) 0°C; d (20°C) 1.207, (8°C) 1.245. Resistant to CO₂; ignites in air. Decomposes extremely violently in H₂O, forming Zn(OH)₂ and C₂H₈. Soluble in ether.

REFERENCES:

- L. E. Krause and A. von Grosse. Chemie d. metallorgan. Verbindungen [Chemistry of Organometallic Compounds], Berlin, 1937 [preparative directions cited from Simonovich. Zh. Russ. Fiz.-Khim. Obsch. <u>31</u>, 38 (1899)].
- II. L. M. Dennis, Z. anorg. allg. Chem. 174, 133 (1928).
- III. Organic Syntheses. Coll. Vol. 2, New York and London 1943/50, p. 184; H. Grubitsch. Anorgan.-prap. Chemie [Preparative Inorganic Chemistry], Springer, Vienna, 1950, p. 458; A. W. Laubengayer and R. H. Fleckenstein. Z. anorg. allo: Chem. 191, 283 (1930).

Zinc Carbonate

ZnCO₁

L $2nSO_4 + 4$ KHCO₃ = $ZnCO_3 + K_3SO_4 + K_4CO_3 + 2$ CO₃ + 2 H₄O (7 H₆O) 367.6 400.3 125.4 174.3 138.2

Neutral $ZnCO_3$ is obtained when zinc carbonate, precipitated at as low a temperature as possible, is allowed to age for a long time at low, gradually increasing temperature in a CO_2 -free atmosphere.

A IN KHCO₃ solution (300 ml.), cooled to 3° C and saturated with CO₃, is added with stirring to 700 ml. of a 0.1M ZnSO₄ solution at the same temperature. The temperature is maintained below 10°C during the first 3-4 days; it is then raised to 20°C and maintained there for an additional 2-3 days until the initial flaky precipitate has been transformed into a finely crystalline deposit. The product is washed several times by decantation with water, taking care to remove the flocculent material floating in the supernatant liquor, and washed free of sulfate on a filter. It is dried in a desiccator at room temperature, or by heating at 130°C.

The x-ray powder pattern of the product heated at 130 °C corresponds to that of natural smithsonite (ZnCO₃), but contains seven additional lines. The yield is satisfactory.

| | ZnCl ₂ + 136.3 | 4 KHCO ₄ + x CO ₂ 400.5 |
|-----------------------|------------------------------|--|
| = ZnCO ₅ + | 2 KCl + | $K_2CO_3 + (x + 2) CO_2 + 2 H_2O$ |
| 125.4 | 149.1 | 138.2 |

Preparation by rapid aging at moderate temperature under CO_2 pressure: 10 mi, of a conc. solution of $ZnCl_2$ is frozen with Dry Ice in a freezing tube. A fourfold excess of solid KHCO₃ and 10 mi. of H₂O are added. A few pieces of Dry Ice are added on top and the tube is melt-sealed while still cold. It is kept at room temperature until the contents melt. The tube is then held at 130°C for two hours.

Departures from the above two procedures result in basic products.

PROPERTIES;

Coloriess. Converts to the basic salt on boiling with water. **Thermal decomposition** begins at 140°C; at 295.5°C the pressure of CO₂ is 700 mm. Solubility 5.7 \cdot 10⁻⁵ g./100 ml. H₂O. Readily

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soluble in acids. d (pycn.) 4.4; d (x-ray) 4.51. Hardness 5 (natural zincspar). Crystal structure: rhombohedral, type G0₁ (calcute type).

REFERENCE:

G. F. Hüttig, A. Zörner and O. Hnevkovsky. Monatsh. Chem. <u>72</u>, 31 (1939).

Zinc Acotate

Zn(CH₁COO),

| $Z_0(NO_3)_2 \cdot 6 H_2O$ | $+ (CH_3CO)_2O =$ | Zn(CH ₃ COO) ₁ | + 2 HNO ₁ + | 5 H ₁ O |
|----------------------------|-------------------|--------------------------------------|------------------------|--------------------|
| 297.5 | 102.1 | 183.5 | 126.0 | 90.1 |

A mixture of 10.2 g. of $Zn(NO_3)_2 \cdot 6H_2O$ and 40 ml. of acetic anhydride is heated. When the vigorous reaction ceases, the mixture is stored in the cold for some time; the crystal slurry is then suction-filtered, washed with some acetic anhydride and ether, and dried in vacuum over KOH and H_2SO_4 . Yield 95%.

PROPERTIES:

Coloriess, hexagonal, prismatic crystals. M.p. 242°C. Sublimes in vacuum without decomposition at lower temperatures; decomposes at temperatures higher than the m.p. d 1.84. Sparingly soluble in cold water, dissolves slowly in warm water. The dihydrate crystallizes from dilute acetic acid, the monohydrate from water and absolute alcohol.

REFERENCE:

E. Späth. Monatsh. Chem. 33, 240 (1912).

Zinc Cyanide

Za(CN)₂

| L. | ZnSO4 | + | 2 KCN | 9775 | $\operatorname{Zn}(\operatorname{CN})_{i}$ | ≁ | K ₂ SO ₄ |
|----|-------------------------------|---|-------|------|--|---|--------------------------------|
| | (7 H ₂ O) 287.6 | | 130.2 | | 117.4 | | 174.8 |

A solution of 10 g. of $ZnSO_4 \cdot 7H_2O$ in 100 ml. of H_2O is mixed (constant stirring) with a KCN solution until no further precipitate is formed (about 5 g. of KCN in 50 ml. of H_2O is needed). The

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1992 ang sa 199**4 a**ng sa precipitate, which settles well on prolonged boiling, is washed repeatedly with hot H_9O and dried either with alcohol and ether or at 70 °C. Yield about 4 g.

E. $Z_{m}(CH_{s}COO)_{t} + 2 HCN = Z_{n}(CN)_{t} + 2 CH_{s}COOH$ US3.5 54.1 117.4 120.1

The $Zn(CN)_{3}$ is precipitated with hydrocyanic acid from a solution of $Zn(OH)_{3}$ in $CH_{3}COOH$. After washing, the product is dried at 110°C.

PROPERTIES:

White, amorphous powder or shiny, rhombic prisms. Insoluble in H₃O and alcohol. Soluble in alkali cyanides and aqueous ammonia; soluble in dilute acids (evolution of HCN). Decomposes at 800°C; d 1.852. Crystal structure: type C3 (Cu₂O type).

REFERENCES:

- L. Ullmann. Enzyklopädie d. techn. Chem. [Encyclopedia of Ind. Chem.], 2nd ed., 10, 718; Loebe. Thesis, Berlin, 1902.
- II. W. Biltz. Z. anorg. alig. Chem. 170, 161 (1928).

Potassium Tetracyanozincate

K₂Zn(CN)₄

L $Z_{R}(CN)_{t} + 2 KCN = K_{t}Z_{R}(CN)_{t}$ 117.4 130.2 247.7

Zinc cyanide is dissolved in the equivalent amount of KCN solution. About 10 min. is required at room temperature; the process may be accelerated by heating. The salt precipitates from the solution on concentrating.

II. $Z_{20} + K_{2}CO_{2} + 4HCN = K_{2}Zn(CN)_{4} + CO_{4} + 2H_{2}O_{5}$ 81.4 138.2 108.1 247.7 44.0

Zinc oxide is suspended in an aqueous solution of the equivalent quantity of K_2CO_3 and treated for several days with gaseous HCN antil completely dissolved. Small crystals of the salt complex precipitate from the concentrated filtrate. They are dried at 165°C.

PTHONTH:

Petassium zinc cyanide, zinc potassium cyanide.

PROPERTIES;

Transparent octahedra. M.p. 538°C; d 1.647. Solubility (20°C) 11 g./100 ml. H₂O, 1 g./210 g. of 88% v./v. alcohol. Readily soluble in liquid NH₃. Crystal structure: type B1 (spinel).

REFERENCES:

I. F. Spitzer. Z. Elektrochem. 11, 347 (1905).

II. W. Biltz. Z. anorg. allg. Chem. 170, 161 (1928).

Zinc Silicate

ZB₂SiO₄

 $2 ZnO + SiO_2 = Zn_2SiO_4$ 162.8 60.1 222.8

I. Two moles of ZnO and one mole of SiO_3 are intimately mixed. The reaction is facilitated by using finely divided starting materials and compressing the mixed powder into 5-g. tablets. The mixture is placed in a platinum boat inside a ceramic protective tube and heated above the melting point of $2n_2SiO_4$ (>1512°C) in a Tammann furnace. The protective tube is closed at one end, which helps to exclude the reducing furnace gases to some extent. The reaction may be observed through a port made of cobalt glass. The melting point is reached when the upright raw material tablet collapses. To prevent evaporation of the ZnO, the heating must be rapid.

II. Tablets made of a mixture of two moles of Zno and one mole of amorphous SiO_2 are heated for four days between 900 and 1000 °C. The x-ray powder pattern of the resultant product indicates a homogeneous material.

III. Pneumatolytic-hydrothermal synthesis from ZnO and ZiO_2 in an autoclave at 365 °C.

SYNONYM:

Zinc orthosilicate.

PROPERTIES:

Colorless. Soluble in 20% HF, decomposed by HCl. M.p. 1512°C; d 4.103. Hardness 5.5; crystal structure: type Sig (Be₃SiO₄ type). At 1432°C, forms a sutscript containing one mole of SiO₃. Phosphoresces on activation with manganese.

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DEVERSIONCES:

- I. W. Bilts and A. Lemke. Z. anorg. allg. Chem. 203, 330 (1932).
- **B.** A. Pabst. Z. phys. Chem. (A) <u>142</u>, 227 (1929). **B.** C. J. van Nieuwenburg and H. B. Blumendahl. Rec. Trav. Chim. Pays-Bas 50, 129 (1931).

Zinc Fluorosilicate

ZnSiF. · 6 H.O

 $Z_nO + H_sSiF_s + 5H_sO = ZnSiF_s \cdot 6H_sO$ 315.5 81.4 144.1 1.02

Somewhat less than the stoichiometric quantity of ZnO is dissolved in aqueous H2SiFe. Complete saturation is avoided because it produces hydrolysis with formation of colloidal silicic acid. The mixture is evaporated on a steam bath in a platinum or lead dish until a film forms on the surface; the film is redissolved with some water and the product is allowed to crystallize over H_SO, in a desiccator.

SYNONYM:

Zinc fluosilicate.

PROPERTIES-

Colorless, rhombohedral prisms, stable in air. Solubility (0°C) 50.3 g. of the anhydrous salt, (10°C) 52.8 g./100 ml, of saturated solution. A saturated solution at 20°C has d~1.4. d (pycn.) 2.139, d (x-ray) 2.15. Crystal structure: trigonal.

REFERENCES:

W. Stortenbecker. Z. phys. Chem. (A) 67, 621 (1909); O. Ruff, C. Friedrich and E. Ascher. Angew. Chem. 43, 1081 (1930).

Zinc Ferrate (III)

ZnFerO,

Ł $ZnO + Fe_2O_3 = ZnFe_3O_4$ 81.4 159.7 241.1

L Zine oxide, precipitated from ZnCl₂ solution and dried in **vacuum over P_2O_5**, is mixed with α - or γ -FeOOH in a ratio of

 $12nO:1Fe_2O_3$, taking into account the water content. The mixture is then screened and weighed out. The powder is mixed for four hours in a Pyrex bottle on a mechanical shaker. Following this, 4-g. portions of the mixture are placed in an open platinum crucible, which is then set in an electric furnace. The reaction may be carried out either at 800°C in a stream of dry air or at 1000°C in the absence of such an air flow. In either case, one hour is required for the reaction.

When ZnO (prepared by heating ZnCO₃ for two hours at 1000°C) and Fe_2O_3 are used instead of the above-specified raw materials, the mixture must be calcined for six hours at 800°C to obtain a ZnFe₂O₄ with a pure spinel lattice.

A solution of 2.4 moles of NaOH in 300 ml. of H_3O is allowed to react with a solution of 0.15 mole of $ZnCl_3$ in 100 ml. of H_3O . The resultant Na[Zn{OH}_3] solution is treated with a solution of 0.3 mole of FeCl₃ · 6 H₃O and 1.2 moles of HCI in 5000 ml. of H₂O (vigorous stirring) and, after stirring two hours, heated for 0.5 hour at 60°C. The mixture is allowed to settle and is then allowed to react with 2N NaOH to a permanent red phenolphthalein color. The product is washed by repeated decantation with 2500-ml, portions of H₂O until the supernatant is free of Cl⁻ (about 15 washings are required), filtered through a sintered glass filter, washed until the solid is free of Cl⁻, and dried in a vacuum desiccator over P_3O_5 and solid KOH. The product then consists of almost black, highly lustrous, brittle pieces. These are crushed, sieved through a 0.15-mm. screen, and redried in the desiccator.

After annealing for one hour at 60°C, two spinel interferences are barely recognizable in the x-ray powder pattern. The spinel pattern becomes fully developed after heating to 500°C.

PROPERTIES:

Dry, brown $ZnFe_3O_4$ is paramagnetic when prepared by either the dry or the wet method. It absorbs more than its equivalent of Fe_2O_3 while maintaining its crystal lattice and becomes ferromagnetic. The magnetizability of these products is maximum at about 70 mole% Fe_3O_3 . d (x-ray) 5.395. Crystal structure: type H1₁ (spinel type).

REFERENCES:

R. Fricke and W. Dürr. Z. Elektrochem. 46, 254 (1939); G. F. Hüttig. M. Ehrenberg and H. Kittel. Z. anorg. allg. Chem. 228. 112 (1936).

Rinmann's Green

A mixture of the carbonates or oxalates of Zn and Co with an equal amount of KCl (e.g., 15 g. of ZnCO3, 3.5 g. of CoCO3, and 18.5 g. of KCl) is heated several hours at high temperature (> 1000°C) in a Pt crucible. (The KCl serves as a flux and mineralizer.) The material should then be cooled under a CO₂ blanket. The reaction is brought to completion by repeating the procedure several times followed by washing. The KCl must be replenished between heatings.

At higher temperatures and on vacuum calcination, the color becomes lighter; it is malachite green in the presence of an excess of Zn, brownish pink with an excess of Cn. Products calcined below 1000*C contain green-black ZnCn₂O₄.

Rinmann's green consists of mixed ZnO-CoO crystals; the green, Co-deficient products (up to about 30% Co) consist of a solid solution of CoO in ZnO (wurtzite lattice). The pink, Co-rich preparations (above 70% CoO) are solutions of ZnO in CoO (NaCl lattice). The intermediate region is heterogeneous.

SYNONYMS:

Cobait green, turquoise green, cinnabar green.

PROPERTIES:

Soluble in weak acids and solutions of $(NH_4)_2CO_3$, d ~ 5.5.

REFERENCES:

J. A. Hedvali, Z. anorg. allg. Chem. 86, 201 (1914); C. Natta and L. Passerini. Gazz. Chim. Ital. 59, 620 (1929).

> Cadmium (needles) Cd. $CdSO_4 = Cd + H_2SO_4 + \frac{1}{2}O_2$ (% H₂O) 256.5 112.4

Two platinum disk electrodes (diameter 4.5 cm.) are placed one above the other (distance of about 5 cm.) in a vertical glass

98.1

cylinder (I.D. 7 cm.). The lower electrode serves as the cathode, the upper as the anode. The electrolyte is a conc. CdSO₄ solution slightly acidified with H_2SO_4 . The Cd is deposited as a fine crystalline powder on the cathode at a current density of 0.1-0.3 amp./cm.² The electrolysis vessel fills up quite rapidly with the silvery crystal powder. From time to time the loose powder is compressed with a glass rod to prevent establishment of a short circuit with the anode.

When the Cd in the electrolyte is depleted to such an extent that H_2 begins to evolve at the cathode, the solution must be replenished with CdSO₄ to avoid formation of a spongy deposit (the latter also appears at excessive current densities).

The compound is used as filler in the Jones reductor.

PROPERTIES:

Silvery-white crystal powder. M.p. 321°C, b.p. 765°C; d 8.642. Bulk density 80%. Solubility (18°C) 5.17 g./100 g. Hg. Soluble in mineral acids. Hardness 2. Electrochemical equivalent 2.097 g. $(amp.-hr.)^{-1}$. Crystal structure: type A3 (Mg type).

REFERENCES:

F. P. Treadwell. Helv. Chim. Acta <u>4</u>, 551 (1921); F. P. Treadwell. Lehrbuch d. analyt. Chemie [Analytical Chemistry], Vol. 2, Vienna, 1949, p. 542.

Cadmium Chloride

CdCl₂

 $Cd(NO_s)_2 + 2 HCl = CdCl_2 + 2 HNO_3$ (4 H₂O) 308.5 72.9 183.3 128.0

Repeated evaporation with very pure conc. hydrochloric aoid converts $Cd(NO_3)_2 \cdot 4H_2O$ to the chloride. The product is recrystallized twice. Partial dehydration is achieved by storing for a prolonged time in a vacuum desiccator containing fused KOH (which is frequently replaced). Final dehydration is achieved by careful heating of the product in a stream of HCl, distilling twice in the same stream, and finally fusing the distillate under pure N_3 .

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$$Cd + 2HCl = CdCl_{*} + H_{*}$$

The reaction between Cd and HCl at 450°C is smooth and uniform. The chloride is distilled twice in a stream of HCl and melted under N_{2} .

28. $Cd(CH_{3}COO)_{s} + 2 CH_{3}COCl \approx CdCl_{s} + 2 (CH_{3}CO)_{s}O$ **290.5** 157.0 183.3 204.2

A warm solution of about 4 g, of cadmium acetate (dry) in anhydrous acetic acid (or a mixture of the latter with acetic anhydride) is treated with a slight excess of acetyl chlorine or with geneous HCl. The white precipitate which appears immediately is centrifuged off, washed once or twice with dry benzene, and dried at 190-120°C.

Cadmium bromide may be prepared by the same procedure from cadmium acetate and acetyl bromide (or HBr gas).

PROPERTIES:

Coloriess rhombohedral leaflets. M.p. 568° C, b.p. 967° C. Solubility (0°C) 90.1 g. (2.5-hydrate), (20°C) 111.4 g. (2.5-hydrate), (100°C) 150 g. (1-hydrate)/100 ml. H₂O. Crystallizes as the monohydrate above 34°C. Solubility (15.5°C) 1.7 g. of anhydrous CdCl₂ per 100 g. of ethanol or methanol. d 4.047. Crystal structure: type C 19 (CdCl₂ type). Method III yields a white, microcrystalline powder which in the cold tends to form gelatinous inclusion products with various solvents (e.g., benzene).

REFERENCES:

O. Hönigschmid and R. Schlee. Z. anorg. allg. Chem. 227, 184 (1936); H. D. Hardt. Private communication; A. R. Pray. Inorg. Syn. <u>5</u>, 153 (1967); E. R. Epperson et al. Ibid. <u>7</u>, 163 (1963).

Codmium Hydroxychloride

Cd(OH)Cl

Of the five basic cadmium chlorides, Cd(OH)Cl has the highest chloride content; it is the stable end product of the hydrolysis of not too dilute solutions of CdCl_a.

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 $CdCl_{z} + NaOH = Cd(OH)Cl + NaCl$ 183.3 49.0 184.9 58.5

A 0.1-1M solution of $CdCl_2$ is treated with 30% of the stoichiometric quantity of aqueous NaOH. The resultant solution should have a pH of 6.6. The precipitate is a labile basic chloride which is converted in stages over a period of a few days to the stable **Cd(OH)Cl.** provided it is in contact with the mother liquor. The incorretical composition is obtained when a 1M solution of $CdCl_2$ is used as the starting material.

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D. $CdO + CdCi_{z} + H_{z}O = 2 Cd(OH)Cl$ 128.4 188.3 18.0 329.8

Cadmium oxide is heated for several days at 210°C with a solution of CdCl_a in a sealed tube.

SYNONYM:

Cadmium chloride hydroxide.

PROPERTIES:

Colorless, elongated, hexagonal prisms. d 4.57. Layer lattice, type E0₃ [Cd(OH)Cl type].

REFERENCES:

- W. Feitknecht and W. Gerber. Helv. Chim. Acta <u>20</u>, 1344 (1937); Z. Kristallogr. (A) <u>98</u>, 168 (1937).
- II. I. L. Hoard and O. D. Grenko. Z. Kristallogr. (A) 87, 110 (1934).

Potassium Cadmium Chloride

CdCl_t · KCl · H₁O

 $CdCl_2 + KCl + H_2O = CdCl_2 \cdot KCl \cdot H_2O$ 183.9 74.6 18.0 275.9

This double salt crystallizes below 36.5 °C from an aqueous solution of equimolar quantities of the components. The anhydrous salt crystallizes at higher temperature.

The compound is used in the Lipscomb-Hulett standard cell (704 mv.).

PROPERTIES:

Fine silky needles. The saturated solution contains the following amounts of the anhydrous salt: $(2.6^{\circ}C)$ 21.87 g., $(19.3^{\circ}C)$ 27.50 g., $(41.5^{\circ}C)$ 35.66 g., $(105.1^{\circ}C)$ 51.67 g./100 g.

REFERENCE:

H. Hering. Comptes Rendus Hebd. Séances Acad. Sci. 194, 1957 (1932). Codmium Bromide

CdBrs

 $Cd + Br_t = CdBr_t$ 112.4 159.8 272.2

Cadmium is brominated at 450°C in a quartz boat placed inside a Vycor tube initially filled with dry No. Nitrogen is then passed through a washing bottle filled with Bra and introduced into the tube. The complete bromination of 3 g. of Cd requires about two hours at 450 °C. Raising the temperature to increase the reaction rate is not recommended, since this may cause appreciable quantities of the metal to distill with the product. The molten CdBr₂ is deep red as long as unreacted metal is present and becomes increasingly lighter as the metal is consumed, so that the end of the reaction may be readily recognized by the final permanent light color. The product CdBra is distilled twice in a stream of Br, by raising the temperature; it is freed of excess Br, by remelting under pure CO2. The entire procedure may be carried out in the apparatus described by O. Honigschmid and F. Wittner [Z. anorg. allg. Chem. 226, 297 (1936)] for the preparation of pure uranium halides; it is also described under UBr. (p. 1440). Alternate method: See under zinc chloride (p. 1070) and cadmium

chloride (p. 1093).

PROPERTIES:

Colorless, bexagonal, pearly flakes; highly hygroscopic. M.p. 566°C, b.p. 963°C; d 5.192. Solubility (18°C) 95 g., (100°C) 160 g. per 100 ml. H₂O. Crystallizes as the monohydrate below 36°C, as the tetrahydrate above this temperature. Solubility (15°C) 26.4 g. of anhydrous CdBr₂/100 g. alcohol. Crystal structure: type C 19 (CdCl₂ type).

REFERENCE:

O. Hönigschmid and R. Schlee. Z. anorg. allg. Chem. <u>227</u>, 184 (1936).

Codmium lodide

CdI:

 $Cd + 1_2 = Cdl_2$ 112.4 253.8 366.3

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Communes shavings (or Cd slurry obtained from CdSO₄ solution + Zn) are shaken in distilled H_2O with the equivalent quantity of resublimed iodine. The shaking may be dispensed with if the mixture is refluxed for two hours. After the color of the liquid disappears, it is filtered and concentrated on a steam bath. The crystals are vacuum-dried for 24 hours over $P_{\rm PO}_{\rm S}$ at 100-150°C.

Carefully dried CdI_3 may be sublimed in a stream of oxygenfree CO_2 . The CdI_3 vapor is condensed in a long glass tube closed off with canvas. This yields "CdI₂ flowers."

II. $CdSO_4 + 2KI = CdI_1 + K_4SO_4$ $\binom{9}{4} H_4O$ 256.5 339.0 366.3 174.3

An aqueous solution of three parts of $CdSO_4 \cdot 8/3 H_3O$ and four parts of KI is evaporated to dryness and extracted with warm absolute alcohol. The CdI_3 crystallizes in colorless lamellae upon cooling of the solution.

Alternate method: See under zinc chloride, p. 1070.

PROPERTIES:

Colorless, lustrous, hexagonal leaflets; stable in air. M.p. 387°C, h.p. 787°C; d 5.67. Solubility (18°C) 85 g., (100°C) 128 g./100 ml. H_2O ; (20°C) 176 g./100 ml. methanol; ~90 g./100 ml. of ethanol. Soluble in ether. Crystal structure: type C 6 (CdI₂) and C2? (second CdI₂ type). d (x-ray) of both structures is identical.

REFERENCES:

- W. Biltz and C. Mau. Z. anorg. allg. Chem. <u>148</u>, 170 (1925);
 E. Cohen and A. L. Th. Moesveld. Z. phys. Chem. <u>94</u>, 471 (1920).
- II. Jahresber, Fortschr. d. Chem. 1864, 242.

Cadmium Hydroxide

Cd(OH),

1. COARSE CRYSTALS

| Cdl. | + | 2 KOH | == | Cd(OH). | + | 2 K.I |
|-------|---|-------|----|---------|---|-------|
| 366.3 | | 112.2 | | 146.4 | | 832.0 |

A solution of 10 g. of CdI_8 in 200 ml. of water is mixed with 320 g. of carbonate-free KOH. The mixture is heated until the first precipitate of $Cd(OH)_2$ redissolves at about 135°C. The heating must be accompanied by continuous stirring to prevent

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the lower layers of the liquid from reaching a temperature high enough to cause partial conversion of the $Cd(OH)_2$ to black, sparingly soluble CdO. The major part of the $Cd(OH)_2$ crystallizes when the solution is slowly cooled. However, a part of the hydrate remains in solution even after complete cooling and may precipitate as amorphous $Cd(OH)_2$ if the product is immediately treated with water. Therefore, the mixture is allowed to stand for 12 hours before attempting to separate the $Cd(OH)_2$ with water.

II. Very homogenous $Cd(OH)_{3}$ is obtained from cadmium acetate and 85% KOH following precipitation of crystalline CdO by the same procedure.

III. FINE CRYSTALS

 $Cd(NO_{3})_{2} \cdot 4 H_{3}O + 2 NaOH = Cd(OH)_{3} + 2 NaNO_{3} + 5 H_{2}O$ 308.5 S0.0 146.4 170.0

A finely crystalline product is obtained by dropwise addition (stirring or shaking) of a boiling solution of $Cd(NO_3)_2$ to boiling, carbonate-free 0.82N NaOH (stoichiometric quantities). The precipitate is repeatedly washed with hot water and vacuum-dried over P_2O_5 at 60°C. (For details, see in the original.)

PROPERTIES:

Nacreous, hexagonal leaflets soluble in acids and NH_4Cl solution. Solubility (25°C) 0.26 mg./100 ml. H₂O; 0.13 g./100 ml. 5N NaOH. Dehydration starts at 130°C, is complete at 200°C, d 4.79. Crystal structure: type C6 (CdI₂ type).

REFERENCES:

- L A. de Schulten. Comptes Rendus Hebd. Séances Acad. Sci. 101, 72 (1885).
- IL R. Scholder and E. Staufenbiel. Z. anorg. allg. Chem. 247, 271 (1941).
- III. R. Fricke and F. Blaschke, Z. Elektrochem. 46, 46 (1940).

Cadmium Sulfide

CdS

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\begin{array}{rcl} CdSO_4 &+ H_8S &= CdS &+ H_8SO_4 \\ (^{\prime\prime}_{1}, H_8O) \\ 250.5 & 22.41. & 144.5 & 98.1 \end{array}
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Finely divided cubic CdS is obtained by precipitation with H_2S of a hot, H_2SO_4 -acidified aqueous solution of CdSO₄. The hexagonal

modification (more or less free of cubic CdS) is obtained from cadmium halide solutions; however, the resultant sulfide is contaminated with strongly adhering halide which cannot be washed out.

Depending on the particle size and the state of the surface. the color of the precipitates varies from lemon yellow to orange. Lemon yellow "cadmium yellow" is prepared by precipitating, with constant stirring, a very diluted neutral solution of CoSOA with an excess of Na₂S solution. The precipitate is then washed free of sulfate.

Dark CdS is obtained by calcining a mixture of two parts of CdCO₃ and one part of sulfur powder in a crucible. The product is pulverized after cooling.

Pure CdS, free of the anions of the precipitating medium, is prepared by bubbling HaS through a solution of Cd(ClO₄)₂ in 0.1-0.3N perchloric acid. Lower acid concentrations yield precipitates which are difficult to filter; the precipitation is incomplete at higher concentrations.

Crystals a few millimeters in size are obtained from HaS and Cd vapor at about 800°C (see Frerichs' method in the literature below).

PROPERTIES:

Lemon-yellow to orange powder. Solubility (18°C) 0.13 mg./100 ml. H2O. Soluble in cone. or warm dilute mineral acids. Sublimes at 980°C. d 4.82. Hardness 3. Crystal structure: cubic type B3 (zincblende type) and hexagonal type B4 (wurtzite type). The cubic modification is converted to the hexagonal by heating at 700-800°C in sulfur vapor. 4

REFERENCES:

W. O. Milligan. J. Phys. Chem. 38, 797 (1934); H. B. Weiser and E. J. Durham. Ibid. <u>32</u>, 1061 (1928); W. J. Müller and G. Löffler. Angew. Chem. <u>46</u>, 538 (1933); E. Dönges. Unpublished; G. Denk and F. Denk. Z. analyt. Chem. 130, 383 (1949/50); R. Frerichs. Naturwiss. 33, 2181 (1946).

CADMIUM SELENIDE CdSe

The preparation is analogous to that of ZnSe (method I, see p. 1078),

PROPERTIES:

Formula weight 191.37. Dark-red powder. d (x-ray) 5.2674 Crystal structure: type B3 (zinchlende type) and B4 (wurzite type).

Cadmium Nitride

Cd₃N₈

$$3 \operatorname{Cd}(\operatorname{NH}_{t})_{t} = \operatorname{Cd}_{3}\operatorname{N}_{t} + 4 \operatorname{NH}_{3}$$

433.4 $365.3 \quad 68.1$

Cadmium amide, $Cd(NH_2)_2$, is thermally decomposed in a vapor pressure endiometer (see Part I, p. 102) at 180 °C while repeatedly removing measured amounts of NH₃. The evolution of NH₃ ceases after about 36 hours. The Cd_3N_3 product decomposes if the temperature is raised higher.

PROPERTIES:

Black; forms oxide in air. d (x-ray) 7.67. Crystal structure: type D5₃ (Mn₂O₃).

REFERENCE:

H. Rahn and R. Juza, Z. anorg, allg. Chem. 244, 111 (1940).

Cadmium Amide

Cd(NH_z),

 $Cd(SCN)_{2} + 2 KNH_{2} = Cd(NH_{2})_{2} + 2 KSCN$ 228.6 110.2 144.5 194.4

Cadmium thiocyanate (7 g.) is placed on filter disk b of vessel • (Fig. 283). About 15 ml. of carefully purified NH_3 is condensed

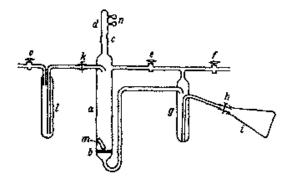


Fig. 283. Preparation of cadmium amide. h and k pinch clamps; istorage vessel for ammonia; m glass slug; n glass bulbs. onto the sait, which then dissolves in the ammonia. A solution of KNH_2 in liquid NH_3 is added to the above mixture through the ground joint c, and the vessel is closed off with ground cap d_s . A fluffy, white precipitate of $Cd(NH_3)_2$ is formed. The amount of KNH_2 used must be somewhat less than stoichiometric as $Cd(NH_2)_2$ dissolves in excess KNH_3 . In addition, no air must be allowed to be present during the reaction; a stream of N_3 is therefore passed through the apparatus when it is opened for any reason.

After thorough mixing of the two solutions, the supernatant liquid containing KSCN and excess Cd(SCN)a in liquid NHa is filtered by suction through disk b. This operation is performed by closing stopcock e and carefully evacuating the apparatus through f; this results in transfer of the liquid from a to g, which is cooled with Dry Ice-alcohol. The liquid is then removed from the system and into flask i by application of slight pressure, achieved by closing f, raising the temperature in g temporarily (remove the cooling bath), and opening the screw pinchcock h. After closing h, the product is washed by producing a slight vacuum in the system and transferring fresh liquid ammonia from storage vessel 1 through screw pinchcock k onto the product in a. Washing is complete when the NHa evaporates without leaving a residue. When this point is reached, all the NHa is removed (by suction) from the product. The latter is then knocked off the walls by means of the glass slug m and transferred to bulbs n. The preparation is carried out at (or near) the boiling point of NH3 (-33.5°C). Very pure N2, introduced through stopcocks o or f_{i} is used as the blanketing gas.

PROPERTIES:

Slightly yellowish, amorphous; rapidly discolors to brown in air. d 3.05.

REFERENCE:

R. Juza, K. Fasold and W. Kuhn. Z. anorg. allg. Chem. 234, 85 (1937).

Cadmium Phosphides

Cd,P., CdP., CdP.

I.

 $3 \text{ Cd} + 2 \text{P} = \text{Cd}_{3} \text{P}_{4}$ 337.2 62.0 399.2

The procedure for the preparation Cd_3P_3 is similar to that for Zn_3P_8 (method I, see p. 1080); that is, it is produced in an

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evacuated quarts tube from Cd metal and red P. The temperature along the tube varies from 400 to 600 °C. The mixture is allowed to react for about nine hours, and the entire tube is then heated for 12 hours at 680 °C. The resultant Cd_3P_2 is resublimed several times over an open flame, and finally sublimed at 680 °C into a slightly colder part of the quartz tube.

E. $Cd + 2P = CdP_{2}$ 112.4 62.0 174.4

A mixture of CdP_2 with Cd_3P_2 is formed by using the procedure given (see p. 1083) for Zn_3As_2 (method I).

 $\mathbf{III.} \qquad \qquad \mathbf{Cd} + 4 \mathbf{P} = \mathbf{CdP_4} \\ \mathbf{112.4} \quad \mathbf{124.0} \quad \mathbf{236.4} \\ \mathbf{112.4} \quad \mathbf{124.0} \quad \mathbf{236.4} \\ \mathbf{112.4} \quad \mathbf{124.0} \quad \mathbf{$

A mixture of 0.6 g. of white phosphorus and 20 g. of a Pb-Cd alloy containing 5% Cd is sealed under a CO_2 blanket in a Vycor ampoule. The ampoule is heated in an electric furnace to 565-575°C (the heatup time is a few hours) and maintained at this temperature for 2.5-5 days. If large crystals are desired, the temperature gradient in the furnace should be small and the cooling slow. The CdP₄ is purified by boiling with glacial acetic acid and H_2O_2 and subsequent treatment with 20% hydrochloric acid.

The starting Pb-Cd alloy is prepared by fusing the two metals under KCN in a porcelain crucible and cutting the product into strips. Commercial phosphorus is purified by melting under dilute chromosulfuric acid and dried under CO_3 .

PROPERTIES:

 Cd_3P_2 : Gray, lustrous needles or leaflets. M.p. 700°C; d (x-ray) 5.60. Soluble in hydrochloric acid with evolution of PH₂, explosive reaction with conc. nitric acid. Crystal structure: tetragonal, type D5₉ (Zn₃P₂).

CdP₂: Orange to red [appears occasionally in an indigo blue modification: B. Renault, Comptes Rendus Hebd, Séances Acad. Sci. <u>76</u>, 283 (1873)]. Tetragonal needles. d (x-ray) 4.19.

CdP₄: Black, highly reflecting crystals. Very unreactive, dissolves in boiling aqua regia. Decomposes into the elements on heating in vacuum. d (pycn.) 3.90. Crystal structure: monoclinic, space group C_{2h}^5 .

HEFERENCES:

- L R. Juza and K. Bär. Z. anorg. allg. Chem. 283, 230 (1956).
- IL M. von Stackelberg and R. Paulus, Z. phys. Chem. (B) 28, 427 (1935).
- III. H. Krebs, K. H. Müller and G. Zürm, Z. anorg. allg. Chem. 225, 15 (1956).

Cadmium Arsenides

Cd.As1, CdA51

| 3 Cd 🕂 | 2 As | = Cd _s As, | Cd + | 2 As = | CdAs. |
|--------|-------|-----------------------|-------|--------|-------|
| 337.2 | 149.6 | 487.1 | 112.4 | 149.8 | 262.2 |

The preparation of Cd_3As_2 is similar to that of Zn_3As_2 (method I): heating the metal in a stream of hydrogen that carries arsenic vapor (see p. 1083).

The phase diagram indicates the existence of CdAs₂, which may be prepared by fusing the components.

PROPERTIES:

Cd₃As₂: Gray. M.p. 721°C. Hardness ≤ 3.5 . d (x-ray) 6.95, d (pycn.) 6.211. Crystal structure: tetragonal, type D5₉ (Zn₃P₂). CdAs₂: Gray-black. M.p. 621°C. Hardness 3.5-4.

REFERENCES:

M. von Stackelberg and R. Paulus. Z. phys. Chem (B) 28, 427 (1935); A. Granger. Comptes Rendus Hebd. Séances Acad. Sci. <u>138</u>, 574 (1904); Zemczuny. Z. Metallographie <u>4</u>, 228 (1913).

Diethylcadmium

Cd(C₄H₅)₄

 $C_2H_3B_7 + Mg = C_2H_3MgB_7$ 109.0 24.3 133.3

 $2 C_{2}H_{3}MgBr + CdBr_{2} = Cd(C_{2}H_{3})_{2} + 2 MgBr_{2}$ 266.6 272.2 141.5 368.3

Anhydrous, finely ground $CdBr_{2}$ (136 g., 0.5 mole) is added in small portions (vigorous shaking and no cooling) to a solution of $C_{2}H_{5}MgBr$ in 350 ml. of absolute ether. The latter reagent is prepared from 29 g. (1.2 moles) of Mg and 131 g. (1.2 moles) of $C_{3}H_{5}Br$, the amount required to dissolve the metal. The inajor portion of the ether is distilled off in a stream of N₂ on a water bath whose temperature does not exceed 80°C. The solid, porous, gray mass left in the flask is then distilled at 1 mm. into a liquid-nitrogen-cooled trap, while the temperature of the oil bath is raised from 20 to 120°C over the one-hour distillation period.

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The clear, completely coloriess distillate is carefully freed of either by distilling the latter in a nitrogen stream; the residue is distilled in N_{B} at 19.5 mm. All the $Cd(C_{2}H_{B})_{2}$ goes over at 64.0°C; it is analytically pure. Yield 90%.

PROPERTIES:

Colorless oil with an unpleasant odor. M.p. -21° C, b.p. (19.5 mm.) 64°C, (760 mm.) 164.7°C. Decomposes at 150°C, explosively at 180°C. May be stored without decomposition in a sealed tube filled with N₂. Funes explosively in air, at first forming white and then (rapidly) brown clouds accompanied by violent detonation. Decomposed by H₂O with a characteristic crackling sound continuing for hours on end. d (21.7°C) 1.653.

REFERENCE:

E. Krause. Ber. dtsch. chem. Ges. 50, 1813 (1918).

Cadmium Carbonate

C9CO*

A solution of $(NH_4)_2CO_3$ is added all at once to a solution of $CdCl_3$, followed by the quantity of ammonia necessary to dissolve the resultant precipitate. The liquid is then heated in an open vessel on a water bath. The $CdCO_3$ separates as shiny crystals.

| L | CdCi _r + | 2 HCl + | 3H10 + | - 2 CO(NH ₂) ₂ : | = CdCO, - | + 4 NH Cl + | CO₅ |
|---|---------------------|---------|--------|---|-----------|-------------|------|
| | 163.3 | 72.9 | 54.1 | 120.1 | 172.4 | 214.0 | 44.0 |

A vertical bomb (wall thickness 3 mm., diameter 25 mm., height about 50 cm.) contains a solution of 10 mmoles of $CdCl_2$ in 30 ml. of H_2O , 0.3 ml. of conc. hydrochloric acid, and a small glass beaker filled with 20 mmoles of urea. A long stem from the bottom of the bomb supports the beaker above the liquid surface. The bomb is melt-sealed and heated at 200°C for 18-24 hours. The yield is almost quantitative.

PROPERTIES:

White powder or rhombohedral leaflets. Sparingly soluble in **B₂C**, soluble in acid. Vapor pressure at decomposition (321°C) 77 **mm.**, (257°C) 760 mm. d 4.256. Crystal structure: type GO₁ (calcite).

ETOR.

REFERENCES:

I. A. de Schulten. Bull. Soc. Chim. France [3] 19, 34 (1898). II. W. Biltz. Z. anorg. alig. Chem. 220, 312 (1934).

Codmium Acetate

Cd(CH₄COO);

 $\begin{array}{rl} Cd(NO_3)_2 \cdot 4 H_2O \ + \ (CH_3CO)_2O \ = \ Cd(CH_3COO)_2 \ + \ 2 HNO_2 \ + \ 3 H_2O \\ 308.5 \ & 102.1 \ & 280.5 \ & 124.0 \end{array}$

A mixture of 5 g. of $Cd(NO_3)_2 \cdot 4H_3O$ and 25 ml. of acetic anhydride is heated; when the vigorous reaction has ceased, the mixture is refluxed 15 minutes. After cooling and suctionfiltering, the white, crystalline precipitate is washed with some acetic anhydride and ether, and vacuum-dried over KOH and H_2SO_4 . Yield 3.6 g. (97%).

PROPERTIES:

Colorless crystals. M.p. 254-256°C; d 2.341.

REFERENCE:

E. Späth. Monatsh. Chem. 33, 241 (1912).

Cadmium Cyanide

Cd(CN):

 $Cd(OH)_{2}$ + 2 HCN = $Cd(CN)_{2}$ + 2 H₂O 146.4 54.1 154.5 36.0

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Evaporation of a solution of $Cd(OH)_2$ in aqueous HCN precipitates $Cd(CN)_2$ in the form of crystals. These are dried at 146°C;

PROPERTIES:

Air-stable crystals; turn brown on heating in air. Solubility, $(15^{\circ}C)$ 1.7 g./100 ml. H₂O. Soluble in KCN solution. d 2.226. Crystal structure; type C 3 (Cu₂O type).

REFERENCE:

W. Biltz. Z. anorg. allg. Chem. 170, 161 (1928).

Potassium Tetracyanocadmate

K.Cd(CN).

 $Cd(CN)_{2} + 2 KCN = K_{3}Cd(CN)_{4}$ 164.4 130.2 294.7

Cadmium cyanide, obtained by precipitation of a CdSO₄ solution with KCN and filtering, is dissolved (shaking) in an aqueous solution of the stoichiometric quantity of KCN. The filtrate is crystallized by evaporation. The product is dried at 105 °C.

STNONYMS:

Potassium cadmium cyanide, cadmium potassium cyanide.

PROPERTIES:

Octahedral, very refractive, air-stable crystals. Solubility (cold) 33.3 g., (b.p.) 100 g./100 ml. H_2O ; (20°C) 2 g./100 g. of 88% v./v. alcohol. M.p. about 450°C; d 1.846. Crystal structure: type H_1 (spinel type).

REFERENCE:

W. Biltz. Z. anorg. allg. Chem. 170, 161 (1928).

Cadmium Thiocyanate

Cd(SCN),

 $CdSO_4 + Ba(SCN)_2 = Cd(SCN)_2 + BaSO_4$ (%, H₂O) 258.5 258.5 228.6 233.4

To a boiling solution of 12.68 g. of $Ba(SCN)_2$ is added, in drops, 12.83 g. of $CdSO_4 \cdot \frac{a}{3} H_2O$ in 100 ml of boiling H_2O , taking care to keep the liquid boiling. After cooling, the precipitate is allowed to settle and the mixture is filtered after standing for some time. The filtrate is evaporated to 80 ml., filtered again, and evaporated to dryness on a water bath.

The required starting solution of $Ba(SCN)_2$ is prepared by dissolving 15.78 g. of $Ba(OH)_2 \cdot 8 H_2O$ in 500 ml. of H_2O and allowing it to react with a solution of 7.62 g. of NH_4SCN in 100 ml. of H_2O , according to the equation

Sa(OH)₂ · **S** H₂O + 2 NH₄SCN = Ba(SCN)₂ + 2 NH₃ + 10 H₂O **Si5.5** 152.2 253.5 34.1 180.2 The mixture is brought to a boll and heated until NH2 ceases to evolve.

SYNONYMS:

Cadmium rhodanide.

PROPERTIES:

Colorless crystal crusts. Soluble in H_3O , alcohol and Hquid NH_3 .

REFERENCE:

H. Grossmann. Ber. disch. chem. Ges. 35, 2666 (1902).

Cadmium Silicate

Cd₂SiO₄

 $2 \text{ CdO} + \text{SiO}_2 = \text{Cd}_2 \text{SiO}_4$ 256.8 60.1 316.9

Like Zn_2SiO_4 , Cd_3SiO_4 is prepared from the oxides by fusion or by hydrothermal synthesis (see p. 1089).

SYNONYM:

Cadmium orthosilicate.

PROPERTIES:

M.p. 1246°C; d 5.833. Phosphorescent after activation with manganese.

REFERENCE:

W. Biltz and A. Lemke. Z. anorg. alig. Chem. 203, 330 (1932); C. J. van Nieuwenburg and H. B. Blumendahl. Rec. Trav. Chim. Pays-Bas 50, 989 (1931).

Cadmium Ferrate (III)

CdFe₁O₄

 $CdCO_3 + Fe_2O_3 = CdFe_3O_4 + CO_4$ 172.4 159.7 288.1 44.0

Finely screened CdCO₂ [or Cd(OH)₂] and γ -FeOOH (p. 1590) in a Cd:Fe ratio of 1:2 are mixed for five hours on a mechanical

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shaker in an atmosphere free of CO_3 and H_2O . The loose powder is divided into 5-g. portions, which are heated for one hour in a platiaum crucible at 800°C [mixtures with $Cd(OH)_3$ at 1000°C] and then allowed to cool to room temperature in a desiccator. The compound cannot be prepared by precipitation.

PROPERTIES:

Dark brown, hygroscopic powder; stable at room temperature. Crystal structure: type H1₁ (spinel type).

REFERENCE:

R. Fricke and F. Blaschke, Z. anorg. allg. Chem. 251, 396 (1943).

Mercury (II) Oxychloride

HgCl_z · 4 HgO

L. To prepare brown $HgCl_2 \cdot 4HgO$, a solution of 15.0 g. of borax in 1.5 liters of water is added to a solution of 10.0 g. of mercuric chloride in 2.0 liters of water (both solutions are at 50-55 °C). The desired compound separates on cooling in the form of thin, flexible flakes 0.1-0.8 mm. long. Depending on the thickness of these flakes, the color of the precipitate varies from golden yellow to black-brown. The yield is about 85%, based on the HgCl₂ used.

IL Black $HgCl_2 \cdot 4HgO$ is obtained when 5.0 g. of finely crystalline brown $HgCl_2 \cdot 4HgO$ is heated for 72 hours in a sealed tube with 10 ml. of 0.1N HNO₃ at 180°C. The product separates in the form of rhombic needles several millimeters long, which are readily isolated from the basic nitrate present in the mixture.

SYNONYM:

Mercuric oxychloride.

PROPERTIES:

L Depending on the thickness, golden yellow to dark brown flakes; elongated brown crystals from concentrated solutions. Soluble in hot water (partial decomposition). The powder pattern distinguishes it from the black form (appearance of lattice defects). Brown $HgCl_2 \cdot 4HgO$ has a remarkably wide phase range, from 2.82 to 4.00 HgO.

II. Black, needle-shaped crystals, sparingly soluble in water, d (pycn.) 9.01. Crystal structure: orthorhombic, space group D_{2h}^{26} .

REFERENCES:

- I. A. Weiss, G. Nagorsen and A. Weiss. Z. Naturforsch. <u>9b</u>, 81 (1954).
- II. A. Weiss. Private communication.

Mercury (II) Bromide

HgBr,

 $Hg + Br_2 = HgBr_2$ 200.6 159.8 360.4

Five parts of Hg are covered with 60 parts of H_2O and allowed to react at 50°C (vigorous stirring) with four parts of Br_2 , which is added dropwise as long as no permanent color is formed. The solution is then brought to a boil, filtered hot, and placed in an ice bath to induce crystallization. The salt is dried at as low a temperature as possible. Purification is by careful double or triple sublimation from a porcelain dish heated on a sand bath and covered with a Petri dish. When very high purity is required (e.g., for conductivity measurements), it may be necessary to repeat the sublimation several times more.

PROPERTIES:

Colorless, lustrous crystal flakes (sublimate and from H_gO), rhombic prisms or needles (from alcohol). Light yellow liquid between m.p. 238°C and b.p. 320.3°C. d²⁰ 5.73; d²⁴⁸ (liq.) 6.11. Vapor pressure (200°C) 24.1 mm., (280°C) 334.2 mm.; sublimes without decomposition. Solubility (25°C) 0.62 g., (100°C) 22 g. per 100 g. H_aO ; (25°C) 30.0 g./100 g. ethanol; (25°C) 69.4 g./100 g. methanol. Specific electrical conductivity (242°C) 1.45 · 10⁻⁴ ohm⁻¹. Its melt is a solvent for a large number of inorganic and organic substances, which impart considerable conductivity to the melt. Cryoscopic constant 36.7 deg. per mole in 1000 g. of HgBr₂. Rhombic layered lattice, space group C_{13}^{22} .

REFERENCES:

W. Reinders. Z. phys. Chem. (A) <u>32</u>, 514 (1900); G. Jander and K. Brodersen. Z. anorg. Chem. <u>261</u>, 264 (1950).

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Potassium Triiodomercurate (II)

KHgI_t · H_tO

 $KI + Hgl_1 + H_2O = KHgI_3 \cdot H_2O$ 166.0 454.5 18.0 638.5

First, 41 g. of KI and 59 g. of HgI_2 are dissolved in 14 (!) ml. of hot H_2O . The beaker should be tared precisely so that evaporating H_2O may be replenished. The salt crystallizes in yellow needles from the cooling solution. The above instructions result from a study of the three-component system HgI_2-KI-H_2O showing that in this system only $KHgI_3 \cdot H_2O$ can precipitate. Yield 9 g.

The salt K_2HgI_4 (without water of crystallization) is obtained from acetone containing exactly 2% H₂O (between 34 and 56°C).

Use: A solution treated with KI is known as Thoulet's solution (see Part I, p. 99); it is also a reagent for alkaloids. Alkaline K_2 HgI, solution is Nessler's reagent.

SYNONYMS:

Mercury potassium iodide, potassium mercurilodide, potassium iodohydrargyrate.

PROPERTIES:

Light yellow crystal needles; becomes orange-red in a vacuum desiccator over H_3SO_4 (reversible loss of H_9O). Decomposes in H_2O with loss of HgI_3 . Soluble in KI solution. Sublimes off HgI_3 on heating.

REFERENCES:

M. Pernot. Comptes Rendus Hebd. Séances Acad. Sci. <u>182</u>, 1154 (1926); <u>185</u>, 950 (1927); Ann. Chim. [10] <u>15</u>, 5 (1931).

Copper (I) Tetraiodomercurate (II)

CusHgl

L

| 2 CuSO ₄ + | K₄HgI₄ + | • SO: + | 2 H2O |
|-------------------------------|--------------------|---------|----------------|
| (5 H ₂ O) 499-4 | 788.5 | 84.1 | 36.0 |
| = Cu ₄ H 835. | gI. + K.S 4 174 | - | H2SO4 196.2 |

A solution of 4.5 g. of HgI_2 and 3.3 g. of KI in 25 ml. of H_2O is filtered and treated with a solution of 5 g. of $CuSO_4 \cdot 5 H_2O$ in 15 ml. of H_2O ; SO_2 is then introduced. The resultant bright-red precipitate is suction-filtered, washed with H_9O , and divide at 100°C. The compound may be recrystallized from hot hydrochloric acid.

u.

 $2 \text{ Cul } + \text{Hgl}_{\pm} = \text{Cu}_{\pm}\text{HgI}_{4}$ $380.9 \quad 454.5 \quad 835.4$

The components are mixed in stoichiometric proportions and fused over an open flame in an evacuated Pyrex glass bomb, which should be as small as possible. Pure Cu_2Hgl_4 is obtained.

An analogous procedure yields AgaHgI4.

PROPERTIES:

Red crystalline powder or small, tabular crystals. d 6.094. Crystal structure: tetragonal. Space group D_{2d}^{1} ; on heating to 70°C, the color changes to chocolate brown with simultaneous enantietropic structure transformation to cubic type B3 (zincblende) in which the cation distribution is random.

REFERENCES:

- I. Cabentou and Willm. Buil. Soc. Chem. France [2] 13, 194 (1870); J. A. A. Ketelaar. Z. Kristallogr. 80, 190 (1931).
- H. H. Hahn, G. Frank and W. Klingler. Z. anorg. allg. Chem. 279, 271 (1955).

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Mercury (II) Sulfide

HgS

BLACK MODIFICATION

 $H_gCl_t + H_sS = H_gS + 2HCl_{271.5} 22.41. 232.7 72.9$

Hydrogen sulfide is introduced into a mercury (II) solution ing 1-2N HCl, absolutely free of oxidizing agents. The transient white to brownish precipitate reacts with additional H_3S to yield black HgS, e.g.,

$$H_{\text{Es}}S_{\text{s}}C_{\text{s}} + H_{\text{s}}S = 3 \text{ HgS} + 2 \text{ HCl.}$$

SYNONYMS:

Ethiop's mineral; mercuric sulfide, black.

NED NODIFICATION

$$H_g(CH_sCOO)_s + H_sS = HgS + 2 CH_sCOOH$$

 $S18.7 22.4 l. 232.7 120.1$

A solution of 35 g. of $Hg(CH_3COO)_3$ and 25 g. of NH_4SCN in 100 ml. of hot glacial acetic acid is prepared. A moderately fast stream of H_2S is then introduced until precipitation is complete. The acetic acid is then slowly evaporated (caution, HCN!), and the black precipitate transforms to the red form. The glacial acetic acid must be present until conversion is complete; overheating must be avoided. During the last stage the paste must be constantly stirred. If this is neglected, the product is dull red or hrown. When the acid has been completely removed and the product cooled, 200 ml, of H_2O is added and the mixture is filtered through a Büchner funnel. The product is washed and dried between two layers of thick filter paper. Yield 25 g.

If HgCl_a is used instead of the acetate, a larger amount of glacial acetic acid is necessary and the boiling must be longer. The final color, however, is never as magnificent as that of the product prepared from the acetate.

Alternate methods: a) A conc. solution of $HgCl_2$ (20 ml.) is poured into 12 ml. of aqueous ammonia (1:2). The resultant precipliate is treated with a somewhat larger quantity of conc. $Na_3S_3O_3$ solution than is necessary for complete solution. The mixture is heated in a dish and evaporated until pasty; the paste is filtered and washed with hot H_2O_2 .

b) A dry method for the preparation of cinnabar consists in subliming black HgS, grinding the sublimate under H_3O , freeing it from excess sulfur by boiling with a solution of K_2CO_3 , washing and drying at 70°C.

SYNONYMS:

Cinnabar, vermilion, Chinese red, cinnabarite.

PROPERTIES:

Black modification: Velvety black amorphous powder (tetrahedral crystals). Soluble in aqua regia and in conc. solutions of alkali sulfides, forming this salts. Unstable. d (x-ray) 7.69. The mineral metacinnabarite crystallizes as type B3 (zinchlende).

Red modification: Scariet powder, darkens in air. Soluble in aqua regia, less readily soluble than the unstable modification in alkali sulfide solutions. Sublimes at 580°C; d 8.09. Hardness 2-2.5. Heragonal, deformed NaCl lattice, type B9 (cinnabarite type).

REFERENCES:

L. C. Newell, R. N. Maxson and M. H. Filson in: H. S. Booth. Inorg. Syntheses, Vol. I, New York-London, 1939, p. 19; O. Hausamann. Ber. disch. chem. Ges. 7, 1747 (1874).

Mercury (II) Selenide HgSe

1.

 $HgCl_2 + H_2Se = HgSe + 2 HCl_{271.5} 81.0 279.8 72.9$

A dilute solution of $HgCl_3$ is added in drops (stirring) to a saturated aqueous solution of H_2Se , so that $HgCl_2$ is never present in excess. Air is carefully excluded. If a conc. solution of $HgCl_3$ is used, the precipitate formed consists of yellow $HgCl_3 \cdot 2HgSe$.

Mercury (II) chloride is added to an equivalent amount of NaCN solution; the mixture is made strongly alkaline with cono. ammonia and an equivalent amount of SeO₂ is added. The mixture is filtered and SO₂ is introduced. The liquid must be maintained alkaline to prevent precipitation of red selenium. The end of the neutralization may be spotted by the reduced rate of absorption of SO₂. The black HgSe is suction-filtered, washed with a dilute ammoniacal NaCN solution followed by H_2O , and dried in a desiccator over P_2O_5 .

III. Hg + Se = HgSe 200.8 79.0 279.6

Stoichiometric quantities of Hg and Se are heated to 550-600°C in a sealed bomb.

The product may be purified by sublimation at 600-650°C in a stream of very pure N_{2} .

SYNONYM:

Mercuric selenide.

PROPERTIES:

Gray-black (the sublimed material is violet-black) regular crystals with a metallic luster. Sublimes without decomposition

5. 45 10

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at about 600 °C in Na, COa or vacuum. Soluble in NH4 HSe, giving a red solution. d 8.266. Hardness (of tiemannite) 2.5. Crystal structure: type B3 (sinchlende type).

REFERENCES:

- L L. Moser and K. Atynski. Monatsh. Chem. 45, 235 (1925).
- II. H. Hahn and G. Störger. Unpublished data.
- III. G. Pellini and R. Sacerdoti. Gazz. Chim. Ital. 40, II, 42 (1910): Chem. Zentralbl. 1910, II, 1741.

Mercury (II) Amide Chloride

HgNH₂Cl

 $H_gCl_1 + 2 NH_2 = H_gNH_2Cl + NH_4Cl$ 271.5 34.1 252.153.5

A solution of 20 g. of HgCl₂ in 400 ml. of H₂O is mixed with 31 ml. of 6N (10%) ammonia. The resultant precipitate is allowed to settle and is then suction-filtered and washed with 180 ml. of cold water. This amount of wash water must be adhered to precisely, since it affects the composition of the product: with larger quantities of H₂O the product assumes a yellow color due to partial formation of NHg₂Cl · H₂O. The product is dried at 30°C (exclusion of light); when it appears to be dry, it is ground and dried further at 30°C. Yield 18.5 g.

SYNONYMS:

White mercuric precipitate (infusible); ammoniated mercuric chloride.

PROPERTIES:

White, light-sensitive powder. Insoluble in H₂O; decomposes in H₂O and alcohol. Completely soluble in CH₃COOH. Does not melt on heating, but volatilizes with decomposition. d 5.38.

REFERENCES:

E. Mannerheim. Pharmazeutische Chemie [Pharmaceutical Chemistry), IV, Exercise Compounds, Collection, 682, p. 63 (1921); J. Sen. Z. anorg. allg. Chem. 33, 197 (1903).

Diamminemercury (II) Dichloride

HgCl, 2 NH,

L

 $HgCl_{z} + 2NH_{z} = HgCl_{z} \cdot 2NH_{z}$ 271.5 34.1 305.6

A solution of 5 g. of HgCl2 and 3 g. of NH4Cl in 100 ml. of In is allowed to react with 20 ml. of 4.5N (8%) ammonia. The

mixture is left to stand six days (frequent shaking). The resultant precipitate consists of small, colorless crystals. It is washed with alcohol and dried in the dark over KOH.

II. In the absence of moisture, the product of theoretical composition is formed in 1.5 days via addition of NH_3 to $HgCl_3$ at room temperature in a vapor pressure eudlometer (cf. Part I, p. 102). The other known ammines are $HgCl_3 \cdot 8 NH_3$ and $HgCl_3 \cdot 9.5 NH_3$.

SYNONYM:

White mercuric precipitate (fusible).

PROPERTIES:

Fine rhomble dodecahedra comprise the crystalline, air-stable, white powder. Melting range 247 to 253 °C under NH₃ at atmospheric pressure. Soluble in CH₃COOH. Stable as a precipitate in a solution containing more than 1.7 g. of NH₃Cl/100 mi. of H₃O. Melts with decomposition on heating. d 3.77. Crystal structure: cubic with random distribution of Hg.

REFERENCES:

I. D. Strömholm. Z. anorg. allg. Chem. <u>57</u>, 86 (1908). IL W. Biltz and C. Mau, Ibid. <u>148</u>, 170 (1925).

Mercury (II) Iminobromide

Hgs(NH)Brs

 $2 \text{ HgBr}_2 + 3 \text{ NH}_3 = \text{Hg}_2(\text{NH})\text{Br}_3 + 2 \text{ NH}_4\text{Br}$ 720.8 51.1 576.1 195.8

I. A solution of 2.16 g. of $HgBr_3$ in 80 ml. of boiling water is mixed with a solution of 0.2 g. of NH_4Br in 100 ml. of 0.1N ammonia. A yellow precipitate forms immediately; it is suctionfiltered while still hot, washed with 250 ml. of cold water, and dried over NaOH. Yield 1.4 g. (81%).

II. A concentrated solution of 1.44 g. of HgBr₂ and 0.9 g. of NH₄Br (total volume about 30 ml.) is added to 2.6 g. of freshly precipitated HgO. The mixture is shaken for about six hours; it clarifies after 2.5 hours. The precipitate is worked up as in method I.

SYNONYM:

Mercuric iminobromide.

PROPERTIES:

Yellow, light-sensitive powder. Soluble in KCN and KI solutions, insoluble in organic solvents. Shaking with cold, aqueous ammonia yields the bromide of Millon's base (see below).

REFERENCES:

- L. W. Rüdorff and K. Brodersen, Z. anorg. allg. Chem. 270, 145 (1952).
- IL A. Meuwsen and G. Weiss, Ibid. 289, 5 (1957).

Millon's Base

$\mathbf{NHg_tOH} \cdot \mathbf{x} \mathbf{H_tO} \ (\mathbf{x} = 1 \ \mathbf{or} \ 2)$

 $2 \text{ HgO} + \text{NH}_{4}\text{OH} = \text{NHg}_{2}\text{OH} \cdot 2 \text{ H}_{2}\text{O} \xrightarrow{110^{\circ}\text{C}} \text{NHg}_{2}\text{OH} \cdot \text{H}_{2}\text{O}$ 453.2 35.1 468.3 450.2

Freshly precipitated HgO (see below) is taken up in carbonatefree, approximately 12N ammonia, and shaken in the dark for 14 days. The resultant light-yellow microcrystalline precipitate is filtered and washed with some water. It is dried over silica rel in a desiccator.

This dihydrate of Millon's base may be converted to the brown monohydrate by brief drying (10 minutes at 110°C). This compound is stable in vacuum over silica gel.

The starting HgO is precipitated at 70°C by addition of a solution of 7.5 g. of NaOH in 20 ml. of $H_{2}O$ to a solution containing 25 g. of HgCl₃ in 200 ml. of $H_{2}O$.

The starting ammonia solution is prepared by passing 51 g. of CO_2 -free NH₃ through 250 ml. of bolled distilled water.

PROPERTIES:

a) Dihydrate: Very fine, yellow, hexagonal crystals, lightsensitive, insoluble in alcohol and ether. Converted to the monohydrate above 110°C. d (x-ray) 7.33. Crystal structure: hexagonal.

b) Monohydrate: Brown, light-sensitive powder. In moist air, the color changes to yellow, with formation of the dihydrate. d (x-ray) 7.05. Crystal structure: hexagonal.

REFERENCE:

W. Bödorff and K. Brodersen. Z. anorg. allg. Chem. <u>274</u>, 338 (1953).

Bromide of Millon's Base

NHg,Br

 $2 \text{ HgBr}_{2} + 4 \text{ NH}_{3} = \text{ NHg}_{2}\text{Br} + 3 \text{ NH}_{4}\text{Br}$ 720.9 68.1 495.1 293.9

Ammonia (5 ml., 24%) is diluted with 400 ml. of water. A solution of $HgBr_2$ in 200 ml. of water, saturated at 20°C, is added with stirring. The resultant yellow precipitate is filtered and washed with water until the filtrate is free of bromide ion. The light yellow product is dried at 110°C and stored in vacuum over silica gel.

The iodide and the nitrate of Millon's base are also readily prepared (see reference below).

PROPERTIES:

Light yellow, finely grained powder. d (pycn.) 7.64, d (x-ray) 7.66. Crystal structure: hexagonal (space group D_{ab}^{+}).

REFERENCE:

W. Rüdorff and K. Brodersen. Z. anorg. allg. Chem. <u>274</u>, 338 (1953).

Mercury (I) Thionitrosylate

$[Hg_{x}(NS)_{1}]_{x}$

| $2 \operatorname{Hg}_2(\operatorname{NO}_3)_2$ | ÷ | $S_4(NH)_4$ | - | $2 \operatorname{Hg}_{2}(NS)_{2}$ | ÷ | 4 HNO, |
|--|---|-------------|---|-----------------------------------|---|--------|
| (2 H ₂ O) 1122.6 | | 188.3 | | 986.7 | | 252.1 |

A solution of 2.3 g. of $Hg_2(NO_3)_3$ (carefully predried over P_2O_3) in about 60 ml, of dimethylformamide is prepared. Any basic nitrate which may precipitate is filtered off. The solution is cooled in a -70°C bath and 400 mg, of $S_4(NH)_4$, dissolved in a few millilitors of dimethylformamide, is added. The resultant yellow solution is slowly brought to room temperature. A yellow precipitate begins to separate at about 0°C. The mixture is allowed to stand 10 minutes and is filtered on a coarse fritted glass filter. The precipitate is washed with dimethylformamide, followed by acetone. The product is dried in high vacuum, first at room temperature, then for a short time at 100°C. Yield 1-1.5 g.

SYNONYM:

Mercurous thionitrosylate.

PROPERTIES:

Solid yellow substance. Insoluble in all common solvents. Stable at room temperature; detonates when held in a flame. Hydrolyzed by bases, evolving NH_3 ; reacts with strong acids, forming basic Hg salts, SO_2 and ammonium salts.

REFERENCE:

M. Goehring and G. Zirker. Z. anorg. alig. Chem. 285, 70 (1956).

Mercury (II) Thionitrosylate

[Hg(NS)₂]₈

 $2 Hg(CH_{3}COO)_{2} + S_{4}(NH)_{4} = 2 Hg(NS)_{2} + 4 CH_{3}COOH$ 637.4 188.3 585.5 240.2

A solution of 27 g. of Hg $(CH_3COO)_2$ in absolutely dry pyridine is prepared. Then 1 g. of $S_4(NH)_4$ in 20 ml. of pyridine is added, resulting in the appearance of a blood-red color, followed soon by separation of a fine-grained yellow precipitate. The mixture is mechanically shaken until the supernatant becomes pure yellow: this requires about two hours. During this operation, the temperature should be maintained at 20-25 °C; the reaction is inhibited at lower temperatures. After the shaking, the deposit is washed several times with pyridine (total 80 ml.) and the solvent is decanted. The remaining pyridine is removed by ether extraction. The product is vacuum-dried over conc. H_2SO_4 . Yield 2 g. (65%).

PROPERTIES:

Finely divided yellow powder. Insoluble in all common solvents. In water, decomposes with blackening. Stable at room temperature, decomposes at about 140°C.

SYNONYM:

Mercuric thionitrosylate.

REFERENCE:

A. Meuwsen and M. Lösch. Z. anorg. allg. Chem. 271, 217 (1953).

Disthylmercury

Hg(C1H4)+

 $2C_{s}H_{s}MgBr + HgCl_{2} = (C_{2}H_{s})_{t}Hg + MgBr_{2} + MgCl_{2}$ 266.8 271.5 258.7 184.2 95.2

Magnesium turnings (25 g.) are covered with 500 ml. of dry ether in a two-liter three-neck flask provided with a dropping funnel and reflux condenser. Ethyl bromide (125 g.) is gradually added in drops from a funnel. The rate of the reaction, which starts after a few minutes, is regulated by the rate of addition. It may be slowed by cooling with water. When the reaction ceases, the solution is boiled for about 30 minutes, cooled and filtered through glass wool.

The ethereal C_2H_5MgBr solution is treated portionwise (stirring) with 97 g. of HgCl₂ in a second three-neck two-liter flask, equipped with a stirrer and a reflux condenser. The addition is spread out over 45 minutes to avoid a too violent reaction. The solution is then boiled for about 10 hours, after which 250 ml of water is slowly added through the condenser to hydrolyze the excess C_2H_{6} -MgBr. The ether layer is separated and dried over CaCl₂. After removal of the ether by distillation, the residue is distilled under reduced pressure. The Hg(C_2H_5)₂ goes over between 97 and 99°C at 100 mm. Yield 55 g. (~60%).

Dimethylmercury may be obtained in a similar manner according to

 $2 CH_3MgBr + HgCl_2 = Hg(CH_3)_2 + MgBr_2 + MgCl_2$.

Storage ampoules are first filled with N_2 or CO_3 to avoid explosions during melt-scaling. To avoid the unpleasant results of shattering of the ampoules on explosion (fiying glass, etc.), the ampoules should be stored in cotton wool inside well-stoppered powder jars.

PROPERTIES:

Almost odorless, heavy liquid. B.p. (760 mm.) 159°C. Stable to H_2O and air. Gradually decomposes when stored in light (Hg drops appear). Almost insoluble in H_2O , sparingly soluble in alcohol, soluble in ether. d (20°C) 2.466. Very toxic.

The danger of poisoning is especially great when the compound is spilled on a porous surface, such as a laboratory bench or wooden floor. The material is inactivated by hot hydrochloric acid or hot mercuric chloride solution (formation of $C_{2}H_{5}$ HgCl).

REFERENCES:

 C. S. Marvel and V. L. Gould. J. Amer. Chem. Soc. 44, 153 (1922);
 E. Krause and A. von Grosse. Chemie der metallorgan. Verbindungen [Chemistry of Oranometallic Compounds], Berlin.
 1937.

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Mercury II Acetote

Hg₁(CH₁COO)₄

| Hg _t (NO ₃), | + 2 CH ₃ COONa | = Hg ₁ (CH ₃ COO) ₂ | $+ 2 \text{NaNO}_{8}$ | | |
|-------------------------------------|---------------------------|--|-----------------------|--|--|
| (2 H ₁ O) 561,3 | 164.1 | 519.3 | 170.0 | | |

A solution of 20 g. of $Hg_2(NO_3)_3$ in 120 ml. of water plus 3.5 ml. of 25% HNO_3 is treated with a solution of 15 g. of sodium acetate in 50 ml. of H_2O . The resultant precipitate is washed with cold water and dried in a desiccator over $CaCl_2$. Yield 13 g.

SYNONYM:

Mercurous acetate.

PROPERTIES:

White, light-sensitive crystal flakes (tinged with gray). Solubility (15°C) 0.75 g./100 ml. H_2O . On boiling and in light the compound in solution disproportionates to Hg and Hg (II) acetate; the mercuric salt then hydrolyzes to a yellow, insoluble basic salt. Readily soluble in dilute acetic acid, insoluble in alcohol and ether. Decomposes on heating, forming a residue of black flakes.

REFERENCE:

Ulimann. Enzykopádie d. techn. Chemie [Encyclopedia of Ind. Chemistry], 2nd ed., IV, 679.

Mercury (II) Acetate

Hg(CH,COO),

 $HgO + 2 CH_sCOOH = Hg(CH_sCOO)_s + H_sO$ 216.6 120.1 318.7 18.0

A solution of 20 g. of yellow HgO in 30 ml. of 50% CH_3COOH is prepared on a water bath. It is filtered through a jacketed filter bested with hot water, and the filtrate is cooled with ice. The crystals are suction-dried and washed with ethyl acetate. The product is recrystallized from hot ethyl acetate or from hot water slightly acidified with acetic acid. The salt is dried in a vacuum desiccator over $CaCl_2$.

Use: As a mercurizing and oxidizing agent and for the ab-

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SYNONYM:

Mercuric acetate.

PROPERTIES:

Nacreous, light-sensitive crystalline flakes. On storage adquires a yellow tinge and an odor of CH_3COOH (formation of a basic salt). M.p. 178-160°C, decomposes at higher temperatures. Solubility (0°C) 25 g., (19°C) 36.4 g./100 ml. H₂O (and about 100 g. at 100°C with partial dec.). The compound in 0.2N aqueous solution is approximately 30% hydrolyzed; the yellow basic salt precipitates on diluting or heating; Soluble in ethyl acetate. d²⁸ 3.286.

REFERENCE:

Gmelin-Kraut. Hdb. anorg. Chem. [Handbook of Inorg. Chem.], 7th ed., V2, 826, Heidelberg, 1914, modified.

Mercury (II) Cyanide

Hg(CN}₁

| 1. | HgO + | 2 HCN 📼 | Hg(CN) _t + | · H'O |
|----|-------|---------|-----------------------|-------|
| | 218.8 | 54.1 | 252.7 | 18.0 |

The crystalline material is obtained by evaporation of a solution of HgO in aqueous HCN. The product is recrystallized, dried at 50°C, ground and redried.

| п. | 9 HgO + | Fe4[Fe(CN)6]5 | + 9H ₆ O = |
|----|------------|---------------|-----------------------|
| | */10 195.0 | 85.9 | 16.2 |
| | 9 Hg(CN): | + 4 Fe(OH); | + 3 Fe(OH); |
| | 227.4 | 42.8 | 27.0 |

One part of HgO is digested for a few hours on a water bath with one part of Prussian blue and 10 parts of H_3O . The crystals separate on evaporation of the solution.

SYNONYM:

Mercuric cyanide.

PROPERTIES:

Colorless, prismatic, tetragonal crystals. Decomposes anto Be and (CN)₂ at 320°C. Solubility (0°C) 8 g., (1002C) 53.9 g./1005002 **H_O:** (19.5°C) 10.1 g./100 g. ethanol; (19.5°C) 44.1 g./200 g. methanol. d 3,996. Crystal structure: type F1₁ [Hg(CN)₂ type].

REFERENCES:

- L W. Biltz. Z. anorg. allg. Chem. 170, 161 (1928).
- B. Gmelin-Kraut. Hdb. anorg. Chem. [Handbook of Inorg. Chem.], 7th ed. V2, 832, Heidelberg, 1914.

Potassium Tetracyonomercurate (II)

K_sHg(CN)₄

 $Hg(CN)_{2} + 2 KCN = K_{2}Hg(CN)_{4}$ 252.7 130.2 382.9

L A solution of stoichiometric quantities of $Hg(CN)_3$ and KCN is evaporated to induce crystallization. The product is recrystallized and dried at 80 °C.

II. Treatment of a suspension of $Hg(CN)_3$ in liquid HCN with the stoichiometric quantity of KCN produces $KHg(CN)_3$, in addition to $K_3Hg(CN)_4$.

SYNONYM:

Potassium mercuricyanide.

PROPERTIES:

Colorless, octahedral crystals. Solubility (20°C) 1 g./35 g. of 89% v./v. alcohol. d 2.420. Crystal structure: type H1₁ (spinel type).

REFERENCES:

L W. Biltz. Z. anorg. alig. Chem. 170, 161 (1928).

IL G. Jander and B. Grüttner. Ber dtsch. chem. Ges. 81, 118 (1948).

Mercury (I) Thiocyanate

Hg₂(SCN)₂

 $Hg_4(NO_4)_2 + 2 KSCN = Hg_4(SCN)_2 + 2 KNO_3$ (2 H₂O) 561.3 194.3 517.4 202.2

A slightly acid solution of $Hg_2(NO_3)_2$, freed of mercuric ions by means of metallic Hg, is treated with somewhat less than the

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stoichiometric amount (~75%) of KSCN solution. A dark-gray difference precipitates at first; after standing for several days (repeated stirring), it becomes completely white. It is washed several times with boiling H_3O .

SYNONYMS:

Mercurous thiocyanate; mercury (1) rhodanide.

PROPERTIES:

Colorless, light-sensitive powder. Insoluble in H_3O , soluble in KSCN solution, precipitating Hg. Decomposes on heating, forming a foamy mass. d 5.318.

REFERENCE:

K. Huttner and S. Knappe, Z. anorg. allg. Chem. 190, 27 (1930).

Mercury (II) Thiocyanate

Hg(SCN)₁

 $Hg(NO_3)_2 + 2 KSCN = Hg(SCN)_2 + 2 KNO_3$ (H₂O) 343.6 194.3 316.8 203.2

A $Hg(NO_3)_3$ solution, acidified with a few drops of HNO_3 , is treated with the stoichiometric amount of KSCN solution. The resultant crystalline precipitate is suction-filtered and washed with H_3O . The product may be recrystallized from hot H_3O or alcohol. Yield 80%.

SYNONYMS:

Mercuric thiocyanate, mercuric sulfocyanate.

PROPERTIES:

Colorless, fibrous needles or nacreous flakes. Solubility $(25 °C)^{\circ}$ 0.069 g./100 ml. H₂O. The solubility in alcohol and boiling H₂O, and in KSCN solution is higher, in ether lower. Decomposes with swelling on heating to 165 °C.

REFERENCE:

W. Peters. Z. anorg. alig. Chem. 77, 157 (1912).

K₁Hg(SCN)₁

 $Hg(SCN)_{2} + 2KSCN = K_{2}Hg(SCN)_{4}$ 316.8 194.3 511.1

A boiling solution of 20 g, of KSCN in 100 ml. of H_2O is mixed with 31.7 g, of $Hg(SCN)_2$. The HgS precipitating on cooling is filtered off. The filtrate is concentrated on a water bath until crystallization. The solution then solidifies on further cooling to a white, fibrous crystalline mass. It is suction-filtered and dried over P_2O_5 .

SYNONYM:

Potassium mercurithiocyanate.

PROPERTIES:

Brilliant white crystal needles. Readily soluble in cold water, soluble in alcohol, insoluble in absolute ether.

REFERENCE:

A. Rosenheim and R. Cohn. Z. anorg. allg. Chem. 27, 285 (1901).

SECTION 21

Scandium, Yttrium, Rare Earths*

K. WETZEL

Pure Scandium Compounds

Scandium may be freed of accompanying elements by extraction of its thiocyanate with ether.

A) PURIFICATION OF SMALL QUANTITIES

One gram of the oxide (which should contain as little Ti, Zrand Hf as possible) is dissolved in dilute hydrochloric acid. The solution is evaporated on a water bath until a moist crystal paste is obtained (see note, p. 1126). This is taken up in 60 ml, of 0.5N HCl. Then 53 g, of NH₄SCN is added (the final volume should be about 100 ml.) and the mixture is shaken with 100 ml, of ether. If a separatory funnel is used, complete phase separation is often diffi-

cult to achieve since the stopcock may become plugged with solid decomposition products of HSCN during the removal of the bottom phase. It is therefore advisable to use a flask such as that in Fig. 284, which has a ground glass stopper at the top, and to use a vacuum in order to transfer the top (or ether) phase into flask c via tube b. Dilute HCl (5-10 ml.) is added to the separated top phase, the ether is evaporated, and the dry residue is treated on a water bath with conc. nitric acid, added in (caution! violent reaction). drops The mixture is then boiled with some additional conc. nitric acid until the orange red HSCN decomposition products disappear. The solution

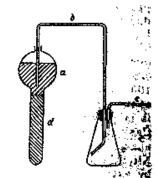


Fig. 284. Ether extraction of scandium thiocyanalist ether solution, b siplish c storage flask, d aqueon solution, c vacuum connection.

*In the following text, the rare earths are designated by general symbol Ln. is diluted with water and pure scandium is precipitated with dilute

This procedure almost completely removes Mg, Ca, Y, the lanthandes. Th and Mn; it also frees the scandium, to a large extent, of Ti, Zr, Hf. U and Fe. However, the product is still contaminated with varying amounts of Be, Al, In, Mo, Re, Fe and Co.

NOTE:

Very impure raw material samples often yield a noncrystallizing sirup on evaporation of the HCl solution; this sirup should not be beated too long because there is a danger of extensive hydrolysis. A small excess of HCl does not interfere at this stage.

B) PURIFICATION OF LARGE QUANTITIES

The crude oxide (60 g.) is dissolved in hydrochloric acid and evaporated carefully on a water bath until a moist crystalline mass is formed.

(If the mass should become sirupy instead of crystalline, the evaporation is discontinued and the mixture is diluted in 400-500 ml. of water. Then dilute ammonia is carefully added until the yellow end-point of tropeolin 00, 30 ml. of 2N HCl is added, and the volume is made up to 600 ml. with water. The purification procedure is then continued as described below.)

The paste is dissolved in 600 ml. of 0.1N HCl. If Ti or considerable quantities of Zr and Hf are initially present, hydrolysis products of these elements may still remain; they are filtered off before the next step. The solution is then allowed to react with 500-550 g. of NH₄SCN and shaken with one liter of ether in a three-liter flask (not a separatory funnel). Just as in method (A), as much of the ether layer as possible is transferred to a second flask containing 100 ml. of a saturated aqueous solution of NH4 SCN. The acid content of the ether layer, which reaches 0.06N (in HSCN) in the first flask, is largely neutralized by slow addition of 27 ml. of 2N ammonia (the flask is vigorously shaken during this addition). The ether is then shaken in a third and fourth flask each time with 100 ml. of 45% NH, SCN solution. The Sc is obtained from this purified ether phase by extraction, in a separatory funnel, with pure water (portions of 250-500 ml.). The extraction is continued until the aqueous layer ceases to yield a precipitate on addition of dilute ammonia (any iron in the starting material will concentration in the first 250-500 mi. of aqueous extract). About 2-3 liters of water is necessary to extract 40-50 g. of Sc_3O_3 from one liter of ether. The aqueous phase remaining in the first flask is now acidified with 30 ml. of 2N HC1 and the operation with one liter of ether is repeated (reuse the aqueous solutions in flasks 2 to 4.) A second repetition of the extraction procedure yields the last traces of Sc.

Such a purification of an oxide initially containing 75-80%, Sc_2O_3 , 8-9% ZrO₂, 0.8-0.9% HfO₂, 1-2% Y₂O₃, 0.5% Dy₂O₃, 1% Er₂O₃, 0.5% Tm₂O₂, 6-8% Yb₂O₃, and 1% Lu₂O₃ gave a 90% yield of Sc_2O_3 . Spectroscopic analysis (x-ray) revealed no other rare earth impurities nor Zr and Hf in this product (limit of detection: 0.1%); the remaining 10% of the scandium oxide present in the raw material was also obtained in greatly concentrated form. After conversion to the oxide, the residue left in the first flask contained less than 0.5% Sc_2O_3 .

Alternate methods: a) Fractional condensation of the chlorides.

b) Fractional sublimation of the acetylacetonates.

c) According to Vickery, pure Sc compounds may be obtained by ion exchange.

REFERENCES:

W. Fischer and R. Brock. Z. anorg. allg. Chem. <u>249</u>, 168 (1942); this paper also reexamines several other procedures for extraction of scandium; R. C. Vickery, J. Chem. Soc. (London) <u>1955</u>, 245.

Treatment of Monazite Sand

Monazite is the orthophosphate of the cerium group of rare earths; it contains oxides of the cerium group (50-70%), oxides of the Y group (1-4%) ThO₂ (1-20%), varying quantities of ThSiO₄, and small amounts of SiO₂, Fe₂O₃ and Al₂O₃.

A) EXTRACTION WITH SULFURIC ACID

The monazite sand is ground in a ball mill (final product approx. U.S. 30 mesh). Conc. H_2SO_4 (3.25 kg.) is heated to 200°C in a sixliter porcelain dish, and 3.5 kg. of ground sand is gradually added in small portions (efficient stirring is necessary). Heating and stirring are continued for 30 minutes after completion of the addition, until a dark gray, quite firm paste is obtained.

The paste is slowly poured (stirring) into 25 liters of cold water, and stirring is continued for one hour. If the solution is still warm after this time, ice is added until the temperature drops below 25°C, since the rare earth sulfates are more soluble in cold than hot water. The residue is allowed to settle, the clear supernatant is decanted, and the solid is suction-filtered and washed several times with cold water. The residue consists of SiO₂, TiO₂, ZrO₂ and unreacted monazite. The residues of several extractions may be combined and subjected to a second H_2SO_4 treatment.

B) PRECIPITATION OF THIS THE FORM OF ThP207

The filtrate, which contains H_2SO_4 , H_3PO_4 . Th and the rare earths, is diluted to 168 liters and stirred for one hour in an earthenware or wooden vessel. The nascent, slightly blue-gray, heavy, gelatinous precipitate is allowed to settle for 8-12 hours. It consists of ThP₃O₇ contaminated with phosphates of cerium and of other rare earths. The precipitation is complete when no additional solid separates on further dilution. The ThP₃O₇ is filtered off and washed with water.

C) PRECIPITATION OF THE BARE EARTHS IN THE FORM OF $N_{4,2}SO_4 + Ln_2(SO_4)_3 + 2H_2O$ OR $Ln_2(C_2O_4)_3 + 5H_2O$

The rare earths are isolated from the filtrate by agitation in the presence of finely ground Na_3SO_4 until the absorption bands of Nd are no longer observable through a 5-cm. layer of the clear supernatant. The precipitate is filtered off, washed and dried at 110°C [if the starting material contains large amounts of yttria earths (i.e., xenotime, YPO₄) it is best to precipitate with solid oxalic acid, since the double sodium yttria sulfates have appreciable solubilities in water].

A first crude separation of the ceria earths from the yttria earths is achieved by adding solid oxalic acid to the filtrate from the double sulfate precipitation. Use of a saturated solution of oxalic acid yields a precipitate which is difficult to filter and necessitates further dilution of the solution.

D) CONVERSION OF THE SULFATES OR OXALATES TO THE OXIDES

The double sulfates or oxalates are mixed with water and stirred to a thick paste, which is allowed to react with slightly more than the stoichiometric quantity of solid NaOH, which is added in small portions with constant stirring at high heat. As the reaction proceeds, the paste becomes increasingly liquid and stirring is easier. The reaction is brought to completion by further heating and stirring for one hour. The hydroxides are transferred to a 30- to 40liter earthenware container and stirred with 20-30 liters of water. The precipitate is allowed to settle, the supernatant is siphoned off, and the washing is repeated until the liquid gives only a weak alkaline reaction. The hydroxides are dissolved in conc. nitric scid (add 3% H_3O_2 if large amounts of Ce are present). This mitrate solution serves as starting material for further workup.

Further separation of the resultant mixture of rare earths and isolation of individual components are described in later procedures in this section; in particular, see the preparation of pure La, Pr and Nd compounds from ceria earths by ion exchange and the preparation of pure Ce, Sm, Eu and Yb compounds.

REFERENCES:

D. W. Pearce, R. A. Hanson, J. C. Butler, W. C. Johnson and W. O. Haas in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 38; S. J. Levy. The Rare Earths, London, 1924, pp. 18, 71, 79.

Treatment of Gadolinite

Gadolinite is an yttria earth-beryllium-iron (II) silicate; its approximate composition is $Y_2Be_3FeSi_2O_{10}$, and it contains up to 50% rare earth oxides and about 10% BeO.

A) EXTRACTION, SEPARATION OF SILICIC ACID

The gadolinite is pulverized in a ball mill to a size passing through a U.S. 140-mesh sieve. Two kilograms of this material are mixed with seven liters of conc. HCl and evaporated (stirring) in a shallow porcelain dish placed on a sand bath; the evaporation is continued until a stiff paste is obtained (1.5 days required). The residue while still hot is taken up in 2-3 liters of hot water, suction-filtered and pressed dry.

To complete the extraction, the residue is again treated as above with 0.5 liter of conc. hydrochloric acid, taken up in one liter of water, suction-filtered, and washed with 0.5 liter of hot, dilute hydrochloric acid. The residue (SiO₂ and impurities not attached by hydrochloric acid) is discarded; it contains only about 0.5% of the rare earths present in the starting material.

B) PRECIPITATION WITH OXALIC ACID

The combined filtrates from (A) are diluted with water to twice their volume and heated to 60° C; a thin stream of a hot solution of 1400-1500 g. of oxalic acid dihydrate in two liters of water is then added with stirring. The mixture is kept warm overnight in a covered container; the precipitate is suction-filtered while still warm and washed with warm water. This yields about 95% of the rare earths initially present. Large quantities of rare earth oxalates are best converted to other compounds by calcining in a stream of air at 600-700°C. The material is spread in a thin layer in a large crucible furnace and heated until the transient gray color disappears again. The oxides can then be readily dissolved in acids. They contain no more than about 0.1% Fe₃O₃ and 0.15% SiO₃.

C) PRECIPITATION WITH NH3

The iron concentrates in the filtrate of the oxalate precipitation so that it constitutes more than 50% of the total metals present. To separate the Be and the rare earths, the latter are precipitated with NH, as the hydroxides (after transient reduction of the iron to the divalent state). The filtrate of operation (B) (two liters) is di-luted with six liters of water in a 10-liter flask. The flask is provided with a dropping funnel, as well as gas inlet and outlet tubes; the gas inlet tube reaches to the bottom of the flask and the outlet terminates at the neck. The solution is heated to 60°C and the necessary amount of KMnO₄ [determined by testing a very dilute sample of the solution with Mn (II)] is added with efficient mixing to oxidize the oxalic acid. The highest possible concentration of KMnO4 should be used. Then 500-700 g. of solid NH4Cl is added and the mixture is brought to a boil while SO2 is passed through. The solution is maintained at the boiling point for an additional 30 minutes, a slow stream of SO₂ being bubbled through all the time. The flame is then removed, the SO_2 is replaced by a stream of Ha, and conc. carbonate-free ammonia is added until no further precipitation occurs. The precipitate should be pure white. A brownish color indicates incomplete reduction of the Fe; a greenish tinge {impure Fe(OH)2] indicates that the amount of NH4Cl added was insufficient. In either case, the addition of ammonia is discontinued, the precipitate already formed is redissolved in hydrochloric acid, and the procedural fault is corrected. If the precipitate assumes a greenish color only toward the end of the operation, this is an indication that Fe(OH), has begun to deposit because an excess of NH₃ is present in solution.

After completion of the precipitation the mixture is allowed to cool to 45°C, and a freshly prepared solution of 70 g. of $Na_2S_3O_4$ in 500 ml. of water and 20 ml. of dilute ammonia is added with efficient mixing. The passage of H₂ is discontinued and the precipitate is suction-filtered and washed with a warm (maximum 45°C) solution of 10 g. of $Na_3S_2O_4$ and 20 g. of NH_4Cl in one liter of water, followed by one liter of pure water. The filtrate and wash water are discarded. The rare earths which have remained in solution after the oxalate precipitation, as well as the Be, are thus quantitatively precipitated. A solution in which the weight ratio BeO: Ln_2O_3 : $Fe_3O_3 \approx 1:0.2:1.6$ yields a precipitate in which this ratio is 1:0.2:0.05-0.03.

D) SEPARATION AND RECOVERY OF THE Be

The moist hydroxide precipitate is dissolved in the minimum amount of warm glacial acetic acid and evaporated to complete drymess on a sand bath. Basic beryllium acetate $Be_4O(CH_3COO)s$ is distilled from the residue at atmospheric pressure (m.p. 254°C; b.p. 330°C; cf. the procedure for the preparation of basic beryllium acetate, p. 901). The residue from this Be separation may be purified by another gadolinite extraction.

REFERENCE:

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Pure La, Pr and Nd Compounds from Cerium Earths by Ion Exchange

Rare earth mixtures are efficiently separated by elution of complexes. Among the complexing agents which are usable as eluents, these which act as chelating agents possess significant advantages. A two-column process is usually employed: the first column is charged with the rare earth mixture and the second column with a suitable auxiliary cation. If the chelating agent used is readily soluble in water (for example, ethanolamine diacetic acid) the material in the second (or bottom) column may be in the H form.

The following process is suitable for rapid laboratory-scale separation of cerium earths: the cerium is removed from the mixture by precipitation with KMnO₄ and Na₂CO₃ (see below, preparation of pure Ce compounds). The remaining compounds are adsorbed on 250 ml. of a cation exchange resin (Dowex 50 or Wofatit KPS-200; particle size 0.2-0.4 mm.). The resin is then placed in an ion-exchange column (I.D. 4 cm.) which is partly filled with water. A second column of the same I.D. is filled in the same manner with 350 ml. of the resin in the Zn form.

The eluent flows successively through the two columns; it contains 2% of nitrilotriacetic acid and is buffered with NH₃ to a pH of 7.0. If the eluate flow rate is not less than 0.5 ml. per minute, there is no danger of formation of precipitates inside the columns. The eluate is collected in fractions; the lanthanides appear in the order of increasing ionic radius. The La, which remains in the columns after elution of the heavier earths, may itself be rapidly eluted with a solution containing 4% nitrilotriacetic acid and 2.4% NH₄Cl (pH 9).

The eluate fractions are brought to a boil and the rare earths: precipitated with oxalic acid. The mixtures are allowed to stand for 20 minutes at 80°C and filtered hot, and the solids are calcined to the oxides. The first fractions, which may contain minute quantities of Zn, are reprecipitated. More than 70% of the nitrilotriacetic acid used in the process can be recovered from the eluate by precipitation with HCl. Starting from 63 g. of the mixed oxide (14.7% La_2O_3 , 23.5% **PreOn.** 54% Nd₂O₃, 5.4% Sm₂O₃, 2.4% heavier earths), this method gave 8.3 g. of La_2O_3 (yield 90%, purity > 99.5%), 10.3 g. of **PreO**₁₁ (yield 70%, purity > 99%) and 30 g. of Nd₂O₃ (yield 68.5%, purity > 99%) in 50 hours of elution.

The method is also applicable to the yttrium earths, although in this case it requires more preliminary effort and takes longer.

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L. Wolf and J. Massonne. Chem. Techn. <u>10</u>, 290 (1958); L. Wolf and J. Massonne, J. prakt. Chem. (4) <u>275</u>, 178 (1956); L. Holleck and L. Hartinger. Angew. Chem. <u>66</u>, 586 (1954); <u>68</u>, 411 (1956); F. H. Spedding and J. E. Powell in: F. C. Nachod and J. Schuber, Ion Exchange Technology, New York, 1956, p. 365; J. Loriers and J. Quesney. Comptes Rendus Hebd. Séances Acad. Sci. <u>239</u>, 1643 (1954); J. Loriers. Ibid. <u>240</u>, 1537 (1955).

Pure Cerium Compounds

PRECIPITATION WITH Na₂CO₃ AND KMnO₄

A nitric acid solution of 250 g. of cerium earths, which should consist only of nitrates, is diluted to one liter and brought to a boil, and the pH is adjusted to 2-3 with aqueous Na_2CO_3 . This already precipitates some of the cerium in the form of Ce (IV) hydroxide. A solution of KMnO₄ is then added until the red color persists, the mixture is reheated to the boiling point, and the cerium is precipitated by adding (with constant stirring) a solution of KMnO₄ and Na_2CO_3 (mole ratio 1:4). The pH gradually reaches 4 and the red color becomes more intense; stirring at the boiling point is then continued for an additional 10 minutes and the precipitate is suctionfiltered and washed with hot water. The filtrate contains minute amounts of cerium, in addition to the other rare earths. If it is desired to isolate the last traces of Ce, the pH of the boiling filtrate is adjusted to 5-6 with aqueous Na_3CO_3 . The resultant precipitate consists of carbonates containing all the Ce present.

The cerium is isolated from the restdues [which consist of Ce (IV) and Mn (IV) hydroxides] by solution of the residues in conc. hydrochloric acid and precipitation in the form of the oxalate. The precipitate is calcined to CeO_3 (96% yield, 99.5% pure).

I. PRECIPITATION WITH CaCO₃ AND KBrO₃

The following procedure is suitable for a raw material mixture containing 40-50% CeO₂: a nitric acid solution containing about 4100 g. of the rare earth oxides (total of 12 liters) is divided in

three equal portions. The solutions are heated in procelain disbes and adjusted to pH 2.7 by adding $CaCO_3$ (mechanical stirring). Then 100 g. of KBrO₃ is added and the solutions are concentrated to one liter (see note below). This procedure is repeated several times to achieve complete oxidation and hydrolysis. If bromine vapor escapes during the evaporation, the pH is readjusted to 2.7 by adding further $CaCO_3$. The mixtures are then diluted to five liters. heated almost to the boiling point, and allowed to settle overnight.

The supernatant liquors are decanted, combined and, after addition of 60 g. of KBrO₃, evaporated to 2-3 liters. The mixture is then diluted to eight liters, brought to a boil, and again decanted.

The combined precipitates are boiled in six liters of water, the supernatant liquor is decanted, and the precipitate is suctionfiltered through a Büchner funnel. The mother liquor is combined with the solution containing the other rare earths.

Other cerium compounds, for example, the basic nitrates, may be purified and converted to the oxides by boiling 50 g, of the moist starting material with 200 ml. of 3N Na₃CO₃ solution. The basic carbonate is filtered off and washed with 50 ml. of water. The product is dissolved in 16 N HNO₃ containing 3% H₃O₂.

This method gives 99.8% pure CeO2 in 97.6% yield.

NOTE:

The Ce (III) seems to oxidize during the evaporation in the hot conc. solution, while the hydrolysis of the resultant Ce (IV) takes place in the hot dilute solution.

III. ETHER EXTRACTION OF Co (IV) NITRATE

Very pure CeO_a may be prepared from the commercial raw material by the following combined procedure: ten parts of orude oxide and seven parts of hydroquinone (reducing agent) are dissolved in boiling conc. hydrochloric acid. The hydroquinone oxidation products are destroyed by oxidative degradation with H_aO_a in ammoniacal solution, followed by evaporation with conc. nitric acid. Since it is accompanied by foaming, this operation must be carried out in a large vessel. If necessary the cerium may also be freed of organic contaminants by precipitation with oxalic acid, followed by solution of the precipitate in conc. nitric acid

If the starting material also contains thorium, the oxalate is boiled with a concentrated, neutral to slightly ammoniacel, solution of ammonium oxalate; the precipitate is suction-filtered and thoroughly washed. Repetition of this operation yields a solution of $(NH_4)_4Th(C_2O_4)_4$ which contains all the thorium initially present.

The nitric acid solution of nitrates, which is obtained in either case, is evaporated to dryness; it is then treated with NH4NO3

17

(Note: weight as the initial CeO₂) and evaporated several times with conc. HNO₃ until orange-red $(NH_4)_2Ce(NO_3)_8$ begins to precipitate from the deep red solution. The precipitate is filtered off on a fritted glass filter (additional double nitrate may be recovered from the filtrate by further evaporation). The product is recrystallized from conc. nitric acid, dissolved in 6N nitric acid (free of nitric oxide), and extracted with peroxide-free ether (attric oxides and peroxides reduce Ce⁴⁺). The residual material in the aqueous solutions should be reoxidized by evaporation with conc. nitric acid and extracted with ether, since the solutions still contain appreciable quantities of Ce³⁺.

The combined ether extracts are distilled, water being added during distillation. The cerium nitrate may be reprecipitated with water containing a hydrazine salt, which serves as a reducing agent.

The resultant cerium nitrate solution, which is about 2N in HNO₅, is filtered and slowly added in drops to a hot, concentrated solution of oxalic acid. The finely crystalline precipitate of cerium oralate is suction-filtered, washed with a large quantity of water, dried and calcined to the oxide.

The oxide may also be obtained by evaporation of the nitrate solution, followed by thermal decomposition of the cerium nitrate.

Preparation of cerium compounds of especially high purity (for neutron bombardment): Peppard et al. recommend extraction of the Ce (IV) from a 10M HNO₃ solution with a 0.75M or 0.30M solution of bls(2-ethyl)hexyl orthophosphate in n-heptane [D. F. Peppard, G. W. Mason and S. W. Moline, J. Inorg. Nuclear Chem. 5, 141 (1957)].

PROPERTIES:

Cerium (IV) oxide is white with a slight yellow tinge; the color is a function of particle size. Even slight contamination with **Pr or Tb** (0.005%) produces a distinct pink color; higher amounts cause a red-brown color. The calcined material is soluble in acids only in the presence of reducing agents. d (x-ray) 7.172. Crystal structure: type C1 (CaF₂ type).

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Pure Samarium Compounds

I. REDUCTION WITH CALCIUM AMALGAM

 $2 \operatorname{SmCl}_{2} + \operatorname{Ca(Hg)} = 2 \operatorname{SmCl}_{2} + \operatorname{CaCl}_{2}$ 513.6 40.1 442.7 111.9

A solution of 180-240 g. of anhydrous rare earth chlorides in 609-700 ml. of absolute ethanol is placed in a thick-wall, rubberstoppered separatory funnel. After addition of 7-10 g. of Ca in the form of a 1% amalgam (see p. 1804 for preparation), the separatory funnel is stoppered and vigorously shaken. Since this reduction to Sm (II) is accompanied by formation of calcium ethoxide and consequent evolution of Ha, the flask must be frequently vented by opening the stopcock (without, however, allowing air to enter). The initially yellow solution soon becomes dark; after a few minutes the color becomes dark brown-red and precipitation of SmCla begins. The Ca becomes exhausted after 20 minutes. The funnel is inverted so that it rests on the rubber stopper, a Bunsen valve is attached to the outlet tube, and the stopcock is opened. After 10 minutes, the CaO present in the mixture is neutralized by adding (through the funnel stem) 2-3 ml. of HCl-saturated anhydrous ethanol, and the funnel is vigorously shaken. The precipitate should turn bright red. After 30 minutes the Hg is separated and the finely crystalline precipitate of SmCla is centrifuged in the absence of air. The mother liquor is decanted and the precipitate is freed of the adhering solution by shaking with air-free absolute ethanol, followed by centrifugation.

Further purification is achieved by taking up the precipitate in water, in which it is oxidized to Sm (III) and forms the basic chloride. Dilute hydrochloric acid is added and the mixture is heated on a water bath until the mercury left in the SmCl₂ has agglomerated and can be filtered off. The yellow solution is concentrated until crystallization just starts, and then saturated with HCl while cooling in ice. The precipitated hexahydrate is dehydrated and again reduced. The SmCl₂ obtained after this last purification procedure contains only a few percent of Eu.

The Eu may be removed by electrolysis of an alkaline scetate solution of the Sm-Eu mixture in the presence of lithium nitrate; a mercury cathode is used. Onstott, starting from a precipitate containing 1.6% Eu₂O₃, was able to obtained a preparation entirely free of Eu in one electrolysis run. R. REDUCTION WITH Mg + HCl

Another process suitable for the separation of Sm from rare earth mixtures consists in reducing the samarium, in the form of hydrated chlorides in ethanol or ethanol-dioxane, by means of Mg + HCl. A mixture containing 3% Sm can be concentrated to 55% Sm in a simple run.

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- 2730 (1948).

Pure Europium Compounds

L EaCl, 2H,0

A conc. solution (d 1.35, 100 ml.) of rare earth chlorides con-taining about 70% Eu (balance Nd, Sm and Gd) is placed together with a few milliliters of conc. hydrochloric acid in a one-liter wide-neck flask. Zinc amalgam granules (100 g., U. S. standard mesh 80) are added, and the flask is stoppered and vigorously shaken by hand. From time to time it is held in front of the slit of a spectrometer to observe the absorption bands. The initially almost colorless solution turns yellowish; after about 30-40 minutes the Eu 5253 Å band disappears, indicating complete reduction to Eu (II). The solution is decanted from the remaining Zn while protected by a CO_2 blanket and poured into a second one-liter flask; the flask is closed with a two-hole stopper carrying a 250-ml. dropping funnel and a gas outlet capillary. Crystallization of $EuCl_2 \cdot 2$ H₂O starts after addition of the first 200 ml. of conc. hydrochloric acid; it reaches a maximum rate after 500 ml. has been added. This procedure precipitates 90% of the Eu present. After 2-3 hours of standing, the well-cooled mixture consists of almost equal volumes of pure white crystals with a faintly blue fluorescence and an essentially colorless mother liquor. The air-sensitive crystals are filtered under CO₂ through a cotion wool filter and suction-dried as far as possible. If oxida-

tion does occur, the filter cake becomes hot and evolves HCl gas, The Eu may be further purified by redissolving the product chloride under CO_2 . The operation should be repeated five times. Finally the product is filtered through a fritted glass filter (under a CO_2 blashet) and washed with 10% methanolic HCl. The alcohol and the HCl can then be removed by slight heating in a fast CO_2 stream.

1136

Another method for removal of traces of other earths present in crude europium consists in reduction of the europium with Zn amalgam in HCl solution. Then the trivalent earths are precipitated with carbonate-free ammonia. The Eu (ii) remains in solution.

II. EoSO.

| 2 EuCl ₃ 516.7 | + Zn = 65.4 | | ł | |
|------------------------------|------------------------|------------------|---|----------------|
| | • H ₂ SO, = | 445.8 = EuSO. | + | 136.3 2 HC2 |
| 222.9 | 98.1 | 248.1 | • | 72.9 |

A solution of 3.5 g of Eu_2O_3 in 5.4 ml of 6N HCl is diluted to about 200 ml. A Jones reductor (height 40 cm., diameter 2 cm.) is filled with 1% Zn amalgam granules (0.5-1 mm.), which are then washed with 200 ml. of 0.1N HCl. When the wash liquor just covers the zinc, the outlet of the reductor is dipped in 50 ml. of 8M H₂SO₄ in a 600-ml. beaker covered with a round piece of paper. Carbon dioxide is then introduced into the beaker to expel the air. The EuCl₃ is passed slowly (2 ml./min.) through the reductor, followed by 150 ml. of 0.1N HCl. Very light, white, hairlike crystals of α -EuSO₄ are the first product. This mixture is heated to 80°C in a CO₂ atmosphere, resulting in conversion of the α -form to the stable β -form, which is less soluble in dilute H₂SO₄ and settles as a dense crystalline mass. The mixture is cooled to room temperature, and the white EuSO₄ is filtered and washed with dilute hydrochloric acid, followed by a few millilliters of HCl-acidified methanol. The CO₂ blanket is not necessary during the filtration. The product may be dried in air at 75°C. The yield is 90% of 99.7% EuSO₄.

PROPERTIES:

White, microcrystalline. Sparingly soluble in water; d (25°C) 4.98. Isomorphous with SrSO4 and BaSO4.

III. EuCOs

 $E_{u}SO_{4} + Na_{4}CO_{2} = E_{u}CO_{5} + Na_{3}SO_{4}$ 248.1 106.0 212.0 142.1

First, 5 g. of EuSO₄ is gradually added to 300 ml. of a vigorously boiling, oxygen-free solution which is 1N in Na₂CO₃ and 0.4N in NaOH (12.6 g. of NaHCO₃ and 10.8 g. of NaOH). After a short time, the solution turns dark; the color disappears on further boiling, and a dense, lemon yellow, crystalline precipitate of EuCO₃ is

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1.41

formed. This precipitate is filtered and dried in air at 75°C. An almost 100% pure product is obtained in 90% yield.

When larger quantities of EuCO₃ are needed, the first fraction of the sulfate ions liberated in this reaction is removed by decanta-tion and further Na_3CO_3 -NaOH solution is added to the residue.

REFERENCES:

- L H. N. McCoy. J. Amer. Chem. Soc. 57, 1756 (1935); 59, 1131 (1937); 63, 3422 (1941); J. K. Marsh. J. Chem. Soc. (London) 1943, 531; G. Wilkinson and H. G. Hicks. Phys. Rev. 75. 1370 (1949).
- IL R. A. Cooley, D. M. Yost and H. W. Stone in: W. C. Fernelius, loorg, Syntheses, Vol. II, New York-London; 1946, p. 70; H. N. McCoy. J. Amer. Chem. Soc. <u>57</u>, 1756 (1935). III. R. A. Cooley, D. M. Yost and H. W. Stone in; W. C. Fernelius,
- Inorg. Syntheses, Vol. II, New York-London, 1946, p. 71.

Pure Ytterbium Compounds

I. ISOLATION OF YTTERBIUM FROM YTTERBIUM EARTHS

IN THE FORM OF Y5SO4

Reduction of Yb2(SO4)3 on a mercury cathode yields YbSO4. The method is particularly suitable for the preparation of pure Yb from ytterbium earth mixtures.

The crude oxide, which must be free of foreign metals [which decrease the overvoltage necessary for the reduction of Yb (III) because they tend to form amalgams], is converted to the sulfate by evaporation with H_2SO_4 . The electrolyte should contain 120 g. of sulfate and 50 g. of conc. H_2SO_4 per liter. The electrolysis is carried out in a thick-wall beaker b (Fig. 285) with its bottom covered with a 1-cm, layer of very pure mercury, A nickel bus bar k connects the mercury pool to the negative side of the power supply. A carbon rod a, partially immersed in a clay cell c filled with dllute H2SO4, serves as the anode. A stirrer t, which agitates both the mercury surface and the electrolyte, prevents the formation of a dense precipitate on the cathode and thus makes possible the preparation of larger quantities of YbSO4. The electrolyte temperature is maintained at 20 °C by external cooling with running water.

The electrolysis is carried out at 72 volts and a current density of 0.05 amp./cm? (about 4-4.5 amp. if the beaker is 19 cm. in diameter). At higher current densities the formation of crystais of YbSO4 is so rapid that they occlude considerable quantities of impurity ions (Tm, Lu, etc.) After a few minutes the

1136

solution turns green. When the cathode becomes covered with a loose layer of YbSO4 2-3 cm. thick, the current efficiency becomes very low and the electrolysis is stopped. Under the conditions described, the process requires 2-3 hours.

The precipitate is collected on a Buchner funnel and washed with water, and the residual water is rapidly removed by suction. Speed is necessary because the oxidation of YbSO4 is accompanied by a marked temperature increase, which could cause decomposition of the product YbSO4 (or Yb₂(SO₄)₃],

The precipitate is dissolved in dilute nitric acid, neutralized with ammonia, and reprecipitated with oxalic acid. The oxide obtained upon calcination of the oxalate still contains traces of the sulfate.

Additional quantities of YbSO4

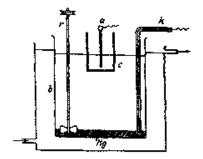


Fig. 285. Electrolytic preparation of ytterbium (II) sulfate. a carbon rod, b beaker, c clay cell.

may be recovered from the spent electrolyte by inclusion in the isomorphous SrSO4. If this is desired, then the electrolyte should contain only 0.5% H₂SO₄. The SrSO₄ solution is prepared by very rapid neutralization of 3 g. of SrCO₃ with the stolchiometric quantity of dilute HaSO4. This solution is added one hour after the start of the electrolysis. The added solution contains slowly crystallizing SrSO4. The addition is repeated twice at intervals of one hour. After 4-5 hours the precipitate, which contains SrSO4 and YbSO4 in a ratio of about 10:1, is filtered off and washed. The YbSO4 is protected against oxidation to Yb (III) by inclusion in the SrSO4 lattice. On calcination in air, YbSO4 is converted to Yb₂O₃ and may be separated from the SrSO, by digestion with conc. hydrochloric acid on a water bath. Some additional SrSO4 may be precipitated from this HCl solution by adding dilute sulfuric acid and allowing the solution to stand 12 hours. After removal of the SrSO4, the Yb is precipitated with oxalic acid in the usual manner. The electrolytic separation of Yb is accompanied by concentra-

tion of Tm and Lu in the residual solution.

Europium and samarium may be separated (as EuSO4 and SmSO₄) from the other rare earth metals by the same method.

PROPERTIES:

Formula weight 269.11. Green Yb^{3+} ions are oxidized by water to Yb^{3+} (evolution of H₂). Solubility in dilute sulfuric sold:

4 g. YbSO₄/liter of 1% H₂SO₄ (0.2N); 8 g. YbSO₄/liter of 5% H₂SO₄ (1N); 20 g. YbSO₄/liter of 12.5% H₂SO₄ (2.5N). Isomorphous with SrSO₄.

R. PURIFICATION OF YE (Snt, Eu) VIA AN AMALGAM PROCESS

 $Yb^{a+} + 3Na(Hg) = Yb(Hg) + 3Na^{+}$

The procedure is suited both for efficient purification of a concentrated ytterbium solution (method a below) and for isolation of Yb from a mixture of neighboring rare earths, as well as freeing the latter from Yb (method b).

a) A product containing about 97% Yb₂O₃ (balance is ytterblum earths), which may be prepared via YbSO4 by the method described under I, is dissolved in acetic acid on a water bath and evaporated until crystallization. A solution of 107 g. of ytterbium acetate in 133 ml. of boiling water is prepared in a one-liter flask. The hot solution is vigorously shaken for two minutes with 250 ml. of 0.5% sodium amalgam (125% of the theoretical Na). During the reaction 3 ml. of acetic acid is added to prevent the formation of hydroxide (formation of NaOH by partial decomposition of the sodium amalgam). It is best not to shake the mixture until the Na is fully spent, since shaking may cause the Yb to partially redissolve in the form of Yb (II) ions (green color of the aqueous layer). In addition, the Yb content of the amalgam should not exceed 1% to avoid solidification. The amalgam is separated from the solution and water-washed twice to remove the acetate. It is then treated with sufficient dilute hydrochloric acid to neutralize the residual Na. Small quantities of Yb which go into solution during this step are precipitated with NaOH. The amalgam is then shaken with encess hydrochloric acid until calomel starts to form. The Yb(OH)s precipitate is added to the HCl solution and the mixture is evaporated to a strup. The precipitating NaCl is filtered off. The filtrate is calcined. Spectroscopically pure Yb₂O₃ is obtained in a yield exceeding 90%.

The acetate solution remaining from the first extraction may be allowed to react, after addition of 3 ml. of acetic acid, with an additional 83 ml. of sodium amalgam. The resultant ytterbium amalgam is worked up as above. The mother liquor is converted to the hydroxide and may be reextracted after dissolving in acetic acid.

b) If complete extraction of Yb from a mixture of ytterbium earths is desired, the solution must be shaken up to 20 times with sodium amalgam and the aqueous layer repeatedly freed of the sodium acetate formed, since high concentrations of the latter interfere with the reaction. Using this method, Marsh was able to reduce the Yb content of a Lu preparation to 0,0033%. Pure compounds of Sm and Eu may be prepared by a basically similar method. The preferential formation of Sm, Eu and Yb amalgams is due to the fact that metallic Eu and Yb always form divalent ions, while Sm does so partially.

REPERENCES:

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- II. J. K. Marsh. J. Chem. Soc. (London) <u>1942</u>, 398, 523; <u>1943</u>, 8, 531; T. Moeller and H. E. Kremers. Ind. Eng. Chem., Anal. Edit. <u>17</u>, 798 (1945).

Metallic Rare Earths

I. REDUCTION OF THE CILORIDES WITH METALS

LANTHANUM METAL, POWDER

| LaCl, | + 3K - | = La + | 3 KCl |
|-------|--------|--------|-------|
| 245.3 | 117.3 | 138.9 | 223.7 |

The Vycor (or similar glass) apparatus shown in Fig. 286 is dried by fanning with a flame under high vacuum. A vacuum pump is connected at d; c and i are closed off with rubber stoppers. The apparatus is filled with pure, dry nitrogen or argon, and a small tube containing distilled potassium is placed in tube b; the neck of the potassium ampoule is broken immediately prior to use. Anhydrous rare earth chloride is introduced into a through tube c (air must be excluded during this operation) and tube c is immediately closed off again. The apparatus is melt-sealed at c and i. and evacuated through d to a high vacuum. Capillary f is heated and bent downward (to position b') and the potassium is slowly distilled from b' into g. This second distillation removes the possibility of traces of potassium oxide coming into contact with the chloride. The apparatus is then melt-sealed at f and e, a small portion of the potassium is distilled into constriction h, and the tube (a-g) is heated to 220-350 °C in an electric furnace. Part of the rare earth chloride is reduced after a short time; an additional fraction of the potassium is then distilled into h, and the tube is reheated in the furnace. This stepwise reduction is continued until most of the rare earth chloride has been converted to the metal. Only then is the remaining potassium distilled by turning the tube upside down and placing almost the entire apparatus (f-a)in the furnace. The potassium is then immediately distilled off

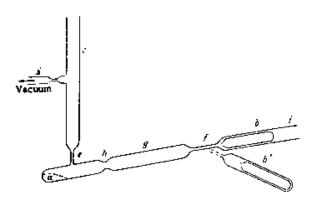


Fig. 286. Preparation of metallic rare earths by reduction of the chloride with metallic potassium. a rare earth chloride; b, b' metallic potassium; c filling tube for the rare earth chloride; d connection to vacuum pump.

again, and the process is repeated several times. This stepwise reduction prevents the reactants from fusing together, and thus ensures completion of the reaction. Finally the tube is gradually pulled out of the furnace, until a potassium mirror no longer forms at the unoccupied spots on the tube between g and h. The product consists of a loose black powder which does not adhere to the glass walls of the tube.

After cooling, tip f is connected via a dry rubber tube to the vacuum-N₂ (or Ar) system and broken off under N₂ or Ar. The alkali metal at g serves as a barrier and traps any traces of water vapor which may be introduced. The tube can now be broken at h without endangering the product, and the mixture of rare earth metal + 3 alkali chloride at a may be poured into a transfer apparatus through which protective gas is flowing (for transfer apparatus see Part I, p. 75 ff., especially Fig. 54).

All the rare earth metals, in the form of powders mixed with alkali chloride, may be prepared by this method. In preparing Sm, Eu or Yb metals (these elements form divalent compounds), a temperature of 250°C must not be exceeded, since at higher temperatures, the direction of the reaction is reversed and SmCl₂, EuCl₂ and YbCl₂ are formed.

CERIUM METAL, SOLID

 $\begin{array}{rrrr} 2 \, \mathrm{CeCl}_{3} \ + \ 3 \, \mathrm{Ca} \ = \ 2 \, \mathrm{Ce} \ + \ 3 \, \mathrm{CaCl}_{2} \\ 493.0 & 120.3 & 230.3 & 333.0 \end{array}$

A crucible of sintered CaO or dolomite is placed in an iron tube provided with a welded-on bottom and a screw lid, and the space between the crucible and the tube is filled with CaO powder. This precaution prevents contact between the reaction mixture and the iron wall if the crucible should break. Since the heat of the reaction between Ca and CeCl₃ is not sufficient for clean separation between the metal ingot and the slag, it is necessary to add a third' component which produces a highly exothermic reaction with Ca, e.g., I₂, S, KClO₃ or ZnCl₂.

For a tube 20 cm. high and 2.5 cm. in diameter, suitable quantities of reactants are 200 g. of CeCl₃, 103 g. of I_3 (mole ratio I:CeCl₃ = 0.625:1.0) and a 15% excess of very pure Ca powder (particles 0.3-2 mm.). The reactants are mixed under anhydrous condition and placed in the crucible; the iron cap is filled with CaO and screwed on. The tube is placed in a furnace heated to 650-750°C. The reaction starts suddenly when the temperature inside the tube reaches 400°C. The yield of Ce metal is 93%. The reaction may be carried out on a larger scale, but due to smaller relative heat losses, only 0.5 mole of I_3 per mole of CeCl₃ and a 10% excess of Ca are needed. The use of sulfur or KClO₃ lowers the yield. The resultant Ce metal contains 1-5% Ca and 0.1-1% Mg.

When smaller quantities of raw materials are used, the reaction temperature must be increased. This is done by replacing the iodine with $ZnCl_2$ (3-6% Zn, based on the amount of Ce). The product is freed of zinc by evaporating it in vacuum. The yield is 90% of Ce containing only 0.002% Zn.

Any Ca, Mg or Zn which may be dissolved in the Ce is removed by placing the product in a crucible made of MgO, CaO, BeO or Ta, which in turn is placed in a second crucible made of graphite. This assembly is placed in a quartz tube with one end closed and the other connected to a high-vacuum pump via a watercooled brass coupling. The coupling is provided with a glass window to facilitate optical temperature measurement. The wellinsulated quartz tube is placed for 30 minutes in an induction furnace heated to 1250°C. The melt is held at this temperature for 10-15 minutes, until cessation of bubbling.

This entire sequence of procedures can be used to prepare La, Ce, Pr and Nd in 99.9% purity. The reaction with Ca converts $SmCl_3$, $EuCl_3$ and $YbCl_3$ to the dichlorides. The preparation of Y fails due to the high melting point of this metal.

II. REDUCTION OF THE OXIDES WITH METALS

SAMARIUM METAL, SOLID

A tantalum crucible (height 20 cm., diameter 2.5 cm.) containing a mixture of 20 g. of Sm_2O_3 and 20 g. of freshly prepared La turnings is heated for 30 minutes at 1450°C in an electric furnace $R_{\rm eff}$, pressure of 0.001 mm. The upper part of the crucible projects

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tina -istat_eri from the furnace and is closed off with a lid carrying a connection to a high-vacuum pump. The Sm is deposited on the cooler parts of the crucible. The method results in a highly pure metal free of La; the yield is 80%.

Pure Yb metal may be prepared by the same method. In a similar preparation the La may be replaced by Ca or Al.

PROPERTIES:

Atomic weight 150.35. Silvery, air-stable metal. More volatile than La metal.

REFERENCE:

A. Jandelli. Atti Reale Accad. Naz. Lincei, Rend. VIII 18, 644 (1955).

II. ELECTROLYSIS OF FUSED CHLORIDES

LANTHANUM METAL, SOLID

The apparatus for melt electrolysis is shown in Fig. 287. The anode is a graphite crucible (inside diameter 40 mm., inside height 80 mm., wall thickness 5 mm., bottom thickness 10 mm.) containing the melt. The current is supplied through a sleeve surrounding the bottom of the crucible; the sleeve is connected to the power supply through an iron rod. The cathode is a Mo rod (diameter 10 mm., length about 100 mm.) friction-fitted into an iron pipe and covered near the top with a tube of sintered corundum cemented in with a talc-waterglass mixture. The rotating cathode should be able to agitate the melt; the current is supplied via a carbon friction contact. To collect the La metal which is thrown off by the spinning cathode and protect it against contact with graphite and the Cl_a formed at the anode, a sintered alumina crucible (upper diameter 40 mm., height 30 mm.) is fitted exactly into the graphite crucible.

The furnace is heated to 1000° C and the crucible is charged with a salt mixture of the following composition: 27.4% LaCl₃, 68.0% KCl, 4.6% CaF₂ (3.75 g, of KCl and 0.25 g, of CaF₂ per gram of La₂O₃). It is advisable to add initially only a small portion of the fluring material. The mixture is allowed to melt and any NH₄Cl present is allowed to escape; the remainder of the flux is then added during the first minutes of the actual electrolysis. The electrolysis is run at 6-8 volts and 40 amp. The highest current efficiencies and product yields are obtained at about 7 amp. per cm.² and 25 amp.-hr. The cathode should rotate at a rate of 1-2 r.p.s. At the end of the reaction, the current is shut off and stirring (rotation of the cathode) is continued for a few minutes. The crucible is then removed, allowed to cool and broken to pieces. The resultant ingot contains more than 99% lanthanum.

With some of the other rare earth metals (Sc, Gd), it is necessary to work below the melting point of the metal. In such cases the metal is deposited on a cathode of molten Zn or Cd, in which the metal dissolves. The Zn or Cd is vacuum-distilled from the product alloy.

PROPERTIES:

Atomic weight 138,92. Iron gray, with a vivid metallic luster when polished; ductile, malleable, Tarnishes rapidly in moist air. M.p. 885°C; d^{ao} 6.18. Crystal structure: α -La, type A3 (Mg type); β -La, type A1 (Cu type).

CERIUM METAL, SOLID

Metallic cerium is obtained via electrolysis of a fused mixture of anhydrous CeCl₃ and KCl-NaCl.

The reaction is carried out in a roughly cylindrical copper vessel, with a wall thickness of 1 mm. (see Fig. 260, p. 957). The inside diameter is about 2.5 cm. At the top, the tube widens to an inverted truncated cone with a base diameter of about 8 cm. The cathode is a carbon rod (diameter 9 mm., length 16 cm.) inserted from below; up to about 1.5 cm, from the upper end of the cylindrical section of the tube, the cathode is wrapped with asbestos cord; this asbestos cord, in conjunction with the unmelted portion of the chloride mixture which rests on it, serves as the bottom of the melting pot. The anode is a somewhat thicker carbon rod inserted from above. The position of the anode may be adjusted by a heightregulating device attached to the side of this crucible. The electrode gap is located approximately at the midheight of the conical melting space.

For small-scale preparations, a thin carbon rod about 3 mm. in diameter and 20 mm. long is clamped between the two cathodes. The crucible is filled with 200 g. of CeCls and 15-20 g. of KCl-NaCl (equimolar mixture) and the crucible contents are melted as rapidly

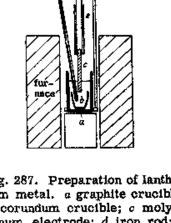


Fig. 287. Preparation of lanthanum metal. a graphite crucible; b corundum crucible; c molybdenum electrode; d iron rod; s corundum protective tube: fthermoccuple.

as possible with a current of 30-40 amp. at 12-15 volts. As soon as the melt thins in consistency, the anode is raised somewhat, the thin carbon rod is removed, and electrolysis is carried out for several hours at 700-750°C. After solidification the metallic ingot is removed and remelted under KCI-NaCl in a silicon carbide crucible.

PROPERTIES:

Atomic weight 140.13. Iron gray, with a vivid metallic luster when polished; may be cut with a knife; somewhat harder than lead; ductile, malleable. M.p. 635°C; d²⁵ 6.92. Tarnishes rapidly in moist air; burns at 160-180°C in a stream of O_2 . Attacked by water (evolution of H_2). Crystal structure: α -Ce, type A3 (Mg type); β -Ce, type A1 (Cu type).

IV. ELECTROLYSIS OF ALCOHOLIC CHLORIDE SOLUTIONS

The electrolysis of an alcoholic solution of a rare earth chloride on a mercury cathode (20 volts, current density 0.02 amp./cm²) yields an amalgam with a rare earth metal concentration of up to 35. The mercury is removed by vacuum distillation, leaving behind the pure rare earth metal.

REFERENCES:

- L. W. Klemm and H. Bommer, Z. anorg. allg. Chem. <u>231</u>, 141 (1937); H. Bommer and E. Hohmann. Ibid. <u>248</u>, 359 (1941); F. H. Spedding et al. Ind. Eng. Chem. <u>44</u>, 553 (1952); F. H. Spedding and A. H. Daane. J. Amer. Chem. Soc. <u>74</u>, 2783 (1952); E. J. Onstott. Ibid. <u>75</u>, 5128 (1953).
- IL A. H. Daane, D. H. Dennison and F. H. Spedding. J. Amer. Chem. Soc. <u>75</u>, 2272 (1953); E. J. Onstott. Ibid. <u>77</u>, 812 (1955).
- III. F. Weibke and J. Sieber. Z. Elektrochem. 45, 518 (1939); F. Trombe. Bull. Soc. Chim. France (5) 2, 660 (1935); W. Fischer, K. Brünger and H. Grieneisen. Z. anorg. allg. Chem. 231, 54 (1937); W. Muthmann et al. Liebigs Ann. 320, 242 (1901); see also Ind. Eng. Chem. 3, 880 (1911).
- IV. V. B. S. Hopkins et al. J. Amer. Chem. Soc. <u>57</u>, 2185 (1935); <u>56</u>, 303 (1934); <u>53</u>, 1805 (1931); Z. anorg. allg. Chem. <u>211</u>, 237 (1933).

Rare Earth Trichlorides

LaCl, (anhydrous)

L REACTION OF THE OXIDES WITH CI2 AND S2CI2

The rare earth oxide (1-2 g.) is placed in a porcelain boat and **chlorissied** for about five hours in a stream of Cl_2 - S_2Cl_2 (prepared

by bubbling Cl_2 through a wash bottle filled with S_2Cl_2 and standing in a 30-40°C water bath). The temperature is slowly raised during the process from an initial 400°C to about 20° below the melting point of the chloride. The chlorides deposit on the bottom as loose powders ready for use in further reactions.

The chlorides of Sm, Eu, Gd, Tb, Dy and Y, which melt below 700°C, are best prepared by dehydration of the hydrated chlorides in a stream of HCl.

II. DEHYDRATION OF THE HYDRATED CHLORIDES IN A STREAM OF HCl

The hydrate of the rare earth chloride (3-5 g.) is dried in a vacuum desiccator and then heated by stages in the region of the individual hydrate transition temperature while a stream of oxygenfree N₂-HCl mixture is passed over it. The boat, which may be of porcelain, quartz, gold or platinum, is placed in a tube of Pyrex, Vycor or quartz. The temperature may be raised beyond the transition region only when no further hydrochloric acid condenses on those sections of the tube which project from the furnace; if this precaution is not observed the chloride melts in the water of crystallization and the product then contains oxychlorides. Dehydration is complete after 30-60 hours. Heating at 300-400 °C in a stream of pure HCl is continued for one hour, and the product is allowed to cool in a stream of N₂. The stopcocks and ground joints which come into contact with the hydrogen halides are greased with a mixture of paraffin and paraffin oil.

The product must yield a clear solution in water. Contamination with traces of oxychloride may be recognized by turbidity of the aqueous solutions.

HL REATING OF THE HYDRATED CHLORIDES WITH NH4CL

Dehydration of the hydrated chlorides may also be achieved by heating with an excess (1-1.5 times) of NH₄Cl. The products, however, always contain small quantities of NH₄Cl.

IV. HEATING OF THE OXIDES WITH NH4CI

A 250-ml. quartz Erlenmeyer flask equipped with an adapter that can be closed off with a small glass cap and can also be connected to a quartz tube (length 25 cm., diameter 3 cm.) is filled with a mixture of 60 g. of the rare earth oxide and 120 g. of NH_4Cl .

The flask, tilted about 30° from the horizontal, is slowly rotated around its axis and heated to 220-250°C on an air bath. Evolution of NH₃ ceases after 6-8 hours. After a short coelding

pariod, the flask is closed with the glass cap while still warm and then allowed to cool completely. The cap is then replaced with the quarts tube. The other end of the tube is connected (via two gas traps) to an oil vacuum pump. The flask is evacuated and surrounded with an electric furnace extending a few centimeters beyond the quartz joint. The mixture is slowly heated to 300-350°C. resulting in evolution of a small quantity of water vapor and NHa. The excess NHACI sublimes into the quartz tube. To prevent cracking of the glass connection, it is sometimes necessary to cool the other end of the tube with a water-cooled lead or tin coll. After 4-5 hours, the mixture is allowed to cool, the quartz tube is cleaned. and the sublimation is repeated. Complete removal of the last traces of NH₄Cl is attained only at 400°C.

The method is particularly suited to the preparation of large quantities of product. The oil pump may be replaced by a jet ejector if an adequate trap filled with a drying agent is inserted in the line.

The above methods are suitable for the preparation of all the anhydrous rare earth chlorides, including that of yttrium, For the preparation of ScCla, see W. Fischer, R. Gewehr and H. Wingchen. Z. anorg. allg. Chem. 242, 170 (1939).

PROPERTIES:

Hygroscopic powders which give clear solutions in water and alcohol. The melting points drop from LaCl₃ (~860°C) to TbCl₃ (~600°C) and rise again to LuCl₂ (~900°C).

REFERENCES:

- L W. Klemm, K. Meisel and H. U. von Vogel. Z. anorg. allg. Chem. 190, 123 (1930).
- IL O. Hönigschmid and H. Holch. Z. anorg. allg. Chem. 165, 294 (1927); 177, 94 (1928); L. Holleck, Angew. Chem. 51, 243 (1938). III. F. Weibke and J. Sieber. Z. Elektrochem. 45, 518 (1939).
- IV. A. Brukl. Angew. Chem. 52, 152 (1939); J. B. Reed. J. Amer. Chem. Soc. <u>57</u>, 1159 (1935); D. H. West and B. S. Hopkins. Ibid. 57, 2185 (1935).

Rare Earth Tribromides

LaBr. (anhydrous)

1. DEHYDRATION OF HYDRATED BROMIDE-NH4Br MIXTURES IN A STREAM OF HB-

A hydrobromic acid solution containing six moles of NH4Br per mole of the rare earth bromide is carefully evaporated to dryness on an air bath, with constant stirring toward the end of the operation. The evaporation should be carried out in a stream of CO_2 . The crumbly salt mixture is dehydrated in a stream of HBr at slowly increasing temperatures. The product must not be allowed to melt under any circumstances! The sublimation of NH₄Br starts at 250°C; its last traces are removed at 600°C.

Very pure tribromides are obtained by dehydration and removal of NH₄Br from the LnBr₃ · 6 H₂O-NH₄Br mixture on heating in high vacuum. For the preparation of ScBr₃, see W. Fischer, R. Gewehr and H. Wingchen, Z. anorg. allg. Chem. 242, 170 (1939).

H. TREATMENT OF THE ANHYDROUS CHLORIDES WITH HBr

The anhydrous rare earth chloride (1-2g.) is heated in a stream of HBr for about seven hours. The temperature is slowly raised from 400°C to slightly below the melting point of the bromide.

PROPERTIES:

Hygroscopic powders. The melting points rise with atomic weight from $SmBr_3$ (~628°C) to $ErBr_3$ (~950°C).

REFERENCES:

- I. G. Jantsch et al. Z. anorg. allg. Chem. <u>207</u>, 361 (1932); G. Jantsch and N. Skalla. Ibid. <u>201</u>, 213 (1931).
- II. W. Klemm and J. Rockstroh. Z. anorg. alig. Chem. 176, 189 (1928).

Rare Earth Triiodides

LnI, (anhydrous)

I. DEHYDRATION OF HYDRATED IODIDE-NH41 MIXTURES IN A STREAM OF HI-H2

A mixture of one mole of $LnI_3 \cdot 6 H_3O$ and six moles of NH₄I is heated in a stream of HI + H₂ mixture with a moderate HI concentration. Under no circumstances should the temperature be raised at a rate fast enough to melt or sinter the product during the dehydration. Because the product is extremely sensitive to O₂ and molsture, great care must be exercised in purifying the gases. Since the last traces of NH₄I sublime only at high temperatures: the mixture is heated to 600°C during the last stage. When the dehydration is complete, the HI is flushed out with N₂. The iodides are stored under N₂.

This method is suitable for the iodides of La, Pr and Nd. Howe ever, SmIs is usually contaminated with some SmIs, which a converted to Sml₃ after elimination of the NH₄I. This is done by beating the product to 500 °C and treating it with iodine vapor. Again, under the conditions of this method, Eul₃ decomposes to Bul₃ and iodine. Because of their tendency to hydrolyze, the iodides of the rare earth metals which are less electropositive than Eu can be prepared only from the anhydrous chlorides. The same applies to Cel₃.

U. REACTION OF THE ANHYDROUS CHLORIDES WITH MIXTURES OF $\mathbf{H}_2 + \mathbf{H}_2$

The anhydrous rare earth chloride is heated for 4-6 hours until 600°C is reached; it is then held at this temperature for 30-40 hours in a stream of HI-H₂ containing as much HI as possible. The iodides are cooled and stored under N₂.

Special care must be exercised with the lower-melting chlorides, since the chlorides no longer react with the HI when enveloped in iodide.

PROPERTIES:

Hygroscopic powders. The melting points drop from LaI_3 (~761°C) to PrI_3 (~733°C) and rise again to LuI_3 (~1045°C).

REFERENCES:

- L G. Jantsch et al. Z. anorg. allg. Chem. <u>185</u>, 56 (1930); E. Hohmann and H. Bommer. Ibid. <u>248</u>, 384 (1941).
- II. G. Jantsch et al. Z. anorg. allg. Chem. <u>201</u>, 207 (1932); <u>207</u>, 353 (1932); <u>212</u>, 65 (1933); E. Hohmann and H. Bommer. Ibid. <u>284</u>, 383 (1941).

Rare Earth Dihalides

LoX: (anhydrous)

The trihalides of Sm, Eu and Yb are converted to the dihalides by beating in a stream of carefully purified H_2 . The temperature should not be raised as high as the melting point of the trihalide, since the molten compounds react either slowly or not at all with H_2 .

All the dichlorides, dibromides and dijodides of Sm, Eu and Yb can be prepared by this method. Note that EuI_2 is formed under the conditions given for the preparation of the triiodides (method ID. Thermal degradation of YbI₂ in high vacuum is the preferable method for obtaining YbI₂. REFERENCES:

W. Prandtl and H. Kögl. Z. anorg. allg. Chem. <u>172</u>, 265 (1928);
 G. Jantsch, H. Rüpnig and W. Runge. Ibid. <u>161</u>, 210 (1927);
 W. Kapfenberger. Ibid. <u>238</u>, 281 (1938);
 G. Jantsch, N. Skalla and H. Jawurek. Ibid. <u>201</u>, 218 (1931).

Cerium (III) Oxide

Ce₁O₁

Reduction of CeO₂ in a stream of H_2 is the best method. It is carried out in a silicon carbide boat. The H_3 must be carefully purified (free of oxygen) and dried. Very pure CeO₃ (3 g.), prepared as described on p. 1133, requires about 80 hours at 1000°C (or 45 hours at 1100°C) for complete reduction. Traces of La and Nd moderately increase the rate of reduction, while Pr and Tb do so markedly. The reduction is complete when the blue-black color of the partially reduced intermediates changes to the pure golden yellow of Ce₂O₃.

PROPERTIES:

Golden yellow (greenish yellow products are incompletely reduced); converts slowly in air to CeO_2 ; rapid conversion, accompanied by a glow, on slight heating. Readily soluble in acids. d (x-ray) 6.856. Crystal structure: type D5₂ (A-sesquioxide type).

REFERENCES:

E. Friederich and L. Sittig. Z. anorg. alig. Chem. <u>134</u>, 316 (1925);
 <u>145</u>, 127 (1925); W. Zachariasen. Z. phys. Chem. <u>123</u>, 134 (1926); G. Brauer and U. Holtschmidt. Z. anorg. alig. Chema. <u>265</u>, 105 (1951); U. Holtschmidt. Thesis, Freiburgi. Br., <u>1952</u>, G. Brauer and U. Holtschmidt. Z. anorg. alig. Chem. <u>279</u>, 129 (1955); D. J. M. Bevan. J. Inorg. Nuclear Chem. <u>1</u>, 49 (1955);

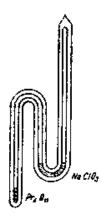
Praseodymium (IV) Oxide

PrO₁

At 400°C, praseodymium oxide preparations achieve a composition corresponding to PrO₃ only under an O₃ pressure of 263 sim. However, at 300°C, only 50 atm. of O₃ suffices. The oxide terms

41**5**1

6 164 W



 Pr_6O_{11} is carried out in the quartz tube shown in Fig. 288. The O_3 is generated by the decomposition of a weighed amount of NaClO₃ in the sealed tube. The amount of chlorate used is calculated beforehand to yield an O_2 pressure of 50 atm. in the sealed tube. After the NaClO₃ is decomposed by local heating, the entire tube is heated to 300°C for 48 hours.

PROPERTIES:

Dark brown powder, easily reduced by H_a to Pr_aO_3 . Crystal structure: type C1 (CaF₃ type). Measurements of the dissociation pressure of O_a indicate that the Pr-O system contains additional stable phases with compositions of $PrO_{1,715}$, $PrO_{1,602}$ and $PrO_{1,633}$.

Fig. 288. Quartz tube for oxidation of praseodymium oxide.

REFERENCES:

J. D. McCullough. J. Amer. Chem. Soc. <u>72</u>, 1386 (1950); W. Simon and L. Eyring. Ibid. <u>76</u>, 5872 (1954); R. E. Ferguson, E. D. Guth and L. Eyring. Ibid. <u>76</u>, 3890 (1954).

Rare Earth Hydroxides

Lu(OH), (crystalline)

Crystalline trihydroxides $Ln(OH)_3$ of the lanthanides (at least those ranging from La to Er) and of Y are prepared by heating the hydroxides under conc. (7N) NaOH: A solution of 2 g. of the nitrate in 2 ml. of water is added to a silver crucible containing a solution of 7 g. of NaOH in 7 ml. of water. The crucible, covered with a silver lid, fits precisely into a pressure tube closed off with a screwed-on cap. The tube is heated for 25 hours at 200°C. The mixture is cooled, the clear supernatant is siphoned off, and the product is washed several times (by decantation) with CO_2 -free water; it is then washed on a filter crucible in the absence of CO_2 and dried by suction. Final drying is achieved by storing the prodact for 24 hours over conc. H_2SO_4 in a vacuum desiccator.

PROPERTIES:

Transparent, hexagonal prisms. Solubility in conc. NaOH increases with the atomic number. The dehydration passes through an intermediate stage, MO(OH), in which the compounds have the PbFCl structure. La(OH)₂ has UCl₃ structure.

REFERENCES:

R. Fricke and A. Seitz, Z. anorg. allg. Chem. <u>254</u>, 107 (1947); R. Roy and H. A. McKinstry. Acta Crystallogr. (Copenhagen) <u>6</u>, 365 (1953).

Lanthonum Sulfide

La₂S₂

 $2 \text{LaCl}_{1} + 3 \text{H}_{2}\text{S} = \text{La}_{2}\text{S}_{3} + 6 \text{HCl}$ 490.6 102.2 374.0 218.8

Anhydrous LaCl₃ is heated in a stream of pure $H_{2}S$. The temperature is maintained at 500-600°C for several hours, followed by heating at 600-700°C overnight. Prior to use, the $H_{2}S$ is dried over CaCl₂ and $P_{3}O_{5}$, liquefied at -78°C (see p. 344 ff.) and evaporated from the liquid [A. Simon, Ber. dtsch. chem. Ges. <u>60</u>, 568 (1927) and this Handbook, Part I, p. 46 ff.] at a flow rate of one bubble per second. The intermediate product is then heated to 800-1000°C for several hours and allowed to cool in a stream of $H_{2}S$.

This method is suitable for all the rare earth suifides, including those of Sc and Y.

 $La_{2}(SO_{4})_{3} + 12 H_{2}S = La_{1}S_{3} + 12 S + 12 H_{2}O$ 566.0 409.0 374.0 384.8 216.2

The recrystallized sulfate hydrates may also serve as starting materials. Except for the fact that the decomposition temperatures of the dehydrated sulfates (given by Brill; see references below), are different, the procedure is similar to that given above for the chlorides. In this case, however, the products are usually contaminated with variable amounts of Ln_2O_2S .

Under these conditions $Y_2(SO_4)_3$ and $Er_2(SO_4)_3$ form Ln_2O_3S exclusively. It is also possible to prepare La_2O_3S by reduction of $La_2(SO_4)_3$ with H_3 at 800 °C.

If the treatment with H_2S is carried out at a lower temperature (580-600°C), the sulfates of La, Ce and Pr form polysulfides. Ln₂S₄, which decompose above 600°C to Ln₂S₃ and S.

The anhydrous rare earth sulfates start to decompose above 600°C, yielding the basic sulfates $Ln_2O_3 \cdot SO_3$, whose decomposition temperatures decrease from La (1150°C) to Yb (900°C).

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PROPERTIES:

Light yellow to light orange, opaque, hexagonal prisms. das

REFERENCES:

- W. Klemm, K. Melsel and H. U. von Vogel. Z. anorg. allg. Chem. <u>190</u>, 123 (1930).
- IL O. Brill. Z. anorg. allg. Chem. 47, 464 (1905); W. Biltz. Ibid. 71, 424 (1911); Ber. dtsch. chem. Ges. 41, 3341 (1908).

Lanthanum Selenides

La₂Se₃, La₂Se₄

 $La_2O_3 + 3H_2Se = La_2Se_3 + 3H_2O_{325,8} + 242.9 + 514.7 + 54.0$

I. Both La_3Se_3 and La_3Se_4 are prepared by high-temperature reaction of the oxide or chloride with H_2Se_4 .

A boat with La_2O_3 is placed inside a quartz tube surrounded by an electric furnace. Several boats containing Se are placed ahead of the oxide and heated with Bunsen burners to a temperature at which the Se slowly evaporates. A stream of carefully purified H_2 is passed through the quartz tube. After treatment for about five hours, during which the temperature of the La_2O_3 is slowly raised from 600 to 1000°C, La_2Se_4 is obtained in quantitative yield.

Heating the polyselenide for 30-60 minutes in high vacuum at 600-800 °C yields La₂Se₃. This operation must be carried out in a porcelain or corundum boat, since quartz reacts to form the rare earth oxide and SiSe₃.

The same procedure is used for Ce_3Se_4 and Pr_3Se_4 . However, Nd yields only Nd₂Se_{3.5}. The other rare earths do not form polyselenides. The sesquiselenides of these elements are best prepared by treating the rare earth chlorides with H₂Se:

$$2 La + 3 Se = La_2 Se_3$$

277.8 236.9 514.7

U. Synthesis from the elements by heating a stoichiometric mixture in a silicon carbide crucible held in an evacuated, sealed quartz tube.

PROPERTIES:

La₂Se₃: Brick red. Insoluble in both cold and boiling water; violently evolves H₂Se in dilute acids; decomposes slightly after several days in moist air. d²⁰ 6.19. REFERENCES:

I and II: W. Klemm and A. Koczy. Z. anorg. alig. Chem. 233, 66 (1937); A. Koczy. Thesis, Danzig, 1936.

La, Ce, Pr and Nd Monochalcogenides

LuS, LuSe, LuTe

These compounds are prepared by synthesis from the elements. The rare earth metal powder, as pure as possible, is placed in one of the arms of an L-shaped glass tube. The other arm contains the stoichiometric quantity of S, Se or Te (1:1 ratio). The tube is meltsealed in vacuum and heated in an electric furnace until the nonmetal is completely consumed. The temperature should reach 400-450 °C by the end of 2-3 days. Powder pattern analysis of the products indicates the formation of nonhomogeneous materials containing Ln_2X_3 and Ln_3X_4 , but not LnX, which starts to form at 1000-1100 °C.

For this reason, the samples obtained at the lower temperature are compressed (10 tons/cm.³) to cylindrical tablets in an atmosphere of CO_2 and sealed (under vacuum) in quartz tubes. The material is then slowly heated to 1000°C in an electric furnace (to 1100°C in the case of the tellurides). The products are 99.2-99.5% pure.

In addition, CeS may be prepared by heating Ce_2S_3 to 2200°C with a small excess of CeH₃; an evacuated molybdenum container is used.

PROPERTIES:

The monosulfides of La, Ce, Pr and Nd are greenish yellow, the monoselenides reddish yellow, the monotellurides blue violet. The sulfides decompose in moist air to form H_2S . Crystal structure: type B1 (NaCl type).

REFERENCES:

A. Jandelli. Gazz. Chim. Ital. <u>85</u>, 881 (1955); E. O. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles and L. N. Lofgren, J. Amer. Chem. Soc. <u>72</u>, 2249 (1950).

Europium (II) Chalcogenides

EuS, EuSe, EuTe

EuCi_t + S (Se; Te) + H_z = EuS (EuSe; EuTe) + 2 HCl 222.8 32.1 (78.0; 127.6) 2.0 184.0 (230.9; 279.5) 72.9 A mixture of EuCl₃ with a several fold excess of S, Se or Eecl₃, heated for several hours to 600°C in a fast stream of purified. Has

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This produces the desired chalcogenides. The S, Se or Te in excess of the desired composition is removed by heating for a few hours more at 820 °C in the stream of H_{g} .

Europium also forms an oxide, EuO, which may be prepared by **beating** $\text{Eu}_{3}\text{O}_{3}$ with La or C.

PROPERTIES:

EuO: dark red or blue depending on the conditions of preparation; d 7.7. EuS: blue black; d 5.7. EuSe: brown black; d 6.4. EuTe: black, metallic appearance. All the Eu (II) chalcogenides crystallize in type B1.

REFERENCES:

W. Klemm and H. Senff. Z. anorg. allg. Chem. 241, 259 (1939);
H. A. Eick, N. C. Baenziger and L. Eyring, J. Amer. Chem. Soc. 78, 5147 (1956); M. Guittard and A. Benacerraf. Comptes Rendus Hebd. Seances Acad. Sci. 248, 2589 (1959); L. Domange,
J. Flahaut and M. Guittard. Ibid. 249, 697 (1959); J. C. Achard. Ibid. 250, 3025 (1960).

Rare Earth Sulfates

Ln₂(SO₄)₃ · nH₂O

The oxide (0.3 g.) is dissolved in 20 ml. of hot 6N H_2SO_4 . The solution is filtered and allowed to crystallize over conc. H_2SO_4 in a vacuum desiccator. The product is filtered through fritted porcelain, washed twice with 10 ml, of water and once with 10 ml. of ethanol, and dried in air for four hours.

The product obtained from La by this procedure is $La_3(SO_4)_3$. #H₂O and from Yb it is Yb₃(SO₄)₃. 11 H₂O. The remaining rare earths and yttrium yield octahydrates.

Cerium sulfate, $Ce_2(SO_4)_3 \cdot 5H_3O_4$ is prepared by heating 3 g. of the chloride with 5 ml. of conc. H_2SO_4 until all the hydrogen chloride has been removed. Then 20 ml. of water is added and the product is allowed to crystallize in a desiccator.

Alternate method: A neutral or slightly acid solution of the sulfate is treated with about 3/4 of its volume of ethanol. The sulfates may thus be isolated rapidly and quantitatively, without the evaporation stage.

Anhydrous rare earth sulfates may be prepared by dehydration of the hydrates at 400-600 °C. The same procedure can also be used with the acid sulfates obtained by evaporating the chlorides with conc. H_2SO_4 . PROPERTIES:

The rare earth sulfates usually crystallize as octahydrates. The anhydrous sulfates are formed in the range of 155 to 295°C; if the dehydration is carried out carefully, it is sometimes possible to detect intermediate stages, such as pentahydrates (Pr. Nd, Er) and dihydrates (La. Ce, Nd, Yb).

REFERENCES:

W. W. Wendlandt. J. Inorg. Nuclear Chem. 7, 51 (1958); W. Biltz. Z. anorg. Chem. <u>17</u>, 427 (1911); O. Brill. Z. anal. Chem. <u>47</u>, 464 (1905).

Rare Earth Nitrides

LnN

Rare earth nitrides may be prepared by heating the metal in a stream of N_2 or NH_3 , or by reaction of the chloride with NH_3 . The preparation of LaN by the first method is given as an example.

LANTHANUM NITRIDE, LaN

Lanthanum filings (several hundred milligrams), prepared from the metal in a stream of N_a , are freed of iron with a magnet and heated in a molybdenum hoat placed in a stream of purified N_a . The azotization requires 2-4 hours at 750°C, 1-2 hours at 900°C.

The nitrides of Ce, Pr, Nd, Sm, Eu and Yh may be prepared by a basically similar method.

PROPERTIES:

Black powder; evolves NH₃ in moist air. Crystal structure: type B1 (NaCi type).

REFERENCES:

B. Neumann, C. Kröger and H. Haebler. Z. anorg. allg. Chem. 207, 148 (1932); W. Muthmann and H. Kraft. Liebigs Ann. 325, 274 (1902); A. Jandelli and E. Botti. Atti R. Acad. Naz. Lincel, Rend. [6] 25, 129 (1937); R. A. Young and W. T. Ziegler. J. Amer. Chem. Soc. 74, 5251 (1952); H. A. Elck, N. C. Baenziger and L. Eyring. Ibid. 78, 5987 (1956); B. M. Ormönit and E. V. Balabanovich. Russian Patent 51,424, Chem. Zentr. 1938, H, 573; W. Klemm and G. Winkelmann. Z. anotherally. Chem. 288, 87 (1956).

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Rare Earth Nitrates

Ln(NO₂), (anhydrous)

 $Ln_sO_s + 6N_sO_s = 2J_m(NO_s)_s + 3N_sO_s$

Anhydrous nitrates of the rare earths may be obtained from the oxides by heating with NH_4NO_3 or, better, by treatment with liquid N_2O_4 . However, $Nd(NO_3)_3$ can be prepared only from Nd_2O_3 and N_2O_4 ; heating Nd_2O_3 with NH_4NO_3 yields $Nd(NO_3)_3 \cdot NH_4NO_3$.

The apparatus for the preparation from the oxides and N_2O_4 is shown in Fig. 289. Drying tower *a*, filled with P_2O_8 , is connected to storage bottle *c* through a vacuum-type stopcock *b*. A mercury manometer, which serves as a safety valve, is attached at *f*, and a McLeod gage is connected to *g* via a cold trap. The 150-mi, steel bomb *h* is equipped with a needle valve at the top and a square thread screw at the bottom; the latter is for the introduction of the dry oxide (about 2 g.) and removal of the reaction product. The bottom neck of the bomb and the corresponding surface of the screw head have machined seats for a lead O-ring. Lead packing may also be used at the junction of the bomb and the needle valve. The metai and glass tubes are connected at *i* by means of a cement seal (for example, Glyptal). Two stopcocks, *c* and *d*, and a cold trap *k* complete the system.

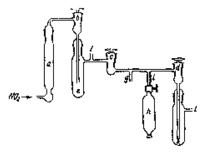


Fig. 289. Preparation of anhydrous rare earth nitrates. a drying tower; b. c. d vacuum-type stopcocks; f. g connections to manometers; h steel bomb; k cold trap.

The apparatus is evacuated through l to about 0.02 mm. Stopcock e is closed and about 30 mi. of liquid N₃O₄ is condensed in eby cooling with liquid N₂. Then c is opened, b and d are closed, and the N₃O₅ is distilled into the steel bomb h (40°C water bath if e, cooling with liquid N₂ at h). The needle value is closed and the bomb disconnected at i. A steel jacket is screwed on and the bomb is heated for 24 hours at 150°C. After cooling, the N₂O₄ is removed (vacuum) via a system of drying towers filled with $Mg(ClO_4)_3$ and collected in a trap cooled with Dry Ice-acceler.

The last traces of N_2O_4 are removed by beating the product in a drying pistol at 137°C (boiling xylene). Very pure nitrates are obtained in 100% yield.

Up to now, this method has been used for the preparation of the nitrates of Y. La, Pr, Nd, Sm and Gd. For the preparation of $(NH_4)_2Ce(NO_3)_6$, see G. F. Smith, V. R. Sullivan and G. Frank, Ind. Eng. Chem., Anal. Edit. 8, 449 (1936), as well as p. 1133 f. of this Handbook.

PROPERTIES:

Loose powders; form clear solutions with water and ethanol (very exothermic process). The nitrate colors differ only slightly from those of the corresponding anhydrous chlorides.

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REFERENCE:

T. Moeller and V. D. Aftandilian. J. Amer. Chem. Soc. <u>76</u>, 5249 (1954); T. Moeller, V. D. Aftandilian and G. W. Cullen in: W. C. Fernelius, Inorg. Syntheses, Vol. V, New York-London, 1957, pp. 37-42; L. F. Audrieth, E. E. Jukkola, R. E. Meints and B. S. Hopkins. J. Amer. Chem. Soc. <u>53</u>, 1807 (1931).

Rare Earth Cyclopentadienides

Lu(C,H₄)1

$LnCl_s + 3 NaC_sH_s = Ln(C_sH_s)_s + 3 NaCl_s$

The anhydrous rare earth chloride, in tetrahydrofuran solution, is treated (stirring) with the stoichiometric quantity of cyclor pentadienylsodium. The solvent is then removed by distillation and the product is sublimed at 200-250°C in vacuum (10⁻⁴ mm.).

Up to now, only the tricyclopentadienides of Sc, Y, La, Ce, Pr Nd, Sm and Gd have been prepared.

PROPERTIES:

Crystalline compounds; begin to decompose above 490 (Insoluble in hydrocarbons, soluble in tetrahydrofuran) **1.3-dimethoxyethane.** Decompose in water to cyclopentadiene and the hydroxide. Quite stable in air, with the exception of $Cic(C_3H_2)_3$.

REFERENCE:

G. Wilkinson and J. M. Birmingham. J. Amer. Chem. Soc. 76, 6210 (1954).

SECTION 22

Titanium, Zirconium, Hafnium, Thorium

P. EHRLICH

1. 20 P

Titonium

Ti

Due to its great affinity for a large number of elements, the preparation of titanium poses considerable difficulties. In particular, N, C and O dissolve to an appreciable extent in the metallic phase, and cause cold-shortness even when present in minute quantities. They cannot be removed either chemically or by sintering or melting in high vacuum. Consequently, the relatively easy conversion of TiO_2 with Ca (method I below) yields only 98% pure metal, even under conditions where the highest purity of apparatus and raw materials is maintained.

Pure metal that is ductile while cold can therefore be prepared only by methods which use halides as the starting materials. However, these procedures, which are based on the reactions $K_2 TiF_6$ (or $Na_2 TiF_6$) + Na (method II) or TiCl₄ + Na (method III below), suffer from the drawback that the deposited metal is usually porous or flaky, which leads to reoxidation during the removal of the alkali halide by-product; it is therefore used only as a crude starting material for the purification process. Nevertheless, careful adherence to a number of precautionary measures permits the preparation, even by these methods, of pure metal which can be cold-worked. The Kroll magnesium process (method IV), which utilizes the reaction between TiCl₄ and Mg, is used at present both in the laboratory and in industry.

The highest purity (0.03% C and ~0.006% N) is attained via the elegant recovery process of van Arkel and de Boer (method \dot{Y} below). This is based on the thermal decomposition of than iodide at 1100-1500°C.

I. PREPARATION OF CRUDE METAL FROM THE OXIDE AND CALCIUM

> $TiO_{2} + 2Ca = Ti + 2CaO$ 79.9 80.2 47.9 112.8

When only crude starting metal for the refining process is desired, the preparation may be simplified and carried out

• bomb made of two steel sections welded together. Section 1 (the one of larger diameter) consists of a tube of type 304L stalaless or low-carbon steel with a welded-on bottom. A wall thickness of 1 mm. is sufficient if the tube diameter does not acceed 25 mm. This section is annealed at 1000 °C in moist Ha (for more efficient removal of the P and C present). A second, crucible-like section, 40-60 mm. long, of exactly the same shape and precisely fitting into the first section (in such a way that the two sections telescoped together make up a vessel closed on all sides), is charged with the starting materials and forced as far as possible into the first section in order to reduce the air space inside to the minimum and to give the tightest possible seal between the two walls. If this is done, then the rims of the two tubes may be welded together without a welding rod; the lower section of the tube, that is, the section encompassing the charge, is cooled in water during the welding operation. One can avoid, to a large extent, the penetration of the welding gases into the bomb either by extending the sealing surface between the two tubes (that is, by using longer tubes for an identical charge), or by crimping the upper rim of the outer crucible around the inner one. As an explosion protection, and to provide a backup to strengthen the bomb walls, a closely fitting external tube or jacket, made of the same material and open at both ends, should surround the bomb. Scaling of the bomb may be prevented by preheating the latter inside a porcelain tube in a stream of Ha; if the heating must be carried out in air, a coat of aluminumbronze paint will prevent too rapid oxidation of the tube.

Following the reaction (see description below) the bomb is allowed to cool completely before being sawed open. The sawing should not introduce any iron filings into the product (avoid tilting the bomb during sawing or cutting at an angle). The reaction product can usually be loosened by gentle tapping with a hammer while the tube is clamped in a vise. Alternatively, the crucible may be sawed open along its length and the steel jacket is just peeled off.

Only Si-free, well-dried TiO_2 starting material should be used, to avoid formation of silicon or silicides. If this precaution is not taken, these impurities are carried over in the subsequent refining process and are incorporated into the titanium ingot. Furthermore, the reduction should be carried out only with distilled Ca: addition of distilled Na is advantageous. Thus, the reduction of 25 g. of TiO_2 with a mixture of 40 g. of Ca and 20 g. of Na yields about 13 g. of crude Ti (with a metal content of about 90%). Heating for 20 minutes at 1000°C suffices for complete reduction. After cooling and opening the tube, the contents are ground to pea size and leached with alcohol, water and increasingly concentrated portions of hydrochloric acid. The residue is washed free of chloride, the water is removed with alcohol, and the product is dried at 110°C.

The preparation of titanium that is malleable when hot (>200°C) by this process is described by Kroll. Pure TiO₂ (770 g.), turnings of distilled Ca (770 g.), and fused and pulverized CaCly/BaCla (750 g./250 g.) are mixed and pressed into briquets, which are allowed to react under 99.2% Ar in an electric furnace at > 700°C. The addition of the salts is necessary to moderate the reaction and, above all, to prevent the formation of CaTiO₃, a product which does not react with Ca even on repeated reduction. The use of CaH₂ in the second reduction has proved useful, since the powdery hydride mixes very readily with the other reactants while the nascent Ha it evolves is a powerful reducing agent, Thus, 348 g. of Ti (from the first reduction stage) + 400 g. of CaCl / BaCl = (3:1) + 50 g. of Ca + 50 g. of CaH, gave a yield of 337 g. of metal after heating for one hour at 1000°C under 99.6% Ar. The very well-sintered product is crushed and washed with water and concentrated hydrochloric acid, yielding fairly homogeneous granules.

The original reference covers the constructional details of the furnace.

With sufficiently small inputs $(20-30 \text{ g. of TiO}_B)$ the second reduction may also be carried out in the welded bomb and without the addition of CaH₂; the temperature should then be 1000°C (see also the procedure for Th, method II).

As in the preparation of the rare earth metals $\{F, H, Spedding et al., Ind. Eng. Chem. <u>44</u>, 553 (1952)} the addition of free lodins to the reduction mixture is recommended, since the large heat of formation of Cal. facilitates fusion of the metal.$

II. PREPARATION OF CRUDE METAL FROM FLUORIDES AND SODIUM

| | $Na_{2}TiF_{4} + 4Na = Ti + 6NaF$ | |
|----|--------------------------------------|-----|
| or | 207.9 92.0 47.9 252.0 | |
| | $K_{2}TiF_{6} + 4Na = Ti + 2KF + 4N$ | яF |
| | 240.1 92.0 47.9 116.2 168 | 1.0 |

The fluorotitanetes are prepared by dissolving pure TiO_2 in an excess of warm 20-40% hydrofluorio acid, treating the mixture with a stoichiometric quantity of NaOH or KOH, evaporating the solution without overheating (at 40-60°C) until saturation, and allowing the product to crystallize. In the case of the potassium salt, the product is the monohydrate; it is readily recrystallized from water. Heating of the air-dried product for two days at 35°C readily yields the anhydride, which in air at 500°C decomposed

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7. 2.9

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to the oxyfluoride. The Na₂TiF_e crystallizes already as the anhydrous salt and may be obtained in 99.9% purity by repeated precipitation with alcohol from aqueous solution. The small amount of water remaining in the product after drying in air is difficult to remove by heating without causing partial hydrolytic decomposition [H. Ginsberg and G. Holder, Z. anorg. alig. Chem. 190, 407 (1930); <u>196</u>, 188 (1931); <u>201</u>, 198 (1931); <u>204</u>, 225 (1932)]. The Na₂TiF₅, in portions of up to 1 kg., may be readily reduced

The Na₃TiF₅, in portions of up to 1 kg., may be readily reduced with a 10% excess of Na in a bomb. The sodium is cut into small cubes and mixed with the hexafluorotitanate. After filling, the bomb is welded as in method I and heated to 1000°C. It is imperative that the fluoride be absolutely dry, otherwise an explosion may occur.

When $K_2 TiF_6$ is used in the same process, a Na excess of only 1% is used, to prevent the formation of too much K, which may cause ignition of the mixture upon opening of the tube.

The one great disadvantage of this process is the fact that removal of the fluorine from the product requires very long boiling with large quantities of water. Direct washing of the fluorine-containing reaction mass with hydrochloric acid is not feasible, since the alkali fluorides react with the acid to form hydrofluoric acid, which dissolves the titanium metal. On the other hand, boiling with water results in considerable oxidation: the Ti thus produced may contain more than 20% of the oxide. After the treatment with water, the metal is boiled a few times with aqueous sodium hydroxide and is then treated with cold, dilute hydrochloric acid (too much Ti goes into solution with warm acid).

III. PREPARATION OF CRUDE METAL. FROM CHLORIDE AND SODIUM

| TiCl | + | 4 Na | = | Ti | + | 4 NaCl |
|-------|---|------|---|------|---|--------|
| 189.7 | | 92.0 | | 47.9 | | 233.8 |

If the reagent quantities are small, the welded steel bomb described in method I can be used. The temperatures must be very high (to start the reaction, the bomb must be red-hot) and thus the TiCl₄ vapor pressure is very high. Larger quantities (500 g. of TiCl₄ + 245 g. of Na) must therefore be heated in a thick-wall steel bomb, the lid of which is sealed on with a copper gasket and secured with a heavy screwed-on cap.

The TiCl₄ pressure in the bomb can be kept low by one of two methods: a) the starting temperature of the reaction may be lowered by the addition of a tablet of $KClO_3$ -Na; the small amount of oxygen introduced is not detrimental provided only crude metal is desired; b) the reaction tube may be constructed in such a way that there exists a temperature gradient and only the sodium is heated to 700-800°C. If the amount of starting material is not too small, the heat of reaction developed in the process is sufficient to cause sintering of the metal; the heat may even be sufficient for partial melting of the charge. The product titanium is first washed with alcohol to remove the excess sodium, then with water to remove salts, and finally with dilute hydrochloric acid. After repeated washing with water, alcohol and ether, the metal is dried in a vacuum desiccator. Assuming the above-mentioned charge of 500 g. of TiCl₄, the product consists of about 31.5 g. of half-fused metal and 4.5 g. of fine powder, as well as 71 g. of lumps and grains whose Ti content ranges between 96 and 99.5%. The powder fraction oxidizes quite readily.

This metal is much better suited as crude Ti for the refining process than the product obtained from the hexafluorotitanate.

In the industrial Degussa process, 46 kg. of Na is heated to 700-800°C. Then, 85 kg. of TiCl₄ is piped onto a layer of molten KCl/NaCl (15/15 kg.) situated below the Na. The resultant metal consists of 98% Ti and 2% Fe.

IV. KROLL MAGNESIUM PROCESS

 $TiCl_4 + 2Mg = Ti + 2MgCl_1$ 189.7 48.6 47.9 190.4

A) PREPARATION OF THE METAL

Magnesium works just as well in the reduction of TiCl₄ as sodium; in addition, commercial magnesium is already very pure and may be handled in air without special precautions. Thus, magnesium is the preferred reducing agent.

The reduction apparatus is shown in Fig. 290.

Since titanium attacks iron at high temperatures, the entire reaction zone of the crucible must be lined with a 1.5-mm.-thick sheet of molybdenum. Although molten Ti also adheres to molybdenum, the two metals can later be separated on a lathe. The TiCl₄ itself does not react at high temperatures with either Fe or Mo; the only precaution necessary is to keep all iron parts inside the furnace oxide-free.

The reaction crucible b, lined with molybdenum sheet c, is charged with 360 g, of very pure Mg blocks (the Mg metal surfaces are precleaned with a file). The adapter cover c, which carries the dropping funnel m and the Ca electrodes, is put in place and the entire system is evacuated to 0.1 mm. Very pure Ar is introduced, and an electric arc is struck and maintained for 10 min. between the two Ca electrodes c; the resultant Ca vapor serves as a scavenger for moisture and impurity gases. Final drying of the Ar is achieved by dropwise addition of a small quantity of TiCl₄ from the small dropping funnel m.

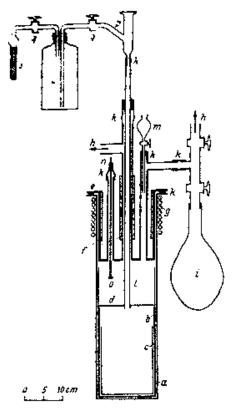


Fig. 290. Preparation of titanium metal from titanium (IV) chloride and magnesium. a) chrome-nickel alloy outer container (Inconel, Nichrome, or other similar alloys may be used); b) iron crucible; c) molybdenum lining; d) ironplate lid; c) adapter cover; () cooling chambers; g) cooling coils (lead); h) vacuum line; i) rubber balloon for Ar: k) rubber connections and seals; 1) iron inlet tube for TiCl₄; m) dropping funnel with TiCla; n) electrodes; o) calcium rods; p) glass adapter for a sight glass; q) stopcocks; r) storage bottle with TiCla: s) $CaCl_2$ tube.

When the alloy container g reaches a temperature of about 700°C, 500 ml. of TiCl₄ is slowly added to the reaction chamber from the storage bottle r. The addition rate is such that it takes 1.5 hours to add all of the TiCl₄. The temperature, which rises to about 1050°C, should be precisely controlled during the entire addition. The remaining 150 ml. of TiCl₄ is then added very slowly over a period of 0.5 hour, the temperature being gradually raised above the boiling point of Mg (to a maximum of 1180°C).

The molten Mg creeps over the surface of the nascent clumps of Ti, thus constantly contacting fresh TiCl₄. In the process small quantities of Mg and MgCl₂ are occluded in the Ti; the final heating of the iron crucible to above the boiling point of Mg is intended to counteract this phenomenon.

The progress of the reaction may be observed through the quartz window set in adapter p. If the rate of addition of TiCl₄ is not precisely controlled, the inlet tube l may become plugged with Ti sponge.

After cooling in argon, the crucible is full of large clumps of light Ti metal embedded in white MgCl₂ crystals. The metal contains extremely finely divided Mg and MgCla; however, no Mg-Ti alloy is formed. This mass is removed from the crucible with the help of a lathe, cutting as far as the molybdenum lining; the pieces of Ti are held so firmly in the surrounding MgCl₂ that metal turnings can be produced without any difficulty. These are first very carefully leached with water, and are then treated with an excess of dilute HCl. Decantation yields about 1% of the product in colloidal form. The smaller turnings are wet-ground in a ball mill and worked up separately. They are unsuitable for the production of ductile Ti. The coarser pieces are crushed to 10-12 U. S. mesh size, and this coarse metal powder is rewashed, separated from the fines, and etched with hot hydrochloric acid (1:3) until the acid becomes deep violet. The acid treatment is necessary because the crushing operation oxidizes the surface of the metal particles (in contrast to the zirconium oxides, the titanium oxides can be removed by acid leaching). After another washing procedure, first in cold 5% hydrochloric acid and then in water, followed by drying, the powder is freed of Fe with a magnet, rescreened, washed with alcohol and dried at 120°C. The vield of Ti metal is 284 g. (95.9%).

Worner, as well as Wartmen et al., has modified the above procedure in several respects. They carry out the reaction in vacuum; however, this necessitates the use of a double-walled container. The addition of TiCl₄ is carried out much more rapidly (80% at 30-40 ml./min., the remainder at 10 ml./min.), so that 1500°C temperatures occur locally, and external heating may be stopped as early as five minutes after the start of the TiCl₄ addition. When the reaction is complete, heating at 900°C is continued for 45 minutes. The reaction product is not leached; MgCl₂ and unreacted Mg are partly removed by evaporation and partly by fusing and draining.

B) REMELTING OR RESINTERING OF THE METAL

The Ti sponge may be converted to solid metal by fusion in an arc furnace, in which either high vacuum or a pure argon (99.92%) atmosphere is employed; the other acceptable procedure is sintering with alternating pressing and heating in high vacuum (10^{-4} mm.) at 1000°C. The Ti powder may also be hot-rolled in air while contained in a welded steel container. In the last case, contamination with Fe is slight and the iron is easily removed by etching the ingot after unwinding the steel sheet. For further details, see the original references.

Assuming that the proper conditions are observed, the product metal is about 99.8% pure, and contains 0.06% Fe, 0.1% O. 0.02% N and 0.02% MgCl₂.

A. THE REFINING PROCESS OF VAN ARKEL AND DE BOER

$$Til_4 = Ti + 2I_7$$

555.6 47.9 507.7

a) The iodides are used for the preparation of small quantities (~20-30 g.) of metal; these highly hygroscopic compounds are not introduced directly as raw ma-

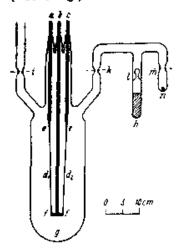


Fig. 291. Preparation of titanium metal by the process of van Arkel and de Boer.
g) pyrex bulb; a, b, c) triangular arrangement of tungsten bus bars; d₁, d₂) tungsten wires; h) iodine storage flask; l) shatter valve; n) steel ball.

terials, but are produced as intermediates during the process in which they form from crude metal and iodine. The most suitable crude titanium for this process is that prepared from TiCl4 and Na. Titanium oxide, nitride or carbide are attacked by the iodine; thus, the corresponding nonmetals are left unchanged and do not incorporate into the growing metal ingot. The weak point of this refining process is that a considerable number of other metals (e.g., Zr, Hf, Th, V, B, Si, as well as AI and Fe if the filament temperature is low) are codeposited with the desired titanium; therefore, these impurities should be removed during the preparation of the crude metal, that is, prior to refining.

The Pyrex thermal decomposition flask is shown in Fig. 291. The tungsten bus bars a, b and c(diameter of each 6 mm.) are arranged in a triangular pattern and sealed into the plass. The Ti de-

sealed into the glass. The Ti deposits on drawn tungsten core wires $(d_1 \text{ and } d_2)$, each 0.04 mm. thick and 400 mm. long.

These wires cannot just simply be stretched directly between the electrodes, as would appear from the drawing. If this were done, the rapid rate of heat conduction through the tungsten rods could cause excessive cooling of the wire ends and consequently prevent the titanium from depositing at the cold spots. This would result in nonuniform deposition, that is, preferential accumulation of the metal on the glowing sections, which would thus become heavier and unbalance the entire wire. Consequently, after a certain time has elapsed, the slightest mechanical shock would be sufficient to break the thin wires and interrupt electrical contact. The critical spots c and f should therefore be strengthened by insertion of reducer pieces made of progressively thinner tungsten wires. The simplest arrangement consists of a 1-mm.-thick wire ring fixed in a slit in the bus bar; this ring, in turn, is fitted with a drilled 0.2-mm, ring to which the glowing wire is attached.

Crude Ti (40 g.) is placed in g and 12 g. of Ia in evacuated space h. The flask is evacuated to $<10^{-9}$ mm, and the metal is degassed by heating to about 500°C. At the same time, the entire glass part of the apparatus (except for the iodine tube) is dried and degassed by fanning with a flame while the reduced pressure is maintained. As soon as a sufficiently high vacuum has been restored, a predetermined starting current (about 0.25 amp.) is applied to the tungsten wires to bring them to a "black body temperature" of 1400 °C, as measured by an optical pyrometer. The system is cooled and sealed at i, the thin glass partition l is broken by means of an electromagnet and steel ball n, and the I_2 from h is allowed to flow into g. A temperature of 200°C is sufficient for a rapid reaction of the iodine with a portion of the Ti, a reaction sometimes even accompanied by the appearance of a flame. Following this the apparatus is melt-sealed at k and heated to 550°C in a furnace; the tungsten wire d_1 is then brought to a glow at the same current as above. The apparent temperature read on the pyrometer is now lower because of the colored vapors rising from the material. This temperature must be held constant during the entire subsequent procedure (by increasing the current as the thickness of the deposited Ti layer increases).

The equilibria prevailing in the system are highly temperaturedependent. Furnace temperatures below 250° C produce TiI₄, which then decomposes on the hot wire in accordance with the above equation. At higher temperatures, TiI₄ reacts with the crude Ti to form TiI₃, which has a considerably lower vapor pressure. Only at temperatures above 500° C does this pressure become large enough to again produce titanium deposition on the glowing wire. The Ti metal formed at higher temperatures is so free of iron that the latter cannot even be detected.

Gases which may still be present in the flask during the refining of the Ti are bound by the metal (thus, a small amount of nitride is often formed). For this reason, the current to the first wire is shut off after a certain time and that to the second wire, d_2 , is turned on; the Ti metal which then deposits on d_2 is completely pure. Because of the gradual build-up of titanium, the current must be raised up to 200 amp, when the ingot reaches a thickness of about 5 mm. This requires about 24 hours; if the starting material is the crude Ti obtained from the hexafluorotitanate, the build-up rate is lower.

The current to the furnace can be gradually reduced to zero in the course of the run, since the growing Ti rod begins to radiate enough heat to maintain the required temperature throughout the system (toward the end of the run, it may even be necessary to cool the furnace space with air).

If the crude metal used in the refining process is prepared from pure starting materials, the resultant smooth Ti rod is almost completely pure, since the tungsten wire substratum constitutes only about 0.01% of the rod. The metal has about the same ductility as Cu, and may therefore be cold-worked and rolled.

The following method is well suited for the conversion of a piece of ductile titanium (it applies also to Zr or Hf) to powder: Ti is treated at 600°C in a stream of H₂. The gas must be extremely pure (see p. 111 ff.). The resultant hydride is brittle and easily ground to a powder. The H₂ may then be removed by heating in high vacuum at 1900°C.

b) This method has recently been used in the U.S. to prepare 700-g. quantities of Ti. The operation is carried out in Pyrex containers 900 mm, long and 200 mm, in diameter, but metal tubes have also been used with great success. For a given size of tube, the metal tubes are much easier to handle and simpler to cool. They contribute to the safety of the operation since an oil bath can then be used. The crude Ti is not placed at the bottom of the tubular vessel but is held in a layer 10-15 mm, thick at the walls by means of a cylinder of perforated Mo sheet. With this arrangement, it is also possible to dispense with the additional furnace heating. The glowing wires, in the form of hairpins, are hung from three tungsten rods; if one wire burns out, two more are still available. Titanium prepared in this manner contains 0.03% C, 0.003% N, 0.002% O, 0.04% Si, 0.04% Fe, 0.05% Al and 0.002% S.

VI. PREPARATION BY ELECTROLYSIS OF MELTS

Because of its high melting point, the Ti formed by electrolysis deposits on the cathode in the form of a solid cluster impregnated with the melt. The presence of even minute traces of moisture or oxygen causes the deposition of a finely crystalline material with a high salt content; suitable operating techniques, however, make it possible to obtain large crystals of pure metal.

c) Crude titanium may be obtained by electrolysis of a solution of TiO or mixed TiO-TiC crystals in a CaCl₂ melt at 700-850°C.

b) The electrolytic decomposition of $K_{2}TiF_{3}$ in a bath of NaCl, on the other hand, yields a very pure, coarsely crystalline metal. In this process the melt becomes enriched in NaF, according to the overall equation

$$K_{g}$$
TiF₄ + 4 NaCl = 2 KF + 4 NaF + Ti + 2 Cl.

while chlorine is evolved on the anode.

c) Another process uses an electrolysis cell in which the cathode chamber is separated from the anode by a diaphragm of sintered alumina; $TiCl_4$ vapor is introduced into a melt of alkali metal chloride or alkaline earth chloride in the cathode chamber. The resultant dissolved lower chlorotitanates decompose to the metal at a later stage of the electrolysis.

d) Metal of very high purity may be recovered from crude titanium or titanium waste by anodic solution of the starting material in a melt of alkali metal chloride containing a small amount of lower titanium chlorides, and reprecipitation of the Ti at the cathode.

VII. REDUCTION OF TiO2 WITH CaH2

A mixture of TiO₂ and CaH₂ (in 40% excess) is heated for one hour in hydrogen at atmospheric pressure (electric furnace, 950-1075 °C); the product is treated with dilute hydrochloric acid. A fine powder, with a metal content of 96%, is obtained; the remainder is mainly H₂ (3%). This process is also suitable for preparation of V. Nb and Ta from their oxides.

PROPERTIES:

Silvery white, ductile metal. M.p. 1730°C; d 4.45. Crystal type A3. Hexagonal α -Ti converts at 885°C to the body-centered cubic form (8-Ti). Electrical resistivity $\rho = 42 \cdot 10^{-6} \Omega \cdot cm$.

Scarcely or not at all attacked by acids and bases; dissolves readily in hydrofluoric acid.

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Zirconium, Hafnium

Zr, Hf

The general remarks concerning titanium apply equally well to zirconium and hafnium. These elements are thus prepared via the same methods and generally in the same equipment as described in detail in the section on titanium. In the following, we shall discuss only those details that differ from the above. Where Hi is not discussed separately, the conditions specified for Zr apply.

ĩ.

$$2rO_t + 2Ca = Zr + 2CaO$$

123.2 80.2 91.2 112.2

Crude starting Zr for the refining process is prepared via the sealed bomb method, with corresponding changes in the amounts of materials used, chiefly the addition of Na, which is highly recommended for the reduction of ZrO_2 (e.g., 20 g. of $ZrO_3 + 20$ g. of Ca + 10 g. of Na); heating to 1300°C produces a metal still containing oxygen. Although this causes coldshortness, the metal becomes malleable somewhat above 200°C.

II.
$$K_{1}Z_{r}F_{t} + 4Na = Z_{r} + 2KF + 4NaF$$

283.4 92.0 91.2 116.2 168.0

Crystalline K_3ZrF_6 (60 g.), prepared by cooling a heated solution of the hydroxide in KHF₃, is heated with 27.5 g. of Na in a scaled bomb at 1200-1300°C. The resultant 18 g. of orude metal is a suitable material for the refining process.

III.
$$2rCl_4 + 4Na = Zr + 4NaCl_{233.0} = 92.0 = 91.2 = 233.8$$

Up to 1 kg. of sublimed $ZrCl_4$, crushed to lumps, and 450 g. of distilled Na may be reacted in one run in a sealed steel tube at 850°C. The bottom of the tube is charged with a layer of Na; this is followed by the reaction mixture ($ZrCl_4 + Na$), topped with a layer of Na. Since the vapor pressure of $ZrCl_4$ is considerably lower than that of TiCl₄, the processing of larger quantities is simpler. The heat evolved in the reaction is so large that partial sintering of the metal occurs.

IV.
$$Z_{T}Cl_{4} + 2Mg = Z_{T} + 2MgCl_{2}$$

233.0 48.8 91.2 190.4

As in the magnesium process for Ti, Zr may be prepared by reduction of ZrCl₄ vapor with Mg in a helium atmosphere (see references below for further details).

V.
$$Z_{rI_4} = Z_r + 2I_2$$

598.9 91.2 507.7

The glowing wire temperatures during refining should be ~ 1400 °C in the case of Zr and ~ 1600 °C in the case of Hf. The Pyrex vessel must be kept at 600 °C. The crude metal obtained from the chloride is the most suitable raw material. Recently Zr has been prepared in large glass vessels in the form of rods weighing up to 200 g.

PROPERTIES:

Silvery white, ductile metals.

| | Formula weight | M.P. | d | α (close-packed hexag.) →β (bcc.) | Redstivity |
|----------------|-------------------|--------|------|--------------------------------------|--------------------------------|
| Z . | 91,22 | 1860°C | 6.50 | 870°C | 41 • 10 ⁻⁶ 9 • 2007 |
| H£ | 178,6 | 2230°C | 13.3 | ~1590°C | 30 • 10 ⁻⁶ 9 • 2007 |

1178

Scarcely or not at all attacked by acids and bases; dissolve readily in hydrofluoric acid. For the pulverization of solid metals via hydrogenation and dehydrogenation (hydrides), see pp. 1170 and 1184.

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Thorium

Th

Despite the close resemblance in chemical behavior of the metals and their compounds, thorium differs from titanium, zirconium and hainium in one respect, and that makes the preparation of the metal much easier. Thus, although the affinity of thorium metal for O, N and C is large, its cubic face-centered lattice cannot accommodate these nonmetals in solid solutions. The result is that, even on incomplete purification, these nonmetals are present only in the form of compounds and in small quantities; they have thus little effect on, for example, the mechanical properties of the metal. For this reason Th may be obtained in a cold-workable form by pressing and sintering the powder.

In contrast to titanium and zirconium, the preparation of thorium metal via reduction of the oxide with calcium (method II) acquires increased importance and rivals the reduction of the tetrachloride with sodium (method I). Melt electrolysis (method III) is another possibility. Neglecting the small oxide content (up to 1%), which in any case has never been determined precisely, the metal obtained by any of the three methods is already quite pure and contains only 0.1-0.2% of other impurities. The Th prepared by the refining process (method IV), is definitely oxygen-free and should in any case yield the purest product.

I. REDUCTION OF THE TETRACHLORIDE WITH SODIUM

$$\begin{array}{rcl} ThCl_4 + 4 Na &= Th + 4 NaCl \\ 373.9 & 92.0 & 232.1 & 233.8 \end{array}$$

Up to 300 g. of oxychloride-free sublimed ThCl₄ may be reacted at 500°C with vacuum-distilled Na (25% excess) in a welded iron bomb (see method I, section on titanium). The iron crucible should be filled with the reaction mixture in the same way as in the reaction between ZrCl₄ and Na, that is, layer by layer. Following the reaction, the bomb is completely cooled, opened and the reaction product treated, first with alcohol (to remove the excess Na), then with water (always maintaining the solution on the alkaline side). After complete removal of the chlorine, the residue is treated with 2N HNO₃ to dissolve any Th(OH)₄ which may be present, filtered with suction, thoroughly washed with water, alcohol and ether, and dried in vacuum at 300°C. The metal yield is 55%, in the form of lead-gray platelets and pellets. The coarsest particles are also the purest and contain 0.1% O (1% ThO₂).

II. REDUCTION OF THE OXIDE WITH CALCIUM

 $ThO_{z} + 2 Ca = Th + 2 CaO$ 284.1 80.2 232.1 312.2

A) PREPARATIVE PROCESS

The process is based on the reduction of very pure ThO₂ with distilled Ca in the presence of anhydrous CaCl₂ heated to 450°C.

1.04

1

The CaCla melts at the temperature of the reaction, affording a liquid reaction medium. The heavy Th product settles to the bottom and is thus protected by a layer of melt. The apparatus is either a steel bomb capped with a threaded conical lid (cf. the paper of Marden and Rentschier) or the simpler welded steel tube described under method I for the preparation of Ti. The charge, which is made up of four parts of ThO_2 , four parts of CaCl₂ and three parts of ground Ca, is vigorously shaken in a closed bottle to achieve the most complete mixing possible. The bomb is filled rapidly, sealed and heated for one hour at 950°C. The tube is then cooled and opened; the resultant pea-sized reaction product is gradually added to water (about two liters per 40 g. of starting ThO₂) with vigorous stirring to prevent a local temperature rise. After the calcium has completely reacted with the water and the evolution of gas ceases, stirring is stopped. the supernatant liquid is decanted, and the solid is washed four times with two-liter portions of water, vigorously shaking each time for 5-10 minutes. The decanted supernatants are lowconcentration suspensions of dark, fine Th. Finally, 200 ml. of water is added to the remaining heavy residue, followed by 25 ml. of conc. nitric acid (vigorous stirring). The odor of acetylene is noticeable, and if the ThO₂ used in the preparation was made from thorium nitrate which contained some sulfate, the odor of H₂S will also be present. After 10 minutes, the solution is diluted tenfold, the product is allowed to settle, the supernatant is decanted, and the acid treatment is repeated once or twice. After thorough washing with water (twice, two liters each time), the product is suction-filtered, treated with alcohol and ether, and dried in vacuum at 300°C. Under favorable conditions, the relatively coarse, dark gray powder is obtained in 90% yield.

Kroll uses the same process with a suitable salt melt. However, instead of working in a sealed bomb, he uses an iron crucible placed in an argon atmosphere.

B) MELTING OF TH POWDER

Small, relatively compact cylinders are formed from thorium powder under a pressure of 6-7 tons/cm³. Crucibles of sintered thoria are suitable melt containers. The cylinder, wrapped in a tungsten wire spiral, is placed inside such a crucible which is set up in a quartz container connected to a high-vacuum pump. The material is heated with a high-frequency induction coil.

The apparatus is evacuated and the sample carefully degassed by slow heating while the vacuum is maintained. With coarse metal powder, this operation requires about half an hour, and longer with fine powders; the reaction is essentially complete when the powder reaches red heat. The temperature is then rapidly increased to melt the metal. Oxidation is prevented if air is excluded from the system until after complete cooling.

Thorium powder with a completely clean surface is noteworthy for its sensitivity to air after high-vacuum degassing at 400°C. This sensitivity is so pronounced that the metal catches fire on coming in contact with air. The material also reacts so vigorously with H_2 that it becomes red hot.

III. ELECTROLYSIS

$$\begin{array}{ccc} \text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O} \rightarrow \text{KTh}\text{F}_3 \rightarrow \text{Th} \\ & 552.2 & 366.2 & 232.1 \end{array}$$

The electrolysis of a solution of $KThF_5$ in a NaCl-KCl melt yields very pure metal, containing only 0.02% C, 0.05% Si, 0.005% Fe and a negligible amount of other impurities.

The $KThF_5$ is prepared by dissolving 400 g, of $Th(NO_3)_4 \cdot 4 H_2O$ in two liters of water and adding, with constant stirring, a solution of 250 g, of KF in 400 ml, of water. The $KThF_5$ precipitate is allowed to settle, washed by decantation until the washings are free of nitrate, suction-filtered and dried for several hours at 125°C.

A cylindrical graphite crucible serves both as the electrolysis vessel and as anode. The inside diameter is 6 cm. and the height 15 cm., with a wall thickness of 1-2 cm. Current is supplied through a strip of Ni sheet wrapped around the upper part of the outside wall. The cathode is a strip of Mo sheet 0.05 mm. thick and 1 cm. wide, which reaches 2.5 cm. from the bottom. The graphite cell stands in a suitable refractory container wound with the heating filament. The entire apparatus is placed inside a sheetmetal vessel filled with thermal insulation (see also the similar arrangement described for the electrolysis of uranium).

A mixture of 250 g. each of KCl and NaCl is melted, and 30 g. of KThF₆ is added. When the melt is homogeneous, electrolysis proceeds, with the above Mo cathode, at a temperature of 775°C. A current of 18-20 amp. is required if the submerged cathode surface area is about 20 cm³. After 20 minutes the cathode is carefully removed from the liquid and replaced with a new piece of Mo, 30 g. of KThF₆ is added, and the electrolysis is continued for 20 minutes more. This procedure may be repeated several times. For preparations on a somewhat larger scale, a larger crucible,

For preparations on a somewhat larger scale, a larger scale, a larger scale, a larger scale, and go of containing about 1 kg. of the melt, and a molybdenum cathode 2.5 cm. wide are used. The procedure is the same, except that the KThFs additions are increased to 60 g., the current to 45 amp., and the cathode area to 50 cm². Eightfold repetition of the operation in this larger equipment permits the preparation of about 130-140 g. of Th (58% yield).

The material adhering to the cathode strip is a mixture of metallic Th and solidified melt. After complete cooling, the salt and the finely powdered, readily oxidized metal fraction are removed by treatment with water. The residual coarse-grained This treated three times with nitric acid (1:10) and washed with water. This metal powder is then suction-filtered, washed with alcohol and ether, and dried in vacuum at 300°C.

IV. REFINING PROCESS

| ThI4 | = | Th | ╉ | 2 I : | |
|-------|---|-------|---|-------|--|
| 739.8 | | 232.1 | | 507.7 | |

The thorium metal prepared by the above process is very pure and absolutely free of oxygen. The procedure is essentially the same as that described for Ti, except that the temperature of the glowing wire is higher (1700°C). The starting material may be any kind of crude thorium, provided it is free of metals which will also deposit on the glowing wire; the product derived from the chloride is very suitable.

PROPERTIES:

Gray powder, solid similar to platinum. Relatively soft and ductile: these properties are unaffected by the presence of small quantities of oxide. M.p. 1830°C; d11.7. Crystal structure: type A1.

Hardly or not at all attacked by dilute acids (including hydrofluoric); dissolves readily in fuming hydrochloric acid and especially in aqua regia. Resistant to strong bases.

Thorium powder may be prepared from the solid via the hydride. The procedure is identical to that described on p. 1170 for Ti and Zr; the hydride should be decomposed above 700°C.

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IV. A. E. van Arkel and J. H. de Boer. Z. anorg. allg. Chemi. <u>148</u>, 345 (1925); N. D. Veigel, E. M. Sherwood and L E. Campbell, J. Electrochem, Soc. <u>102</u>, 687 (1955).

Separation of Zirconium and Hafnium

Hafnium does not occur as a separate mineral, but appears in nature as the always present companion of Zr; the Hf/Zr weight ratio is usually in the range of 0.01-0.025. The preparation of Hf or the purification of Zr thus always involves the isolation of Hf from the crude chlorination product or from commercial Zr compounds. The following fractionation processes are of practical importance:

| I. | Crystallization | IV. | Ion exchange and adsorption |
|----|-----------------|-----|--------------------------------|
| п. | Precipitation | v. | Partition between two solvents |
| ш. | Distillation | | |

1. CRYSTALLIZATION

This method, which is unwieldy and applicable only to the separation of very small quantities of material, has been abandoned for all practical purposes.

II. PRECIPITATION

Good separation is obtained by precipitation of the phosphates; the hafnium concentrates in the less soluble fractions. A detailed description of the recovery of Hf from cyrtolite, a silicate of very high Hf content (5.5% HfO_3), is given in E. M. Larsen, W. C. Fernelius and L. L. Quill in: L. F. Audrieth, Inorg. Syntheses, Vol. III, New York-Toronto-London, 1950, p. 67.

III. DISTILLATION

Since the vapor pressures of $ZrCl_4$ and $HiCl_6$ are virtually the same, the process makes use of their adducts with PCl_6 or $POCl_3$. When a 50-plate glass column is used, the more volatile Hf compound concentrates in the first distillation fraction (5%) of the total; 2.5% to 16% HiO_2); the residue remaining after distillation of 40% of the total feed contains only 0.2% HiO_2 .

This process seems to have recently assumed a greater industrial importance.

IV. ION EXCHANGE AND ADSORPTION

This process, which was introduced in 1948 by Street and Seaborg for the separation of milligram quantities of Hf and ZP: becomes important in preparative work only when the small Hf fraction, and not the predominant Zr, may be retained on the column. This is achieved by selective elution of the Zr with $1N H_2SO_4$ (which involves the formation of an anionic complex) from a column of synthetic cation exchange resin (method a) or by selective adsorption of Hf on silica gel from an anhydrous methanolic solution of the tetrachlorides (method b). Although the latter process permits larger throughputs and shorter residence times, work with anhydrous methanol involves difficulties, and the further treatment of the eluate is more troublesome. Method b becomes applicable chiefly in those cases when one is forced to deal with tetrachlorides, for example, when the latter are precipitated by chlorination of minerals.

a) Dowex 50 or Zeocarb 225 (350 g., with a particle size of 0.5 mm.) is treated with water for several days and then placed in a tube 120 cm. long and 2.5 cm. in diameter. A solution of 20 g. of $ZrO(NO_3)_2 \cdot 2H_2O$ in one liter of 2N HNO₃ is passed very slowly through the column. (If the nitrate is not available, 24 g. of $ZrOCl_2 \cdot 6H_2O$ is precipitated as the hydroxide, washed thoroughly, and dissolved in one liter of 2N HNO₃.) The material absorbed on the column is eluted with 1N H₂SO₄ (flow rate of 100 ml./hr.). The Hf concentrate begins to appear when 95-98% of the Zr has been recovered (passage of about nine liters of the acid); the HfO₂ content in the Zr salt eluted prior to this point is less than 0.01%.

[For faster throughput rates, one can use the "breakthrough method," in which the initial adsorption on the resin is omitted; the resultant separation is, however, poorer. One proceeds as follows: a solution of 2.5 g. of $ZrO(NO_3)_2 \cdot 2H_2O$ per liter of 1N H₂SO₄ is passed through the above column at a rate of about 200 mL/hr. Before the "breakthrough point" is reached (after the passage of about nine liters), the solution leaving the column contains mainly Zr and a small amount of Hf, whose concentration in the Zr slowly increases to 0.1%. If only seven liters is collected, the product recovered from the solution consists, for example, of 8.2 g. of oxide containing 0.047% of HfO₂.]

After removal of the Zr, the Hf adsorbed on the column is eluted with stronger sulfuric acid (>1.2N); a solution of 0.05 moles of oxalic acid in one liter of 2N H_2SO_4 is an especially good eluent. Thus 63 mg. of Zr-free HfO₂ may be obtained in a 30-g. column, starting from 70 mg. of HfO₂ containing 8% ZrO₂; the material is passed through the ion-exchange column in the form of a solution of HfOCl₂ · 8H₂O in 675 ml, of 1N H₂SO₄.

b) Silica gel (1000 g.) with a specific area of 720 m. $^{2}/g$. Is purified by treatment with nitric acid (1:1) and washing with water, activated by heating for four hours at 300 °C, and suspended in dry methanol; this suspension is placed in a tube 120 cm. long and 5.0 cm. in diameter. The column then contains about 700 ml. of methanol.

Zirconium tetrachloride (400 g., equivalent to 210 g. of ZrO_2), with a Hf/Zr weight ratio of approximately 0.02, is dissolved in two liters of anhydrous methanol; the solution is allowed to stand for three hours and is then filtered. The filtrate advances through the column at an average rate of 20 cm./hr. (400 ml./hr.).

[The highest separation is achieved during the initial stages, as the following data illustrate:

Cumulative throughput, in g. ZrO_2/g , silica gel 0.05 0.1 0.2 0.25 % Hf in Zr leaving the column 0.05 0.1 0.35 0.6

Thus, one can collect an eluate containing 140 g. of ZrO_2 (equivalent to 265 g. of $ZrCi_4$) with a total Hf concentration of less than 0.1%.

Oddly, much better results are obtained when the operation is conducted on a larger scale. Thus a column 10 cm. in diameter and 150 cm. long charged with 8 kg. of silica gel yields, at correspondingly higher throughputs but otherwise unchanged operating conditions, 1.6 kg. of Hf-free $ZrCl_{4-}$

At the point when only about 200 g. of $ZrCl_4$ (equivalent to 100 g. of total oxide) remains in the column, the HfO_2 concentration in this residue becomes 10%. Further concentration is attained by elution of the column with a solution of 2.5 moles of HCl/liter of methanol (preferential desorption of the $ZrCl_4$). Depending on the duration of this treatment, the final elution with 7N H₂SO₄ yields, for example, 60% of the absorbed Hf as a 30% product, or 20% of the metal as a 60% product. These concentrates constitute a very suitable starting material for the extraction process described below.

The silica gel may be reused after reactivation.

V. PARTITION BETWEEN TWO SOLVENTS

The process is based on the preferential ether extraction of Hf from aqueous thiocyanate-containing solutions of Zr and Hf. Addition of acids or salts alters the equilibrium. Thus the presence of ether-insoluble sulfate ions shifts the distribution of Zr and Hf in favor of the aqueous phase, while the addition of acid or NH₄SCN achieves the opposite effect. Since no separation can be achieved by a single-stage extraction, a multistage process must be used. The process is designed to achieve maximum separation by combining the above factors, i.e., by varying the additives in the initial and final stages. Hydrolytic reactions have also been used to advantage in this separation. The following procedure has proven effective for the processing of a raw material containing ~ 20% MfO₂. The ether phase, which is 1N in HSCN, is prepared by shaking one liter of ether with an acidified solution of NH₄SCN (90 g. of NH₄SCN + 1/2 mole of H₂SO₄); the sulfuric acid is added in small portions during the shaking. A mixed oxide $Zr(Hi)O_3$, calcined at not too high a temperature, yields on evaporation with conc. H₂SO₄ a product of the approximate composition 1 $ZrO_2:2SO_3$. This product, in a concentration of 40-50 g. of oxide/liter of H₂O, is used as the starting material.

Is used as the starting material. One liter of this freshly prepared solution (do not heat to dissolve) is treated with 600 g. of NH₄SCN and vigorously shaken for one minute with one liter of the above ether preparation. After standing for five minutes, the ether layer is siphoned off and transferred to the next stages of the process, where it is treated with solutions of the following composition:

| Stage No. | 2 | 3 | 4 | |
|---------------------|-----|-----|-----|-----|
| $(NH_4)_3SO_4$ (g.) | 80 | 80 | 80 | ••• |
| $(NH_4)SCN$ (g.) | 50 | 25 | 0 | |
| H_3O (ml.) | 500 | 500 | 500 | |

The initial extraction is repeated ten times, each time with a new batch of the ether-HSCN phase. Each of the resultant ether extracts (fractions 2-10) is then passed through all the successive stages of the process. The aqueous solutions in each stage are, of course, used over and over again; that is, the new ether fraction is treated with the thiocyanate solution remaining in that stage from the extraction of the previous ether fraction. However, it is recommended that the NH₄SCN concentration in the aqueous solutions of stages 2 and 3 be gradually increased (always retaining the thiocyanate gradient shown in the table) and that thiocyanate be gradually added to the succeeding stages. The solution of the last stage must, however, always consist of 80 g. of $(NH_4)_2SO_4$ in 500 ml. of water, so that the ether leaving the system is always washed free of Zr and Hf. Thus, new last stages must be continually added to the solution from stage 3 becomes that of stage 2, the solution from stage 4 is shifted to stage 3, and so on down the line. A new thiocyanate-free aqueous stage is then added at the end of the series.

The Hf + Zr concentration and the Hf/Zr ratio must constantly be checked in each stage, since the separation depends on a large number of interdependent factors. Thus, the temperature greatly affects the partition coefficients, an effect which can be compensated for by changes in the volumetric ratios between the phases or by addition of salts. Some hydrolysis may occur in stage 1; it is recognizable by the appearance of heavy turbidity or precipitation in the aqueous layer, and may necessitate an intermediate treatment (precipitation with ammonia, followed by solution of the precipitate with H_2SO_4).

As has been emphasized before, the process is particularly effective with partially concentrated hafnium products, as shown by the following data. Starting from 40 g, of a product with a HfO_3 concentration of 18%, the aqueous layers of the various stages, after shaking with 10 liters of ether, contained the following proportions of HfO_3 :

| | 1 | 2 | 3 | 4 | 5 | 6 |
|----------------------|----|-----|---|------|-----|-----|
| Oxide (g.) | 28 | ~4 | - | 2 | 0.6 | 0.2 |
| HfO ₂ (%) | ~7 | ~20 | | > 40 | >50 | >70 |

The corresponding figures obtained from a starting material containing 50% HfO_a were:

HfO₂ (%) 25 ~50 ~80 ~99 >99

Alternate methods: a) U.S. authors have used processes involving fractional extraction of the aqueous phase with benzene solutions of diketones [thenoyl trifluoracetone: E. H. Huffman and L. J. Beaufait, J. Amer. Chem. Soc. <u>71</u>, 3179 (1949); trifluoroacetylacetone: B. G. Schultz and E. M. Larsen, J. Amer. Chem. Soc. <u>72</u>, 3610 (1950)]. One disadvantage of the thenoyl trifluoroacetone process may be that the Zr, which is usually the major component, is preferentially extracted into the benzene phase.

b) A process in which aqueous solutions of the chlorides are countercurrently extracted with methyl isobutyl ketone in the presence of thiocyanates and thiocyanic acid has attained industrial importance [W. Fischer, H. Heitsch and G. Otto, German Patent 1,010,061, Oct. 18, 1955; Nuclear Sci. Abstr. <u>10</u>, 371 (1956)].

c) The nitrates of Zr and Hf can be selectively partitioned between aqueous nitric acid and organic solvents, particularly tributyl phosphate and ketones, the Zr being preferentially extracted into the organic phase {R. P. Cox, H. C. Peterson and G. H. Beyer, Ind. Eng. Chem. 50, 141 (1958); Chemie f. Labor und Betrieb, August 1958, 340; W. Fischer and H. Heitsch, German Patent 1,007,306, Nov. 16, 1954; F. Hudswell and J. M. Hutcheon, Proc. Internat. Confer. Peaceful Uses of Atomic Energy, Vol. 8, 563, New York, 1956; J. Huré and R. Saint-James, ibid., 551.]

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Titanium, Zircanium and Thorium Hydrides

Ti∕H

Hydrogen dissolves in the Ti metal lattice until a composition $TiH_{0,5}$ is reached; this produces a hydride with a considerable homogeneity in the range of TiH-TiH₂. The upper hydrogen concentration is attainable only with Ti and H₂ of the highest purity, while operating under conditions of extreme cleanliness.

The metal form best suited for the hydrogenation is Ti sponge. Titanium sheet starts to absorb H_3 at 300°C and does so rapidly beginning at 400°C. Partially hydrogenated Ti reacts with carefully purified H_2 even at 20°C. Hydrogen is released from highly hydrogenated products by reheating to above 400°C in high vacuum; complete desorption is achieved at 1000°C.

When it is required to absorb only a predetermined quantity of H_2 , the following procedure may be employed. The metal is weighed into a boat of sintered clay (or, better, of stainless steel, provided traces of Fe in the product are not detrimental) placed in a quartz tube connected to the system with a ground joint. The apparatus consists of a glass burette with 0.1-ml. divisions provided with a leveling tube and Hg reservoir and connected to an electrolytic H_2 generator; this apparatus is attached to a high-vacuum system. The quartz tube volume is measured, and the metal is degassed by heating to 550°C. Hydrides with the desired H_2 content are obtained by varying the absorption temperature and the quantity of bydrogen introduced.

Zr/H, Th/H

The preparation of Zr and Th hydrides is similar to the above procedure. Zirconium reacts very rapidly beginning at 700°C and at atmospheric pressure is capable of dissolving 1.95 atoms of H per atom of Zr. Thorium starts to absorb H_2 at 400°C; the maximum H_2 concentration corresponds to a hydride composition of TbH_{3.24}.

PROPERTIES:

Gray powder of somewhat lighter color and lower density than the parent metal powder. In contrast to the Ti and Zr hydrides, Th hydrides of high hydrogen content are labile and ignite spontaneously in air.

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A. Sieverts et al. Z. phys. Chem. <u>145</u>, 227 (1929); Z. anorg. allg. Chem. <u>153</u>, 289 (1926); <u>172</u>, 1 (1928); <u>187</u>, 155 (1930); <u>199</u>, 384 (1931); G. Hägg. Z. phys. Chem. (B) <u>11</u>, 433 (1931); T. R. P. Gibb and H. W. Kruschwitz, J. Amer. Chem. Soc. <u>72</u>, 5365 (1950); R. E. Rundle, C. G. Shull and E. D. Wollan. Acta Crystallogr. (Copenhagen) <u>5</u>, 22 (1952).

Titanium (II) Chloride, Bromide and Iodide

TiCl₁, TiBr₁, TiL

 $TiCl_4 + Ti = 2 TiCl_7$ 189.7 47.9 237.6

A weighed quantity (2-3 g.) of TiCl₄ is placed with the appropriate precautions in a thick-wall quartz tube, and the stoichiometric quantity of Ti filings is added. The tube is cooled in a Dry Icealcohol bath, thoroughly evacuated by means of an oil pump, and melt-sealed in such a way that its total length is 12-15 cm. It is then placed in a very slightly inclined position in a tubular electric furnace so that the Ti metal is located at the higher end and the chloride at the lower. The Ti is in the hottest part of the oven (at 800-900 °C), while the section containing the TiCl₄ is in a cooler zone (at about 200 °C). An explosion shield is recommended. If one uses a mixture such as Ti + 2 TiCl₃ the procedure is less dangerous but more involved.

A mixture of black and purple substances (TiCl₂ and TiCl₃) is observed after 24 hours. As soon as all unreacted TiCl₄ disappears, the reactor tube is pushed deeper into the furnace, which results in a gradual disappearance of the reddish component. To achieve complete homogeneity, the mixture is heated for an

Ia.

189.7

÷

additional 4-5 days at 600-700°C. The product is black and may be dislodged from the wall by gentle tapping (the reaction with the quarta wall proceeds to only a very slight extent). The quartz tube is sawed open; the black powder is dropped into a transfer apparatus (Fig. 54, p. 75) and reheated in vacuum for 15-30 minutes at 200°C to remove the moisture absorbed during the transfer. The product is then ready for further processing.

Ib. To prepare larger quantities of $TiCl_2$ by the same method, it is advisable to use a vertical reactor tube, in which the molten dichloride is formed on passage of $TiCl_4$ vapor over titanium filings heated to a high temperature. A layer of Ti filings about 30 cm. high is placed on a perforated carbon plate in a fused quartz tube 110 cm. long and 4.5 cm, wide. Just underneath the carbon plate there is a graphite crucible supported by a pistonlike arrangement; this crucible collects the droplets of the product. The entire arrangement is placed in a tubular furnace; the temperature at the metal level is 1050°C, while that at the level of the collecting crucible is 900°C. After thorough flushing with Ar, gaseous TiCl₄ is introduced from above in a slow stream of Ar. At the end of the reaction the graphite crucible is removed from the furnace in an atmosphere of a protective gas, and the solid block of TiCl₂ is removed by gentle tapping.

Tibr, Til.

These compounds are synthesized in a similar manner, except that the halogens, rather than the tetrahalides, are used as starting materials.

$$Ti + Br_{g} = TiBr_{g};$$
 $Ti + J_{g} = TiI_{g}$
47.9 159.8 207.7 47.9 253.8 301.7

After weighing and before addition of the Ti filings, the Br_3 must be cooled to $-78\,^{\circ}$ C, since liquid Br_3 and Ti react with ignition even at room temperature. This phenomenon also occurs in the sealed tube as soon as the Br_3 starts to melt. The tubes, however, are capable of withstanding the pressure. With I_3 , on the other hand, the conversion to tetraiodide starts only after slight heating. In both cases, further treatment is similar to that of the chloride. The quartz tube wall is attacked even less by the bromide than with the chloride, while the iodide does not react with quartz at all.

L

$$2 \text{TiCl}_{1} = \text{TiCl}_{2} + \text{TiCl}_{4}$$

308.5 118.8 189.7

A high vacuum is created in a quartz tube, one end of which is filled with Ticl, and heated to 475°C, while the other is maintained

×,

at -78 °C. The TiCl₄ formed via the disproportionation condenses at the cold end. Complete decomposition of 1 g. of TiCl₃ requires about 12 hours. When the reaction is over, the tube end containsing the TiCl₄ is sealed off from the remainder. Since the decomposition reaction 2 TiCl₂-TiCl₄ + Ti sets in below 475 °C, pure TiCl₂ cannot be obtained by this method; the product always contains 2-3% of free titanium.

On the other hand, this method may be very successfully used for the preparation of TiBr₃. At temperatures slightly above 400°C, half a gram of TiBr₃ will decompose completely in 18 hours according to the equation $2 \text{TiBr}_3 = \text{TiBr}_3 + \text{TiBr}_4$. However, the disproportionation $2 \text{TiBr}_2 - \text{TiBr}_4 + \text{Ti sets in above}$ 506°C, so again free titanium may be present in the product.

III. Very pure and finely divided $TiCl_9$ may be obtained by reduction of $TiCl_9$ with H_2 in an electrical discharge produced without electrodes.

PROPERTIES:

TiCl₂: Black crystals; ignites in moist air; soluble in H₂O, evolving H_2 (the same properties apply to TiBr₂ and Til₂). d (TiCl₂) 3.13, (TiBr₂) 4.31, (Til₂) 4.99.

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- I. W. Klemm and L. Grimm. Z. anorg. allg. Chem. <u>249</u>, 198 (1942); P. Ehrlich, H. J. Hein and H. Kühnl, Z. anorg. allg. Chem. <u>292</u>, 139 (1957); for TiI₂, see also J. D. Fast. Recueil Trav. Chim. Pays-Bas <u>58</u>, 174 (1939); for TiCl₂, see especially D. G. Clifton and G. E. McWood, J. Phys. Chem. <u>60</u> 311 (1956).
- II. R. C. Young and W. C. Schumb, J. Amer. Chem. Soc. <u>52</u>, 4233 (1930); W. C. Schumb and R. F. Sundström. J. Amer. Chem. <u>55</u>, 596 (1933); see also W. Klemm. Angew. Chem. <u>69</u>, 683 (1957).
- III. V. Gutman, H. Nowotny and G. Ofner. Z. anorg. allg. Chem. 278, 80 (1955).

Titanium (III) Chloride, Bromide and lodide

TiCle, TiCle · 6 HeO; TiBre, TiBre · 6 HeO; Tile

TiCl_a

I.

$$2 \text{ TiCl}_{4} + H_{2} = 2 \text{ TiCl}_{3} + 2 \text{ HCl}$$

379.4 2.0 308.5 72.9

a) The procedure developed by Schumb et al. was modified Klemm and Krose as follows.

The apparatus is shown in Fig. 292. Parts a, c, and d are made of fused quarts, while the container f is Pyrex. Before the start of the reaction the entire system is thoroughly dried with a stream of H_2 . About 25 g. of TiCl₄ is then added through b, the furnace is rapidly heated to 600°C, and the cooling water for the rurace is rapidly neared to so C, and the country water for the finger *d* is turned on (Schumb et al. use a system made of high-melting glass and heat to 650 °C only). The TiCl₄ in *a* is heated almost to the boiling point while a stream of H₂ is passed through the flask; the product is free of TiCl, only if an excess of TiCla is present in the reaction chamber. The unreacted TiCl4 is collected in container f, which is cooled with Dry Ice. After all the TiCl₄ has been distilled out of flask a, the current to the furnace is shut off; it should cool rapidly, since the insulation consists only of a thin asbestos layer. When the temperature drops to 120°C, the water flow to the cold finger is stopped, the finger is dried with an air stream, and the furnace is kept at 120 °C for several hours in order to free the product deposited on the tip of the finger of TiCl₄. The TiCl₄ left in the remaining section of the apparatus is distilled off by fanning with a flame. The system is then allowed to cool in a stream of H2, followed by a fast stream of CO_a . The container f is then disconnected at e and replaced with a transfer device (Fig. 54, p. 75); the cork stopper carrying the cold finger is pulled out from the reactor to a distance sufficient for insertion of a scraper; the TiCla is scraped off the finger and dropped by tapping into the transfer container. The yield of the pure product is 2-3 g.

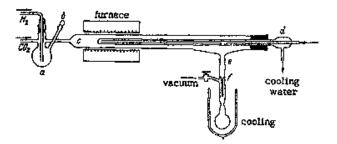


Fig. 292. Preparation of tianium (III) chloride according to Klemm and Krose. a) flask, b) charging adapter for TiCl₄, c) reaction tube, d) cold finger, f) container

b) Larger quantities (150-200 g.) of less pure product (98%) can be prepared in one day in the apparatus of Fig. 293 via reduction of TiCl₄ with H_2 on the surface of a glowing tungsten wire.

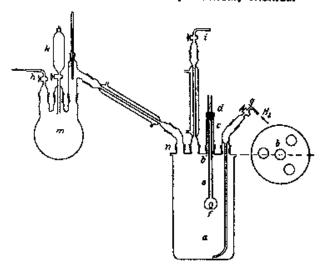


Fig. 293. Preparation of titanium (III) chloride according to Sherfey. a) Pyrex reactor; e) tungsten rods, about 6 mm. in diameter; /) tungsten wire coil; m) flask for distillation of TiCl₄.

The four-liter Pyrex reaction vessel a is provided with a flat-ground lid with four openings, one in the middle and the other three arranged symmetrically around it. The central 34/45 ground joint b carries a tubular adapter c closed off with a two-hole rubber stopper d through which two tungsten rods e (6 mm. in diameter) are inserted. The rods are interconnected by a tungsten wire, the thickness and length of which are determined by the available power supply. Thus, heating a wire 1 mm. In diameter and 30 cm. long to the required temperature of 1000-1100°C requires a current of 36 amp. and 8.6 v. Thinner wires should not be used, if at all possible, since they may burn out during the run; longer wires increase the process rate.

The apparatus is thoroughly flushed with pure, dry H_2 , which is introduced at g and which leaves at h. When all the moisture has been removed, stopcock h is closed and i is opened, without interrupting the stream of H_2 . Then TiCl₄ (one liter = 1700 fit is introduced from dropping funnel k into distilling flask m and except for a small residue, redistilled into the reaction vessel a: The distillation apparatus is then removed and the opening at n is rapidly closed off.

Only the lower third of reaction vessel a is beated with a heating mantle. The boiling TiCl4 then condenses on the lid and the

1126

side walls-cooled with a fan if necessary-and, while flowing down, washes off the nascent $TiCl_3$. If the $TiCl_4$ boils too violently, the solid $TiCl_5$ particles may come in contact with the hydrogen stream, be entrained by it and plug the reflux condenser (the condenser serves only as a safety vent).

When the boiling of the TiCl₄ (in the fast hydrogen stream) has reached a steady state, the tungsten wire is heated to red best. The reduction starts immediately and is accompanied by the appearance of violet vapors of TICl₃, which condense on the walls and are largely flushed down to the bottom of the TICl₄containing flask. Since there is a possibility that air may enter the system whenever there is a sudden cooling and resultant temporary vacuum, the H2 flow rate must be carefully maintained the air is undesirable since it may oxidize the glowing wire to the point of burnout and may also cause hydrolysis). When the TiCl, ceases to flow unhindered along the walls of the vessel. the reaction is stopped by turning off the current to the glow wire, and the flask is allowed to cool in a stream of H2. The TiCl. may be distilled directly from the reaction beaker by replacing the lid used in the reaction with a one-hole cover. However, it is simpler to transfer the reaction mixture to a sideneck distilling flask and heat to 150°C on an oil bath. The last traces of adsorbed TiCl4 are removed by heating in vacuum to 200°C; other volatile contaminants are removed at the same time. About 150 g. of TiCl3, corresponding to a yield of 10% (or 90% based on the amount of TiCl, actually consumed in the reaction), is obtained. Because it contains a small quantity of TiCl₂, the product has a reducing value of 101.5%. It usually ignites even in moist air, and even more rapidly when it is still warm; transfer must therefore be carried out carefully, in an inert atmosphere.

The difficulties involved in welding on the tungsten coil may be circumvented by means of the following arrangement. Two copper tubes (diameter 6 mm., length about 30 cm.) are electrically insulated from each other and commented in the adapter c_1 just above c they are provided with side fittings for connection to cooling water. The cement may be an epoxy resin such as Araldite 121 R with hardener 951.* The upper ends of the copper tubes, which serve as bus bars, are interconnected by means of a short piece of rubber tubing; the lower ends are closed off. A strip of molybdenum sheet (0.2 mm, thick, 6 cm, long) is soldered on at the lower end of each of the two copper tubes to support the fungates wire. A firm electrical contact between the wire (which is wound into five or six coils) and the molybdenum strips is achieved by threading the wire ends through a series of small holes in the strips, followed by bending the ends over and crimping to the strips.

п.

$3 \operatorname{TiCl}_4 + \operatorname{Ti} = 4 \operatorname{TiCl}_9$ 1_{10} : 58.9 4.8 61.7

If pure Ti metal is available, the TiCl₃ may be prepared in a thick-wall pressure tube made of fused quartz or Vycor in accordance with the above equation. The procedure is essentially the same as that described for the preparation of TiCl₂. A large amount of TiCl₂ forms initially; this stage may be recognized by the black color and moist appearance of the product, due to unreacted TiCla. After the initial reaction the reactor tube is gradually (over several hours) pushed completely into the furnace, which is maintained at 600°C. Should a temperature gradient exist in the system, the TiCl₃ will sublime, in the form of violet, leaflike crystals, into the center of the pressure tube. The tip of the tube is then broken off under a blanket of protective gas; the other end, which may contain some residual unreacted Ti, is also broken off, and the TiCla is dropped into a transfer device (cf. Part I, p. 75), in which it is heated for an additional few minutes in vacuum to 100-150°C by fanning the vessel with a flame; the small amount of TiCl4 which evolves shows that the reaction did not go to completion. The reactor walls are attacked only at the spot where the Ti metal was placed, and then only very slightly.

ш.

| | 3 TiCL | ÷ | Sb | S TiCl, | Ŧ | SPC1* | |
|-------|--------|---|------|-------------|---|-------|--|
| 1/10: | 58.9 | | 12.2 | 48.3 | | 22.6 | |

The reduction of TiCl₄ to TiCl₃ with Sb does not require a complicated apparatus and may be carried out as follows:

A solution of $SbCl_3$ (d 1.265) is reduced with Zn dust. The resultant Sb is washed several times with 0.1N HCl until free of Zn, then treated with alcohol and ether, and finally dried in a stream of CO_2 . Antimony prepared by other methods does not reduce TiCl₄ as efficiently.

Freshly distilled TiCl₄ (28 g.) is placed in a bomb tube and the Sb (6 g.) is added; the reactor tube is melt-sealed and beated for five hours at 340°C. After cooling, both tube ends are broken off and the moist mass, in a stream of CO₂, is transferred to a three-neck flask via an adapter at neck a. Then CCl₄ is added from a dropping funnel attached to neck b while the mixture is agitated with a stirrer inserted through the center neck; this dissolves out the unreacted TiCl₄. The mixture is allowed to

settie, an adjustable siphon tube is inserted at a, and the supermatual liquid is forced out by CO_3 pressure applied through b. The operation is repeated until the product is free of TiCl₄. The SbCl₃ formed in the reaction is removed in the same manner by exhaustive extraction with ether, the last traces of which are evaporated by heating on a water bath in a stream of CO_3 . The TiCl₃, in the form of a violet powder, is transferred to storage under a blanket of CO_3 . The yield is quantitative.

IV. Alternate method: Finely divided, very pure TiCl₃ may be prepared by reduction of TiCl₄ with H_{2} in an electric arc.

TiBn

L. The preparation of TiBr_3 by method I_d is similar in its essentials to that used for TiCl_3 , except that the removal of TiBr_4 after completion of the reaction must be carried out at a higher temperature (250 °C).

The preparation by method Ib uses the same apparatus as that for TiCl₃. Since TiBr₄ is a solid at room temperature, the reflux condenser must be cooled with hot water or steam. The TiBr₄ is poured hot into the distillation flask and allowed to solidify before the apparatus is flushed with H₂.

II. Sublimed $TiBr_3$ crystals are synthesized from the elements under the same conditions as those given for $TiCl_3$.

Til,

I. Direct synthesis from stoichiometric quantities of the elements by heating in a scaled tube is similar to the preparation of $TiCl_3$ or $TiCl_2$ from $Ti + TiCl_4$. As long as the tetraiodide still accompanies the diiodide and the triiodide, the product is a solid cake which is difficult to break up by tapping. Toward the end of the reaction, after heating for several hours at 700°C, the product can be pulverized by vigorous shaking. The reaction may be completed at 180°C (reduce the temperature over a period of several days). The reaction is tested for completion by pulling out the tip of the tube from the furnace (maintained at this temperature) and cooling it with a piece of moist filter paper. The reaction is complete if after several hours only a very slight film of TiL is observed (the film quantity is negligible compared to the total imaterial in the reactor).

PROPERTIES:

TiCl₂: Formula weight 154.27. Violet-red to black crystals; sublimes in vacuum at 425-440 °C; decomposes to TiCl₂ + TiCl₄

1192

above 450°C. Readily soluble in H_2O . d 2.66. Crystal structure: type D 0_5 .

TiBr₃: Formula weight 287.65. Bluish-black crystals; decomposes to TiBr₂ + TiBr₄ at 400°C. Less soluble in H₂O than TiCl₃.

Til₃: Formula weight 428.66. Violet-black needle-shaped crystals; stable up to 300°C on heating in high vacuum; decomposes to Til₂ + Til₄ above 350°C. Dissolves slowly in H₂O without evolving H₂.

REFERENCES;

- Ia. C. Young and W. C. Schumb. J. Amer. Chem. Soc. 52, 4233 (1930); W. C. Schumb and R. F. Sundström, J. Amer. Chem. Soc. 55, 596 (1933); W. Klemm and E. Krose. Z. anorg. Chem. 253, 209 (1947); H. Hartmann, H. L. Schläfer and K. H. Hansen. Z. anorg. allg. Chem. 284, 153 (1956); for TiBr₃ see also: R. C. Young and W. M. Leaders in: W. C. Fernelius, Inorg. Syntheses, Vol. H. New York-London, 1946, p. 116.
- Ib. J. M. Sherfey. J. Research Nat. Bur. Standards <u>46</u>, 299 (1951); Inorg. Syntheses, Vol. VI, New York-London, 1960, p. 57; P. Ehrlich, G. Kaupa and K. Blankenstein, Z. anorg. allg. Chem. <u>299</u>, 213 (1959).
- II. W. Klemm and E. Krose. Z. anorg. Chem. <u>253</u>, 209 (1947); P. Ehrlich and G. Pietzka. Unpublished experiments; for Til₃, see also J. D. Fast. Recueil Trav. Chim. Pays-Bas <u>58</u>, 174 (1939).
- III. M. Billy and P. Brasseur. Comptes Rendus Hebd. Seances Acad. Sci. 200, 1765 (1935).
- IV. T. R. Ingraham, K. W. Downes and P. Marier. Canadian J. Chem. <u>35</u>, 850 (1957); Inorg. Syntheses, Vol. VI, New York-London, 1960, p. 52.

TiCl, - 6 H₂O

 $\begin{array}{l} \mathrm{TiCl}_4 \rightarrow \mathrm{TiCl}_3 \rightarrow \mathrm{TiCl}_3 \cdot 8 \ \mathrm{H_2O} \\ 189.7 \quad 154.3 \qquad 262.4 \end{array}$

Titanium (III) chloride may be prepared by cathodic reduction of TiCl₄ in a hydrochloric acid solution; if the concentration of TiCl₃ in the solution is sufficiently high, the hexahydrate precipitates on saturation with HCl. The crystallization is apparently inhibited by the presence of tetravalent titanium, and total reduction of the solution is therefore necessary.

The procedure, according to W. Fischer, is as follows.

11.126

÷,

5A)

A thick-wall cylindrical battery jar (diameter 7 cm., height 9 cm.) serves as the electrolytic cell. The center of the cell is occupied by a clay cylinder (diameter 4.5 cm., height 12 cm.). The cylinder is beld in place by a cork ring with three additional holes, two for carbon anodes (placed opposite each other on the diameter) and the third for an outlet tube for the Cl_2 evolved during the electrolysis. The clay cylinder is closed with a three-hole rubber stopper, which contains an inlet tube reaching almost to the bottom of the cylinder, a short outlet tube, and a lead wire to the Pt catbode. Also recommended is the insertion of an additional glass tube, used for occasional sampling of the solution as a check on the degree of reduction.

To start with, TiCl. (19 g.) is added in drops with efficient cooling and vigorous stirring to 27 ml. of 25% HCl solution. The insoluble hydrolysis products which may be formed are filtered off through fritted glass. The clear solution is placed in the clay cylinder, and the anode chamber is filled to the same level with 25% hydrochloric acid. At 12 v. and a current density of 2.5 amp./10 cm.² of the Pt cathode, the electrolysis should require about four hours. The jar is meanwhile cooled with ice (or, if necessary, with ice-salt). Toward the end of the run, HCl is added to the solution until saturation. The hexahydrate TiCl₃·6H₂O crystallizes best when the solution is not agitated; therefore, the introduction of HCl should be interrupted for 10 minutes every half hour. If the reduction is complete, the product crystallizes within one hour, forming a solid crystalline mass. It is placed on a coarse fritted-glass filter under CO₂ and the mother liquor is removed by suction. The precipitate is washed with some saturated HCl solution, followed by ether, and the crystals are dried in a vacuum desiccator over soda lime. The TiCl₃·6H₂O then consists of small crystals.

PROPERTIES;

Pale-violet, hygroscopic crystals, readily soluble in water. Decolorizes slowly by oxidation in dry air, rapidly in moist air, with formation of white TiO_3 hydrate.

If a saturated solution of $TICl_3$ is covered with ether and saturated with HCI, a green, very unstable isomeric hexahydrate is formed [A. Stähler and H. Wirthwein, Ber. dtsch. chem. Ges. 35, 2619 (1905)].

REFERENCE:

Private communication from W. Fischer, Hannover.

TiBr, · 6 H₂O

$$\begin{array}{rcl} \text{TiBr}_{\bullet} \rightarrow & \text{TiBr}_{\bullet} \rightarrow & \text{TiBr}_{\bullet} \cdot 6 \text{ H}_{\bullet} \text{O} \\ \text{367.6} & & \text{395.7} \end{array}$$

Titanium (III) bromide $TiBr_3 \cdot 6H_2O$ is prepared in exactly the same way as $TiCl_3 \cdot 6H_2O$. A solution of 37 g. of $TiBr_4$ in 25 ml of 34% hydrobromic acid is poured into the clay cylinder and reduced for three hours at a current intensity of 2.5 amp.

PROPERTIES:

Reddish-violet crystals. M.p. 115°C. Soluble in H_2O , methanol, absolute alcohol and acetone; insoluble in CCl₄ and benzene. Decomposes in absolute ether.

REFERENCES:

The same as for TiCl₃.6H₃O; see also J. C. Olsen and E. P. Ryan, J. Amer. Chem. Soc. <u>54</u>, 2215 (1932).

Titanium (IV) Chloride

TiCL

 $TiO_2 + 2C + 2Cl_2 = TiCl_4 + 2CO$ 79.9 24.0 141.8 169.7 56.0

PREPARATION

a) An intimate mixture of 30 g. of commercial TiO_2 (sold under the trade name "synthetic rutile"; if natural rutile is used, it must be preground for 24 hours in a ball mill until a very fine powder is obtained), 15 g. of charcoal or carbon black, and 0.05 g. of manganese dioxide catalyst is stirred to a paste with water and 0.3 g. of soluble starch. The mixture is heated in a drying chamber with occasional stirring until a material consisting of agglomerated particles is produced; this is placed in a clay crucible, covered with a layer of carbon black, and thoroughly calcined by means of a blast burner.

The chlorination is carried out in a quartz tube (20 mm. I.D.) to which an 8-mm, quartz tube is sealed at a 45° angle. The narrower tube is inserted into a 150-mi. distilling flask, which serves as the receiver.

The larger tube is charged with the TiO₂ + C mixture and the entire apparatus is dried by fanning with a flame, while a stream of CO₂ is flowing through. The receiver is immersed in an icesait mixture, and the reactants are slowly heated to 450° C in a stream of Cl₂. In the absence of a catalyst, or if the TiO₂ is insufficiently ground, heating to 1000° C is necessary. From time to time, particularly toward the end of the run, the tube section between the furnace and the receiver is fanned with a flame to distill off any condensed TiCl₄ and to prevent plugging with FeCl₃. At a flow rate of three liters of Cl₂ per hour, the reaction requires 4-5 hours for completion. The receiver is removed and the product TiCl₄ is freed of dissolved Cl₂ (and COCl₂, if present) by drawing a stream of dry air through the tube. The yield is about 40 g.

h) A simple laboratory apparatus, which can be used for the preparation of most anhydrous chlorides (solid, liquid and gaseous). has been described by Kroll (see Fig. 294). It is made of fused quartz, which is better than porcelain since it is attacked at much higher temperature and even then produces only a single contaminant (SiCl4). The apparatus consists of a single tube in two sections, one wide and one narrow, and containing a cold finger in the large-diameter section; the latter section serves as a condensing chamber for the distillate or sublimate. The heating arrangement is divided into two parts. The heating section for the narrower tube reaches well into the wide-tube section, to prevent the chlorides from condensing in the transition section. The large-diameter section may be heated slightly if the need arises; it is only partially covered by the heating element and its exposed part may be cooled by placing it in a wooden box filled with Dry Ice; this may be necessary in the preparation of chlorides which are difficult to condense (e.g., BCla). Chlorides which are liquid at room temperature (e.g., TiCl4) condense on the cold finger and flow into the receiver, the reactor in this case being slightly inclined. Nonvolatile chlorides deposite as solids on the finger.

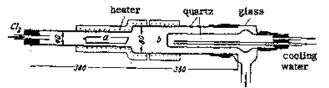


Fig. 294. Preparation of anhydrous chlorides according to Kroll. The main tube and the cold finger are made of fused quartz. a) reaction chamber; b) condensing chamber. Dimensions in mm.

If the raw materials for TiCl₄ are very pure TiO₂ and sugar charcoal calcined in a stream of Cl₂, then the prepurification described below becomes unnecessary. The solid charcoal may be dispensed with if the chlorine stream also contains CCl_{\bullet} or $S_{2}Cl_{2}$.

See also the preparation of ZrCl4.

PREPUBLIFICATION

The crude product is decolorized and contaminants such as $FeCI_3$, $VOCI_3$, etc., are removed by adding 1 g. of Cu powder (Na amalgam or Hg may also be used) and heating the liquid to 90-100 °C for 15 minutes with occasional shaking.

[If Cu turnings are used, the amount specified above must be increased tenfold. Oleic acid and its salts and other organic compounds, in quantities of less than 1%, are also efficient decolorizing agents [C. K. Stoddard and E. Pietz, U. S. Bur. Mines Rep. Invest. $\underline{4153}$, 40 (1947)].

According to British Patent 588,657 the following purification procedure is particularly well suited for the removal of traces of vanadium. The product containing 0.072% V is mixed with 0.1% of Fe stearate and treated with $H_{\rm s}S$, causing precipitation of a black-brown sulfide; the latter is filtered off. The TiCl₄ then contains only 0.002% V.]

After heating with copper, the $TiCl_4$ is cooled and suction-filtered through a very dry filter funnel, and the filtrate is transferred for further purification (removal of $SiCl_4$ and dissolved nonvolatile hydrates) to the distillation apparatus described below (Fig. 295).

A) ATMOSPHERIC PRESSURE DISTILLATION

The neck of distilling flask a is closed off with a ground stopper provided with a small hook, from which a thermometer is suspended on a Pt wire. The side arm passes through a condenser jacket; a small bulb b (the receiver for the forerun) and an outlet tube c filled with P_2O_n are sealed on as shown. In the initial stage of the run, the system ends in a second distilling flask s equipped with a break-seal valve f (see Part I, p. 63), via which the flask is later connected to additional pieces of glassware. The apparatus is set up to point i and flasks a and e are dried by fanning with a flame while a stream of air is passed through. Then TiCl, is placed in flask a and the latter is heated on an oil bath. The forerun is collected in b, which is then sealed off, while the main fraction of the material is distilled into e, which is then sealed off at d. This operation is followed by an additional distillation at atmospheric pressure: flask e is melt-sealed at i to the system shown on the right side of Fig. 295A; this part of the apparatus is very thoroughly dried by alternately evacuating the system and allowing dry air to enter. The thin-wall break-see

where is then shattered at the prescratched point g by moving the barmer λ by means of a magnet. The forerun from this distillation is collected in k and the main fraction of the distillate in receiver m, which is then melt-scaled at point l.

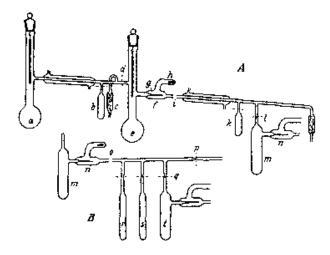


Fig. 295. Purification of titanium (IV) chloride by distillation: A) at atmospheric pressure; B) in vacuum.

B) VACUUM DISTILLATION

Vessel *m* is melt-sealed at *o* to the rest of the apparatus shown in Fig. 295B, and the entire system is dried by fanning with a flame while a high vacuum is maintained. The TiCl₄ is then introduced into *m* and frozen with liquid nitrogen, the breakseal value *n* is broken by the method described above, the system is evacuated to 10^{-4} mm. and sealed at *p*. A forerun is collected in *r* by cooling this trap and gradually heating flask *m*; the connection to *r* is then sealed off. The main fraction of the product may now be distilled in one batch, that is, by collecting in cooled receiver *t*, sealing off at *q*, and repeating the vacuum distillation; or the TiCl₄ may be distributed into several batches and collected in traps s_1 , s_3 , s_3 , etc.

PROPERTIES:

Colorless, acrid liquid; fumes strongly in moist air. M.p. -24.8°C, b.p. 136°C; d 1.73.

Hydrolyzes almost completely on solution in water; if the hydrolysis is depressed by addition of acid or if only small quantities of water are used, oxychlorides may form as intermediates. Readily forms adducts with ammonia, pyridine, nonmetal chlorides, etc.

REFERENCES:

Preparation: a) Private communication from W. Fischer, Hannover. b) W. Kroll. Metall u. Erz <u>36</u>, 101, 125 (1939); see also A. Köster. Angew. Chem. <u>69</u>, 563 (1957).

Prepurification: A. V. Pamfilov, A. S. Chudyakov and E. G. Standel. Zh. Prikl. Khimii 142, 232 (1935), and other papers of A. V. Pamfilov published in that period.

Distillation: K. Arii. Sci. Rep. Tohoku Imp. Univ. 22, 959 (1933); the apparatus described may be used for the distillation of other highly corrosive liquids, such as POCl₃, SOCl₂, etc.
Purification of TiCl₄ for atomic weight determinations is described by G. P. Baxter, J. Amer. Chem. Soc. <u>45</u>, 1228 (1923); <u>49</u>, 3117 (1926); E. H. Archibald, The Preparation of Pure Inorganic Substances, New York, 1932, p. 184.

Ammonium Hexachlorotitonate

(NH₄)₁[TiCl₄]

This is a good, easily measured starting material for preparing hydrochloric acid solutions of titanium, since it forms concentrated, stable solutions in water or dilute hydrochloric acid.

> $TiCl_{4} + 2 NH_{4}Cl = (NH_{4})_{5}[TiCl_{5}]$ 189.7 107.0 290.7

The preparation comprises precipitation of (NH₄)₂[TiCl₈] from an HCl-saturated solution, using a special apparatus which may also be employed in many other syntheses.

A 200-ml. wide-neck Erlenmeyer flask is used to hold 100 ml, of solution. The flask is closed off with a closely fitting three-hole rubber cap ("fermentation cap"). A glass stirrer; preferably of the twist drill type, is inserted in the center hole; a drop of glycerol is used for lubrication and gas seal. The use of a ground joint sealed to a mercury-seal agitator is also reocommended. Laborious centering of the stirrer is avoided and easy assembly and dismantling of the apparatus promoted by coupling the stirrer to the motor shaft (or the speed reducer shaft) by means of a piece of strong, rigid rubber vacuum bose? The direction of rotation of the stirrer is such that the center of

the liquid is pushed down; higher agitation rates can be reached with this arrangement without danger of splashing, and the stirring is also more efficient.

The flask is supported at the neck by a clamp which holds it in a cooling bath at a depth so that it is covered with coolant to just below the clamp level while still leaving enough coolant underneath the flask to provide cooling of the bottom.

The gas inlet tube need not dip into the solution, since the rate of absorption of HCl in the vigorously stirred liquid is so rapid that it is almost controlled by the input rate alone; possible plugging of the inlet tube is also avoided by not letting the tube dip into solution. The HCl addition rate is controlled to avoid the formation of a mist above the stirred mixture, a point at which evaporation losses just begin. The greater the stirring rate, the higher the rate at which the HCl may be introduced, and the sooner the end of the run. Complete saturation of 100 ml. of precipitation solution requires less than one hour.

The HCl flow rate is sharply reduced toward the end of the run. The progress and termination of the HCl absorption can be followed by means of bubble counters inserted ahead of and behind the precipitation flask.

The HCl generator must be capable of yielding a continuous stream of gas and must also allow a wide range of adjustment in the flow rate; in addition, it should be easy to start, give an air-free gas stream as soon as possible after the start, and stop generating gas shortly after being turned turned off. The generator described on p. 280 fulfills these conditions less well than the apparatus developed by W. Seidel [Chem. Fabrik 11, 408 (1938)], in which conc. hydrochloric and conc. sulfuric acids react to give a good yield of HCl; this is accomplished by dropping the acids separately onto a packing of glass beads.

If only small quantities of HCl are required, the most convenient generator is still the Kipp, which utilizes the reaction of conc. sulfuric acid with lumps of NH_4Cl , particularly since the gas does not have to be dried. However, foaming is quite pronounced at larger HCl flows.

Returning now to the precipitation of $(NH_4)_2[TiCl]_5$, gaseous HCl is introduced at 6°C into a solution of 6 g. of TiCl₄ in 100 ml. of aqueous (7:1) hydrochloric acid containing about 4 g. of NH₄Cl. The HCl gas is added until saturation. Then the HCl flow is stopped, but stirring is continued until complete precipitation. If the precipitation rate is low, the yellow $(NH_4)_2[TiCl_6]$ is obtained in the form of coarse crystals averaging 0.1 mm.

The precipitate is separated from most of the mother liquor by a short suction filtration through coarse fritted glass (without allowing air to be drawn through the compound), and the crystals are then pressed between two pieces of filter paper. If an asbestos filter is used, the compound must be repeatedly boiled with cono. hydrochloric acid and then very thoroughly washed.

PROPERTIES:

Yellow octahedra, probably of the $K_{2}[PtCl_{6}]$ structure. May be stored for an indefinite period if moistened with hydrochloric acid and kept in a closed container; on washing with anhydrous ether and drying over conc. $H_{2}SO_{4}$ in a vacuum desiccator, decomposes with pronounced evolution of HCl. In moist air, forms a white hydrolysis product, which is unusual in still being soluble in water.

REFERENCES:

A. Rosenheim and O. Schütte. Z. anorg. Chem. <u>26</u>, 239 (1901);
 W. Fischer and W. Seidel. Z. anorg. allg. Chem. <u>247</u>, 383 (1941);
 W. Seidel and W. Fischer, Z. anorg. allg. Chem. <u>247</u>, 367 (1941).

Titanium (IV) Bromide

TiBr4

I.

 $TiCl_4 + 4 HBr = TiBr_4 + 4 HCl$ $189.7 \quad 323.7 \quad 367.6 \quad 145.8$

Due to the long time required (30 hours), the original method described by Thorpe in 1856 (bubbling of HBr through warm TiCl₄ until the boiling point of the solution equals that of TiBr₄) has been modified as follows.

Receiver b of the apparatus shown in Fig. 296 is cooled with liquid nitrogen or Dry Ice, and pure, dried HBr is condensed in until enough liquid is present. The section above d is then broken off, TiCl₄ is added to a, and the apparatus is resealed at c. Stopcock f is closed, i is opened, and TiCl₄ is slowly distilled into container b, which is cooled with Dry Ice; the initial reaction is quite violent. By periodically removing the coolant, it is possible to bring the reaction to completion. The gas mixture evolved (essentially HCl) is vented through stopcock i, while the HBr is condensed in c by proper cooling. The mixture is allowed to warm up to room temperature in order to accelerate the reaction, and the condensation of fresh HBr into the flask is repeated several times. Finally, vessel b, which contains an already very pure crude product, is sealed off at g; if desired, flask c may be sealed at point h to a distillation apparatus (such as the one described in the proparation of TH_4) and the $TiBr_4$ further purified by vacuum distillation.

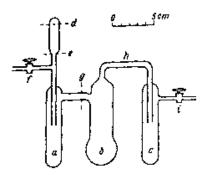


Fig. 296. Preparation of titanium (IV) bromide.

11.

 $T_iO_2 + 2C + 2Br_z = T_iBr_4 + 2CO$ 79.9 24.0 319.7 367.6 56.0

The already-described method of preparation of TiCl₄ is modified only to the extent that the stream of Cl₂ is replaced by dry CO₂ which passes through a 60°C wash bottle containing 135 g. of Br₃; the bromine-saturated CO₂ then passes over the reaction mixture (30 g. of TiO₂ + 15 g. of wood charcoal), which is heated to about 600°C. A mixture of TiBr₄, CBr₄ and free Br₂ collects in the receiver. The last two products are distilled off in a stream of pure CO₂ bubbled through the melt, leaving the TiBr₄ as the residue. Cooling to room temperature produces a solid mass, which may be purified by multiple distillation. The yield is 80 f_4 .

п.

$$Ti + 2Br_2 = TiBr_4$$

47.9 319.7 267.6

If metallic Ti is available, the compound may be easily synthesized from the elements (see the procedure for the preparation of titanium dihalides). A weighed amount (5-6 g.) of freshly distilled Br_2 is placed in a thick-wall quartz tube cooled with Dry ice, crude Ti is added (somewhat more than the stoichiometric quantity), and the tube is sealed under high vacuum. The Br_2 begins to melt on removal of the coolant; the reaction starts immediately and flames appear. After completion of the reaction the tube is opened and the TiBr₄ is distilled off; it may be purified by multiple distillation (see TiL₄).

PROPERTIES:

Amber yellow, octahedral crystals. M.p. 40°C, b.p. 230°C; d 3.25. Extremely hygroscopic, absorbs moisture with hydrolytic decomposition. Very readily soluble in alcohoi, moderately in ether; soluble in 34% hydrobromic acid and in conc. hydrochloric acid. Crystal structure: type D1₁.

REFERENCES:

- W. Biltz and E. Keunecke. Z. anorg. allg. Chem. <u>147</u>, 171 (1925); W. Klemm, W. Tilk and S. von Müllenheim. Z. anorg. Chem. <u>176</u>, 1 (1928).
- See also J. C. Olsen and E. P. Ryan, J. Amer. Chem. Soc. 54, 2215 (1932), as well as R. C. Young in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 114.
- III. See also J. M. Blocher Jr., R. F. Rolsten and I. E. Campbell, J. Electrochem. Soc. <u>104</u>, 553 (1957).

Purification of TiBr, for atomic weight determination is described by G. P. Baxter and A. Q. Butler, J. Amer. Chem. Soc. 50, 408 (1928); E. H. Archibald, The Preparation of Pure Inorganic Substances, New York, 1932, p. 185.

Zirconium (IV), Hafnium (IV) and Thorium (IV) Chlorides and Bramides

ZrClo, HfCle, ThCle, ZrBro, HfBro, ThBro

ZrCi,

| ZrOr | + | $2\mathrm{C}$ | + | $2 \operatorname{Cl}_1$ | ZrCL | + | 2 CO | |
|-------|---|---------------|---|-------------------------|----------|---|------|--|
| 123.2 | | 24.0 | | 141.8 | 233.0 | | 56.0 | |

An intimate mixture of one part of pure ZrO_8 and two parts of calcined carbon black or sugar charcoal is placed in a porcelain boat and heated at 500°C in a stream of Cl₃; or, preferably, ZrO_2 with no admixtures is chlorinated in a Cl_2 -CCl₄ gas mixture produced by passing Cl₂ through a wash bottle (70°C) filled with CCl₄. The initial chlorination temperature is 350°C, but is gradually raised to 700°C.

The equipment is similar to that described on p. 889 for the preparation of BeCl₂, except that, when working with Cl_3-CCl_4 , a trap for the unreacted CCl₄ must be inserted in line after tube A. Since ZrCl₄, which sublimes at 331°C, is difficult to recondense, it is advisable to use a long tube (600 mm.), preferably of Vycor. The additional resublimation at 300-350°C is carried out in a stream of H₂, a treatment which more effectively removes the oxide and FeCl₂ present.

Alternate method: The industrial chlorination of ZrC prepared from ErSiO₄ is described by W. J. Kroll et al. [Trans. Electrochem. Soc. <u>89</u>, 263 (1946); <u>92</u>, 187 (1947); J. Electrochem. Soc. <u>94</u>, 1 (1948)].

PROPERTIES:

White crystalline powder. Sublimation point 331° C, m.p. (under pressure) 438° C; d 2.80. Yields a mist of hydrochloric acid in moist air; violently decomposed by H₂O, forming the oxychloride. Soluble in alcohol and ether. Crystal structure: type D I₁.

RfCl, ThCl,

The same general method is used for $HfCl_4$ and $ThCl_4$; in the case of ThCl₄, the Cl_2 - CCl_4 mixture should be replaced with Cl_2 - SCl_2 , since this allows reducing the temperature to 700°C instead of 900°C.

Z.B., HfBr., ThBr.

The preparation of the bromides in a Br_s-saturated nitrogen stream requires high temperatures if practical reaction rates are to be achieved. The oxide-carbon mixture must usually be heated to about 1100°C; this temperature is easily attained with a gas-air blast burner provided the quartz reactor is embedded in porous, refractory gravel ("Diatomite" gravel). The preparation of HiBr, and the lower bromides HiBr, and HiBr.

The preparation of HiBr, and the lower bromides HiBr, and HiBr, is described in W. C. Schumb and C. K. Morehouse, J. Amer. Chem. Soc. <u>69</u>, 2696 (1947).

REFERENCES:

D. Lely and L. Hamburger, Z. anorg. Chem. <u>87</u>, 209 (1914);
A. Voigt and W. Biltz. Z. anorg. allg. Chem. <u>133</u>, 277 (1924);
O. Hönigschmid, E. Zintl and F. González, Z. anorg. allg. Chem. <u>139</u>, 293 (1924); J. H. deBoer and J. D. Fast, Z. anorg. alig. Chem. <u>187</u>, 177 (1930); W. Fischer, R. Gewehr and H. Wingchen, Z. anorg. allg. Chem. <u>242</u>, 161 (1939); J. P. Coughlin and E. G. King, J. Amer. Chem. Soc. <u>72</u>, 2262 (1950); for the bromides, see also R. C. Young and H. G. Fletcher ia: H. S. Booth, Inorg. Syntheses, Vol. I, New York-London, 1939, pp. 49, 51.

Thorium Chloride

ThCl. 8 H₁O

A solution of thorium hydroxide in excess hydrochloric acid is evaporated until sirupy and is then allowed to cool and crystallize.

Further purification, in particular, removal of Fe and SiO₂, is best achieved by shaking with an ether-aqueous hydrochloric acid mixture. The experimental arrangement is the same as described for the preparation of $(NH_{4})_{2}$ [TiCl₆], p. 1199.

The crystals are dissolved in the minimum quantity of 6N HCl, filtered through asbestos, and shaken twice with ether to remove the iron. Silicic acid precipitates during the evaporation and is also filtered off. The filtrate is cooled to 0°C, and HCl gas is passed through until saturation. An equal volume of ether is added and the mixture is treated with additional HCi until homogeneous. Pure white crystals of ThCl₄ · 8 H₂O crystallize; these are filtered, washed with other, and dried.

PROPERTIES:

Formula weight 518.08. Deliquescent in moist air, readily soluble in water and alcohol. Soluble in ethylenediamine.

REFERENCES:

C. B. Kremer. J. Amer. Chem. Soc. <u>64</u>, 1009 (1942); T. Muniyappan. Master's Dissertation, University of Illinois, 1955.

Titanium (IV), Zirconium (IV) and Thorium (IV) Iodides

Til, (ZrL, Thi)

Syntheses I and II (described below) start from crude Ti (prepared from TiCl₄ and Na), which is allowed to react with I_2 vapor, while in method III a commercial fine Ti-Al alloy powder (Altam 70%, i.e., containing 70% Ti) is boiled in a solution of I_2 in CS₂. Upon removal of the solvent, the AII₃ is bound in a non-volatile complex KAII₄, while the TiI₄ is distilled off. This method is recommended for larger-scale preparations.

 $T_{1}^{*} + 2I_{2} = TU_{4}$ 47.9 507.7 555.0

I. Crude Ti (20 g.) is treated with dilute hydrofluoric acid, washed with distilled water and alcohol, and dried. It is then placed in the center bulb e of the apparatus shown in Fig. 297, which is sealed off at f as close to the bulb as possible. The apparatus is made of high-melting glass, preferably fused quartz ware if highest purity is to be obtained. Filling tube a is closed off with a rubber stopper; the system is evacuated and dried by fanning with a flame while vacuum is maintained. The stopper at a

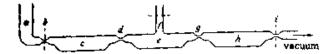


Fig. 297. Preparation of titanium (IV) iodide according to the method of Blocher and Campbell,

is removed for a while, and doubly sublimed, carefully dried I_2 (100 g.) is added via tube a. The I_2 is melted and transferred as a melt into bulb c, which is then sealed off at b. Bulb c is cooled with Dry Ice; the system is evacuated to 10^{-3} mm, and sealed at i. The center bulb is heated to 525° C, and the two side bulbs are alternately heated and cooled with air, to produce a slow stream of I_2 vapor which flows back and forth over the heated metal. The reaction is complete after three passes. The conversion is quantitative, based on the metal content of the Ti. Nonmetallic impurities are left as a residue in e. If the compound is to be resublimed or subdivided into portions, additional bulbs are fused onto h as described in the preparation of BeCl₂ (p. 889).

II. If a particularly pure product is desired, one may proceed as follows: 2 g, of Ti powder is placed in section a of the Pyrex apparatus shown in Fig. 298 and heated for one hour at 500°C in

high vacuum (provided by a pump attached at o). The material is then cooled to room temperature, and thin glass partition d is broken by means of a magnet and steel ball g (which is then removed from the system by sealing off at h; bulb b, which contains 10 g. of In is thus connected to the rest of the apparatus. The latter is now sealed off at i and the pump is turned off. The Ia vapor reacts immediately (sometimes slight heating is necessary) with the Ti to give a quantitative yield of Til. (in the preparation of Zrla, it is necessary to heat the apparatus for several hours in an electric furnace at 200°C). When the reaction is complete, the apparatus is sealed off at m. After breaking partition j. the gases liberated during the reaction are removed by means of a high-vacuum pup connected at q. The system is rescaled at k, the Til, is sublimed from a into c by heating the former, and constriction . is scaled off. The pump may new be connected at p, e broken, and any gas

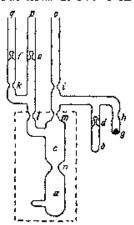


Fig. 298, Preparation of titanium (IV) lodide according to Fast: d, e and f are break-seal valves; g is a steel ball. evolved during the sublimation removed. The compound may then be removed, as desired, through p. If the Til, is to be stored, the system is sealed off at l.

The preparation of ZrI4 or ThI4 is similar.

III. in the method of Blumenthal and Smith, the apparatus (Fig. 299) consists of a two-liter, long-neck, round-bottom flask a, two smaller round-bottom flasks b and c (500 ml., 250 ml. respectively), a condenser and a receiving flask d (250 ml.). The multihole rubber stopper in the large flask carries the following: 1) an annular heating device consisting of a glass tube g which terminates at the bottom in a closed sphere: steam is introduced via a thin inner rubber tube which reaches down to the sphere; 2) a dropping funnel; 3) a reflux condenser; and 4) a glass tube with a largerdiameter filter section (the latter is in flask a and is filled with glass wool). All openings to the atmosphere are protected with drving tubes filled with silica gel. Before the start of the preparation, 10 g, of KI is placed in flask b. The apparatus is assembled and dried by fanning with a flame while a stream of air is drawn through. The rubber stopper is raised rapidly and 127 g. of In dissolved in 600 ml, of CS, and 50 g, of finely powdered Altam 70% alloy (equivalent to 1/2 mole of free Ti, the remainder being the oxide) is added to flask a. The solution is brought to a boil by passing steam through the heating device. The heating is

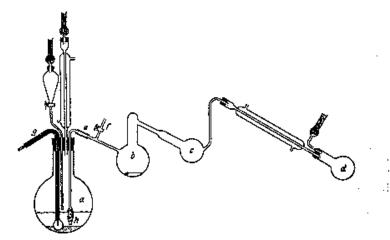


Fig. 299. Preparation of titanium (IV) iodide according to Blumenthal and Smith: *e* rubber connection with pinchcock; *g* steam heater consisting of an outer glass tube with a sphere and an inner rubber tube; *k* filter with glass wool packing.

. 6 .

continued for one hour with occasional shaking, resulting in quantitative formation of the iodides (Til, and Alla). These are soluble in CS.

The mixture is cooled to room temperature and compressed dry air is introduced via the reflux condenser, forcing the solution through the glass wool filter and into flask b. This transfer is carried out in stages, since the iodide solution in flask b must be concentrated from time to time by distilling excess CS a into flask d. Finally, three 190-ml. portions of CS, are added to rinse out the last traces of product in a; these are also transferred to b:

The rubber connection e is closed off with a clamp and flask a is removed from the system. Flasks b and c are heated in a water bath to 80°C until all the CS a distills into d. A slow stream of dry N₂ is introduced through stopcock f, and flask b is strongly beated with a burner while flask c is cooled with cold water: this causes the All, to react quantitatively with the KI to form nonvolatile KAll4; the Til4 meanwhile distills into c. The distillation is ended when colored vapors can no longer be observed.

The crude product (90% yield) contains 95.1% Til4, 4.6% free I_2 and 0.3% iodides of other metals. Since 98% of the CS₂ is recycled, and since KI and I_2 may be recovered from the KAll₄ melt by air oxidation:

 $4 \text{ KAII}_{s} + 3 \text{ O}_{s} = 4 \text{ KI} + \text{ AI}_{s} \text{ O}_{s} + 6 \text{ I}_{s}$

the process is suited for the preparation of large quantities of Til4.

IV. Alternate method: If metallic Ti is not available, Til, may be prepared by the method of Hautefeuille (1867). The procedure is similar to method I for the preparation of TiBra.

The tetraiodides of Ti, Zr and Th may be produced from the oxides with the aid of All ...

PROPERTIES:

Red-brown octahedra crystallizing in type D 11, but transformed on prolonged storage to a modification with a lower degree of symmetry. M.p. 150°C, b.p. 377°C; d 4.40. Fumes strongly in air; dissolves rapidly in water with hydrolytic decomposition.

REFERENCES:

- i. J. M. Blocher and L. E. Campbell, J. Amer. Chem. Soc. 69. 2106 (1947); V. Gutmann and H. Tannenberger, Monatsh. Chem. 87, 423 (1956).
- IL. J. D. Fast. Z. anorg. allg. Chem. 239, 146 (1938).
- III. W. B. Blumenthal and H. Smith, Ind. Eng. Chem. 42, 248 (1950). W. W. Biltz and E. Keunecks. Z. anory. allg. Chem. 147, 171

(1925); W. Klemm, W. Tilk and S. von Müllenheim. Z. anorg. allg. Chem. <u>176</u>, 1 (1928); M. Chaigneau. Comptes Rendus Hebd. Séances Acad. Sci. <u>242</u>, 263 (1956); S. Ramamurthy. J. Sci. Industr. Res. <u>14B</u>, No. 8, 414.

Titanium (III) Oxychloride

TiOCI

 $TiO_1 + 2TiCl_2 = 2TiOCl + TiCl_4$ 79.9 308.5 198.7 189.7

A quartz tube is thoroughly baked while under high vacuum. It is then charged (under a nitrogen blanket) with TiCl. (50% excess) and TiO₂. The tube is evacuated (10⁻⁵ mm.), sealed off and placed in a furnace with a temperature gradient so that one third of the tube, containing the TiOs-TiCIs mixture, is at 650°C while the remainder is at 550°C. The reaction ends in about 12 hours; the excess TiCl₃ and a small amount of yellowish-brown orystals of TIOCI pass into the cold zone. The hot zone contains a brown, finely crystalline cake of TiOCl. If heating in the temperature gradient is continued for several days all of the TiOCI migrates to the colder zone and deposits as beautiful long crystals. The TIOCI is isolated by distilling the TiCl. into the empty half of the tube, freezing it there, and cutting the tube in two. The mixed crystais of TiOCI and TiCl, are then treated with dimethylformamide, in which TiCi, dissolves readily, forming a blue solution. The TiOCI residue is repeatedly washed with dimethlyformamide, followed by alcohol and ether, and dried in vacuum.

The compound may also be prepared by a similar procedure via the reaction of TiCl_a with Fe₂O₃, SiO₂, H₂O or O₂.

PROPERTIES:

Golden-yellow to red-brown crystals; decomposes slowly in air. Decomposes to TiO₂ and TiCl₄ on heating in an open annealing tube.

REFERENCE:

H. Schäfer, F. Wartenpfuhl and W. Weise, Z. anorg. allg. Chem. 295, 268 (1958).

Titanium (IV) Oxychloride

TiOCl_t

I.

 $3 \text{ TiCl}_{4} + \text{As}_{9}\text{O}_{8} = 3 \text{ TiOCl}_{2} + 2 \text{ AsCl}_{3}$ $189.7 \quad 197.6 \quad 134.8 \quad 181.3$

An excess of TiCl₄ is treated with As_2O_3 , resulting in a highly exothermic reaction which goes to completion if caking of the

solid product is avoided. The yellowish substance obtained is freed of $AsCl_3$ and excess $TiCl_4$ by suction filtration in the absence of air and thorough washing with absolute pentane or CCl_4 . Residual solvent is removed by vacuum distillation at room temperature. The product contains traces of arsenic.

II. $TiCl_1 + Cl_1O = TiOCl_2 + 2Cl_2$ 189.7 86.9 134.8 141.8

A stream of Cl_2O diluted with dry O_2 is introduced through a large-diameter inlet tube into a two-neck 250-ml. flask containing about 100 ml. of TiCl₄ (the TiCl₄ is distilled into the flask under conditions of complete exclusion of moisture). The gas is prepared by passing a stream of O_2 -Cl₂, predried with P_2O_5 , over HgO. The latter is contained in a glass tube provided with a cooling jacket and able to rotate (Liebig condenser).

Plugging of the inlet tube with solid TiOCl₂ is prevented by sealing a glass spatula to the bottom of the flask in such a way that it projects a few centimeters into the tube. Occasional rotation of the flask around the inlet tube then keeps the latter free.

The O_3 -Cl₃O mixture is bubbled in until the formation of a crystalline paste makes this impossible. The mixture is allowed to stand overnight, whereupon any small quantity of hypochlorite still present decomposes to Cl_3 and additional TiOCl₃. The product is filtered in the absence of moisture and washed several times with high-purity CCl₄ which has been distilled over P_2O_6 ; the product is freed of the CCl₄ by evaporating the latter in a stream of a dry gas, and is then kept in vacuum for a short time.

The yield is practically quantitative, based on $Cl_{2}O$; based on TfCl₄ actually used, it is about 50%.

PROPERTIES:

Pale yellow, hygroscopic, crystalline powder. Sparingly soluble in CCl₄, benzene and similar solvents, moderately soluble in ethyl acetate, readily soluble in ethereal hydrochloric acid (decomposition), Hydrolyzes in moist air, giving a white color. Dissociation to TiCl₄ and TiO₂ begins at 180°C. d 2.45.

REFERENCES:

- 1. P. Ehrlich and W. Engel. Z. anorg. allg. Chem. 322, 217 (1963).
- II. K. Dehnicke. Angew. Chem. <u>75</u>, 417 (1963); Angew. Chem. (International Ed. in English) 9, 325 (1963).

Zirconium Oxychloride ZrOCh · 8 H.O

The anhydrous compound is unknown. Of the existing hydrates, with 2. 3, 5, 6 and 8 moles of H_2O , the last is the most important,

since it crystallizes as a sparingly soluble compound from aqueous solutions containing HCl. In a solution containing about 1.2 g, of $ZrOCl_2 \cdot 8H_3O$ per 100 ml. of H_2O , the flat minimum section of the solubility curve corresponds to a concentration of 7-8 moles of HCl/liter at 0°C. The octahydrate is readily recrystallized and can therefore be prepared in very pure form.

PREPARATION

$$Z_TO_t \rightarrow Z_TOCl_t \cdot 8 H_tO$$

123.2 322.3

I. Since zircon $2rSiO_4$, a mineral found in nature, is more difficult to work with, it is better to start from zirconia $2rO_2$ (baddeleyite), which is calcined, finely ground (the coarser particles are screened off with silk gauze), and converted to the sulfate by evaporation or treatment for several days with an excess of warm conc. H_2SO_4 . The solid residue, which consists of $2r(SO_4)_2$ and unreacted $2rO_3$, is taken up in water (the solid is added in small portions to prevent heating of the solution). The sulfate dissolves slowly, and its solution may be aided by acidifying the water with some hydrochloric acid. The resultant milky suspension, which contains solid undissolved $2rO_2$ and SiO_3 (or $2rSiO_4$), is allowed to stand for several hours and filtered.

The weakly acidic sulfuric acid solution is precipitated with ammonia and the hydroxide is filtered off. If the precipitate still exhibits a high Si content, it is dissolved in conc. hydrochloric acid and the solution is evaporated to dryness; this procedure is repeated several times. On redissolving in water, SiO_2 and some basic zirconium chloride become the insoluble residue. If no Si is evident in the hydroxide, the fresh gel is dissolved in cold hydrochloric acid and the oxychloride is allowed to crystallize by adding conc. hydrochloric acid or saturating with HCl. The crystals are filtered and washed with 8N HCl.

II. When the starting material is high in SiO_8 and, in general, if a platinum dish is available, the $2rO_8$ may be evaporated with a mixture of conc. H_3SO_4 and 40% hydrofluoric acid instead of with pure H_3SO_4 . The temperature required for this procedure is lower than in the preceding method. The subsequent steps are as described in method I.

III. The octahydrate $ZrOCl_8.8H_3O$ may also be prepared as follows. A suspension of freshly precipitated zirconium hydroxide in H_3O is dissolved in cold dilute hydrochloric acid; after filtering, the $ZrOCl_8.8H_8O$ is crystallized by evaporation (if necessary, by

adding cone, hydrochloric acid). The starting zirconium hydroxide is prepared by precipitating a solution of $K_3 Zr F_8$ with ammonia; the precipitate, which contains a basic fluoride, must be treated for a short time with conc. $H_3 SO_4$ (to remove the HF) and redissolved in $H_2 SO_4$. The pure hydroxide is precipitated with ammonia.

IV. ZrCl₄ is dissolved in water (do not heat to dissolve—if necessary, add some hydrochloric acid); the solution is filtered and the oxychloride is precipitated by making the solution 7-8N in NCL.

The crude chlorination products of those zirconium-containing minerals that are difficult to break down must be rechlorinated with Cl_{a} at 1000°C, yielding crude chlorides, which can then be purified via method IV.

PREPARATION BY RECRYSTALLIZATION OF THE OXYCHLORIDE.

V. The fact that $2rOCl_2 \cdot 8H_2O$ dissolves readily in water and is insoluble in 7-8N (25-30%) hydrochloric acid allows this compound to be used as an intermediate in the purification of Zr salts. Although complete isolation of zirconium cannot be achieved, this method eliminates not only Al, Fe, Nb, Ta, the rare earths and many other elements, but also Ti, the removal of which otherwise involves great difficulties. Thus, for example, the Al content may be reduced from 0.035% to 0.0015% by only one recrystallization; the decrease in Fe content is of the same order of magnitude. Reprecipitation of the oxychloride is thus more effective than that of the sulfate, described on p. 1232.

Since the molar solubility of $HfOCl_3$, SH_2O is identical to that of the Zr salt, the Hf/Zr ratio remains unchanged.

The strongly acidic HCl solution of ZrOCl_3 . 8H₂O is evaporated on a water bath until crystallization is incipient and is then treated with an equal volume of conc. hydrochloric acid; the mixture is heated (do not allow too much HCl to escape) and, if necessary, 25% hydrochloric acid is added to the warm mixture until solution is complete and the mixture contains, at most, 39 g. of oxychloride, i.e., 15 g. of ZrO₂ per 100 ml. The solution is mechanically stirred and its temperature is allowed to drop to a point where it still feels warm to the hand; it is then cooled with ice. After stirring for 30 minutes at 0°C, the product is filtered through a mediumporosity fritted glass and washed with 25% hydrochloric acid precooled to 0°C.

The filtrate still contains about 1.5 g, of the oxychloride (or 0.6 g, of ZrO_2) per 100 ml.

VI. A simpler method gives a less complete precipitation. One proceeds as follows.

First 25 g. of $2rOCl_{3} \cdot 8H_{2}O$ is dissolved in a mixture of 6 mi. of conc. hydrochloric acid and 100 ml. of $H_{2}O$. The solution is heated to 70 °C and filtered. The filtrate is concentrated to 75 ml. and allowed to cool without stirring. The crystallizing salt is suction-filtered on a fritted glass and washed with a cold 1:1 alcohol-conc. hydrochloric acid mixture, in which the oxychloride is very sparingly soluble. The yield is 10 g. of purified material; an additional 7 g. may be recovered from the mother liquor by further evaporation and crystallization.

SYNONYM:

Zirconyl chloride.

PROPERTIES:

Tetragonal prisms or needles. Deliquescent in moist air, evolves HCl and becomes dull in dry air. Soluble in H_{aO} (slight hydrolysis) and alcohol. Lower hydrates are formed on heating in a stream of HCl. Liberates HCl on heating in air and the solubility in water is gradually lost; reverts to the oxide on calcination.

Precipitation of an alcoholic solution with ether or acetone yields dizirconyl chloride $2r_2O_3Cl_2 \cdot 5H_2O$, which is sparingly soluble in water. The same compound deposits when a dilute aqueous solution of zirconyl chloride is allowed to stand for a month.

Hafnium Oxychlaride

The preparation and properties of HfOCl₂·8H₂O are virtually identical to those of the Zr compound.

REFERENCES:

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- III. F. P. Venable and J. M. Bell, J. Amer. Chem. Soc. 39, 1599 (1917); M. M. Smith and C. James. J. Amer. Chem. Soc. 42, 1765 (1920); O. Hönigschmid, E. Zintl and F. González, Z. anorg. allg. Chem. <u>139</u>, 293 (1924).
- IV. See also H. von Siemens and H. Zander. Wissenschaftl. Veröffentl. Siemens 2, 484 (1922); W. B. Blumenthal, J. Chem. Education <u>39</u>, 607 (1962).
- V. W. Fischer and M. Zumbusch. Z. anorg. allg. Chem. 252, 249 (1944); see also O. Hönigschmid, E. Zintl and F. González. Z. anorg. allg. Chem. 139, 293 (1924) or E. H. Archibald. The Preparation of Pure Inorganic Substances, New York, 1932, p. 187.

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Lower Titanium Oxides

TiO, Ti₁O₁

L. The surest preparation of defined lower Ti oxides involves sintering with metallic Ti.

Filings are prepared from a Ti sheet and ground to pinhead size; a magnet is used to free them from the Fe picked up during the machining operation. The filings are etched with dilute hydrofluoric acid, rinsed with acetone, and rapidly dried. They are mixed with TiO_3 in proper amounts and the mixture is pressed into tablets or rods; these are heated in high vacuum to $1600^{\circ}C$ in the arrangement illustrated in Fig. 300.

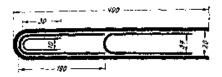


Fig. 300. Synthesis of lower titanium oxides (dimensions in mm.).

Two Tammann crucibles (10 mm, and 14 mm, I.D.), made of sintered clay, are placed one inside the other, and the assembly is placed in a tube (20 mm, I.D. and 400 mm, long) made of the same material and closed at one end. The 14-mm, crucible is loosely covered by the closed end of an identical crucible, as shown. The outer (20 mm, I.D.) tube is connected to a high-vacuum system via a ground joint cemented on with picein. This arrangement of three concentric tubes is needed because the outer corundum tube is not vacuum-tight at the reaction temperature of 1600°C. The gas used for flushing the annular space between the surrounding graphite heater and the inner corundum tube is bydrogen, which diffuses inside. Thus, in new tubes, the inside pressure rises from a satisfactory high vacuum to 1 mm. within 10 minutes at 1600°C; the pressure rises even more rapidly in older tubes. The pump must therefore be left on during the entire heating period. The above arrangement of cracibles prevents the hydrogen from diffusing to the reactants before it can be removed by the vacuum pump.

The mixture is heated at 1600°C for 15 minutes in a Tammana furnace; this is obviously insufficient to bring about complete reaction. The Ti is not completely consumed, but it becomes so brittle that it is readily pulverized in an agate mortar. This fine powder is reheated and the product is then homogeneous,

If Ti powder is used as the starting material, a single but longer heating run is sufficient (1/2 hour at 1600°C).

Materials with a low oxygen content are best subjected to a preliminary homogenization treatment, either by high-frequency heating in high vacuum, or by so-called button-melting in an electric arc, which is familiar in titanium metallurgy.

The above procedure is generally applicable and may be used for the preparation of lower oxides of other elements closely related to titanium, e.g., Zr, Hf, V, Nb, etc.

In many cases it has proved more convenient not to start each run from the metal; in those cases, a larger quantity of the lowoxygen compound is prepared and then used as a stock raw material.

II. Reduction of TiO₂ in a stream of H₂ at 1250°C yields a product of composition TiO1.8, at 1430°C and longer reaction times up to $TiO_{1.46}$. At 1000°C, the reduction of TiO_3 in a $TiCI_4$ -saturated stream of H₂ also yields a small amount of violet-colored Ti_2O_3 , besides the other products.

III. When TiO₂ is reduced with carbon, the formation of mixed TIO-TIC crystals cannot be entirely prevented. According to Shomate, heating in vacuum at 1400°C for 20 hours yields Ti2Os via the reaction 2 $TiO_2 + C = 2 Ti_2O_2 + CO$, in agreement with the observations of Junker, who found that significant amounts of carbide are formed only above 1600°C.

PROPERTIES:

TiO: Formula weight 127.80. Golden yellow powder. M.p. 1750°C; d 4.89. Crystal structure: type B1 (NaCl type). The rock salt phase is homogeneous over a wide range of compositions $(TiO_{1,3}-TiO_{0,6})$. TiO dissolves in dilute hydrochloric and sulfurio acids with partial oxidation: $Ti^{3+} + H^+ = Ti^{3+} + \frac{1}{3} H_2$. Ti_3O_3 : Formula weight 143.80. Dark violet powder. M.p.

~1900°C; d 4.49. Crystal structure: type D51. A.S. 4.

REFERENCES:

I. P. Ehrlich, Z. Elektrochem, <u>45</u>, 362 (1939); see also S. Andersson, B. Collén, U. Kuylenstierna and A. Magnéli, Acta Chem. Scand. <u>11</u>, 1641 (1957).

- **U. E. Friederich and L. Sittig. Z. anorg. alig. Chem. <u>146</u>, 127 (1925); Y. Belyakova, A. Komar and V. Mikhailov. Metallurg <u>14</u>, 23 (1939); G. Lunde. Z. anorg. alig. Chem. <u>164</u>, 341 (1927); G. Brauer and W. Littke. J. Inorg. Nuclear Chem. <u>16</u>, 67 (1960).**
- III. C. H. Shomate. J. Amer. Chem. Soc. <u>68</u>, 310 (1946); E. Junker.
 Z. anorg. allg. Chem. <u>228</u>, 97 (1936).

Titanium (IV) Oxide

TiO,

Titanium (fV) oxide crystallizes in three modifications of decreasing stability: rutile, anatase and brookite. Whether the synthesis of brookite has been achieved is still in doubt. Anatase is formed via the hydrolysis of Ti halides at not too high a temperature (600°C) or via low-temperature calcining (~700°C) of precipitated titanic acid. The lattice is stabilized by adsorbed anions, among which the most effective are sulfate and phosphate. Pure TiO₃ calcined at high temperature always yields the rutile lattice.

I.

Very pure TiO_2 is readily prepared by hydrolysis of preparified and repeatedly distilled $TiCl_4$. The chloride is hydrolyzed in Pyrex vessels cooled in ice and the residual titanic acid is precipitated by addition of ammonia. The mixture is boiled for one hour, filtered and thoroughly washed until free of chloride (if necessary, the precipitate is redissolved in hydrochloric acid before washing, and precipitated with ammonia). The precipitate is dried at 107°C and calcined for one hour at 800°C. The product should be ground to a fine powder, rewashed until free of chloride, and calcined at 1000°C. After calcination, the TiO_2 so prepared is white or light gray. A yellow tinge indicates traces of iron.

Alternate methods:

II. A more readily filtered precipitate is obtained when the precipitation is carried out in the presence of $(NH_4)_3SO_4$. Commercial TiCl₄ (900 g.) is slowly added to one liter of distilled water, and the solution is purified by boiling for 10 minutes and removing SiO₂ and any insoluble impurities by filtration. A solution of 1300 g. of $(NH_4)_3SO_4$ in two liters of distilled water acidified with 25 ml. of conc. hydrochloric acid is treated in a similar manner. The two solutions are cooled, combined with stirring, and brought to a boil. The pH is adjusted to 1.0 by addition of

ammoniz. At pH<1, the yield is lower, while at pH>1 the Fe content of the product may exceed 0.003%. Further treatment is the same as in (I). The yield is almost quantitative, and a rutile powder with a TiO₂ content exceeding 99.8% is obtained.

III. K₃TiF₆ → TiO₃ 240.1 79.9

A solution of $K_2 TiF_6$ (which has been recrystallized several times) in hot water is prepared, and ammonia is added to precipitate the snow-white TiO_2 -aq. The precipitate is thoroughly washed, dried and calcined.

IV. $TiOSO_4 \cdot 2H_5O \rightarrow TiO_2$ 196.0 79.9

This may be achieved by hydrolysis of titanium sulfate solutions on prolonged boiling. However, this procedure is not recommended since it requires a long time (eighthours) and the resultant precipitates are difficult to filter; precipitation with ammonia at the boiling point is preferred.

V. $TiCl_{\pm} + O_{\pm} = TiO_{\pm} + 2 Cl_{\pm}$ 189.7 32.0 79.9 148.8

The following procedure for the preparation of rutile differs fundamentally from the previous methods. Absolutely dry O_2 and TiCl₄ vapor are passed for 20 hours through a 20-mm,-I.D. porcelain tube heated to 650-750°C. Coloriess to light-yellow, lustrous crystals of rutile are deposited on the white reactor walls. Unreacted TiCl₄ is collected in a receiver cooled with ice-salt. Toward the end of the preparation, pure O_2 is passed through the tube, and this stream is continued while the mixture is cooling.

SYNONYM:

Titanium dioxide.

PROPERTIES:

Rutile: type C4, d 4.22; anatase: type C5, d 4.06; brookite: type C21, d 4.13. M.p. 1870°C; thermal dissociation above 1800°C is evident from the appearance of a bluish tinge and a lower melting point.

Amorphous TiO_2 is also insoluble in water and dilute acids. It dissolves slowly in hot conc. H_2SO_4 , better in alkali hydrogen

sulfates. The solubility is strongly dependent on the prior thermal treatment.

REFERENCES:

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- II. W. B. Blumenthal, Ceramic Age 51, 320 (1948).
- IV. Tscheng Da Tschang, Buil. Soc. Chim. France [5] 3, 271 (1936); A. W. Czanderna, A. F. Clifford and J. M. Honig. J. Amer. Chem. Soc. 79, 5407 (1957).
 - V. H. Rheinboldt and W. Wisfeld. Ber. dtsch. chem. Ges. 67, 375 (1934).

Titonium (IV) Oxide Hydrate

TiO₂ · n H₂O

I. Compounds belonging to the system TiO_2-H_3O prepared in the usual way (e.g., by precipitation with ammonia from an aqueous solution of K_3TiF_6) may be regarded as composed of TiO_2 and labile H_2O . Part of the water, however, is bound and localized; its amount depends on the method of preparation. Precipitated, hydrated TiO_2 either exhibits an amorphous x-ray pattern or consists of anatase containing adsorbed water; similar lattices are formed by the products of hydrolysis of $Ti(SO_4)_2$ solutions (refluxing for four hours), while hydrolysis of $TiCl_4$ and $Ti(NO_3)_4$ solutions under identical conditions yields rutile.

II. "Orthotitanic acid" $H_4 TiO_4$ or $TiO_3 \cdot 2 H_3O$ seems to form only under certain definite conditions; using the Wilstätter acetone method at low temperature (0°C), it was possible to prepare a compound of composition $TiO_3 \cdot 2.16H_2O$.

BEFERENCES:

- For general references, see R. Fricke, Das System TiO₃/H₂O in R. Fricke and G. F. Hüttig, Hydroxyde und Oxydhydrate [Hydroxides and Oxide Hydrates], Leipzig, 1937, p. 211.
- L. H. B. Weiser and O. W. Milligan. J. Phys. Chem. 38, 513 (1934); O. Glemser. Z. Elektrochem. 45, 820 (1939); W. Biltz, G. A. Lehrer and O. Rahlfs. Z. anorg. allg. Chem. 244, 281 (1940).
- II. R. Schwarz and H. Richter, Ber. dtsch. chem. Ges. <u>62</u>, 31 (1929); R. Willstätter, Ibid. 57, 1082 (1924).

Peroxotitanic Acid

H.TiO,

According to Schwarz and coworkers, 5 g. of titanic acid hydrate (Merck) is dissolved in 10 ml. of warm conc. $H_{g}SO_{45}$ the solution is diluted to three times its volume with water, cooled to -10° C, placed in a dropping, funnel, and added to a solution of 8.6 g. of $K_{2}SO_{4}$ in 15 ml. of 30% $H_{2}O_{2}$. The mixture is cooled to 0° C and allowed to stand in the cold for 1/2 hour; it is then precipitated by addition of about one liter of ice-cold acetone pretreated with $H_{2}O_{2}$ until the appearance of the color of titanium sulfate (alcohol may cause partial reduction of the solution, yielding a product deficient in active oxygen). The precipitate is filtered with suction and washed with ice-cold absolute ether until the filtrate gives a negative reaction with permanganate. The product is dried for several hours in high vacuum at the lowest possible temperature, yielding yellow-red potassium peroxytitanyl sulfate corresponding to the formula $K_{2}[TiO_{2}(SO_{4})_{2}] \cdot 3 H_{2}O_{2}$.

According to K. F. Jahr (see FIAT-Review, Anorganische Chemie, Part III, p. 173) the color is due not to the complex anion, but to the peroxytitanyl cation itself. See also E. Gastinger, Z. anorg. allg. Chem. 275, 331 (1954).

In the preparation of the corresponding zirconium and hafnium salts, which are white but have an analogous structure, the indicated concentrations of the reactants must be very strictly adhered to.

If the complex salt is to be used immediately, purification by thorough washing suffices. The precipitate is dissolved on the filter in ice water and the solution is poured into 10 liters of icecold water. Gradual deposition of the pure white precipitate sets in after some time and the precipitation is complete after about 24 hours. The product is purified by filtering, washing with fee water followed by acetone; any adsorbed water is removed by agitating in a shaker flask (three times with 100 ml. of acetone, once with 100 ml. of absolute ether, three times with petroleum ether—all washing operations at 0°C). The remaining petroleum ether is removed by suction and the product is left for about 0.5 hour in a vacuum desiccator which does not contain a drying agent.

The peroxide hydrates of Zr, Hf and Th are prepared by treating a solution of the sulfate (5-10%, based on the oxide content) with an excess of 30% H_2O_2 , cooling to -20°C, and precipitating with ammonia below 0°C. The slimy precipitate is removed by scotion from the cooled container with the aid of a filter candle and washed with ice water. The only suitable drying method is the ammonia extraction process described by W. Blitz [Z. Elektrochem. 33, 491 (1927)].

PROPERTIES:

 $Ti(OH)_3 \cdot OOH$: Slightly hygroscopic, lemon-yellow powder, Gradually loses its active oxygen at room temperature, with resultant decoloration. Readily soluble without decomposition in dilute H_3SO_4 ; loses oxygen gradually in water.

REFERENCES:

R. Schwarz and W. Sexauer, Ber. dtsch. chem. Ges. <u>60</u>, 500 (1927); R. Schwarz and H. Giese. Z. anorg. allg. Chem. <u>176</u>, 209 (1928); see also R. Schwarz and F. Heinrich, Z. anorg. allg. Chem. <u>233</u>, 387 (1935).

Zirconium (IV) Oxide

ZrO,

 $\begin{array}{rcl} \operatorname{ZrOCl}_{2} & 8 \operatorname{H}_{2} \operatorname{O} \twoheadrightarrow & \operatorname{ZrO}_{2} \\ & 322.3 & 123.2 & 355.4 & 123.2 \end{array}$

Zirconium (IV) oxide is formed when zirconium oxide hydrates or zirconium salts of volatile, oxygen-containing acids (nitrates, oxalates, acetates, etc.) are dehydrated and then calcined.

Usually the oxychloride or sulfate is thermally decomposed between 600 and 1000°C. Either salt must be prepurified by repeated recrystallization. In the case of the sulfate, the thermal decomposition removes the last traces of SO₃ with some difficulty.

The amorphous ZrO_2 , which is the first product obtained on beating the oxychloride (300°C), converts at 500°C to the tetragonal modification, which then contains only traces of Cl. Above 600°C the material is monoclinic.

Alternate methods: a) For the almost complete decomposition of $ZrOCl_3 \cdot 8H_2O$ with superheated steam (accompanied by evolution of HCl and formation of ZrO_3) see Akhrap-Simonova.

b) The preparation of ZrO_3 by removal of silicon from $ZrSiO_4$ with SiO is described by Zintl et al.

PROPERTIES:

White powder. M.p. 2680°C, b.p. 4300°C; d 5.73. Exists in several modifications. Crystal structure: tetragonal and monoclinic.

The chemical behavior is strongly affected by the nature of the prior thermal treatment. If the compound has been heated to moderate temperatures, it dissolves quite readily in mineral acids; after heating to high temperatures, it is soluble only in hydrofluoric acid and conc. H_2SO_4 ; after melting, it is attacked only by hydrofluoric acid. Decomposes readily in alkali hydroxide or carbonate melts, in which it forms acid-soluble zirconztes.

REFERENCES:

O. Ruff et al. Z. anorg. allg. Chem. <u>133</u>, 193 (1924); <u>180</u>, 19 (1929);
W. M. Cohn and S. Tolksdorf, Z. phys. Chem. (B) <u>8</u>, 331 (1930);
G. L. Clark and D. H. Reynolds. Ind. Eng. Chem. <u>29</u>, 711 (1937);
L. K. Akhrap-Simonova. Zh. Prikl. Khimii <u>11</u>, 941 (1938); E. Zintl, W. Bräuning, H. L. Grube, W. Krings and W. Morawietz. Z. anorg. allg. Chem. <u>245</u>, 1 (1940); A. W. Henderson and K. B. Higbie. J. Amer. Chem. Soc. <u>76</u>, 5878 (1954).

See also R. Fricke, Das System ZrO_9/H_3O in R. Fricke and G. F. Hüttig, Hydroxyde und Oxydhydrate [Hydroxides and Oxide Hydrates], Leipzig, 1937, p. 219, especially for the formation of oxide hydrates.

Hafnium (IV) Oxide

HfO,

Hafnium (IV) oxide is prepared by calcination of the hydroxide, oxalate, oxychloride or sulfate at 500-1000 °C. The crystallization of the oxide starts at 400 °C.

PROPERTIES:

White powder. M.p. 2780°C; d 9.68. Essentially identical with ZrO₂ in chemical behavior. It probably forms the same types of crystal lattice.

REFERENCE:

G. von Hevesy and V. Berglund, J. Chem. Soc. (London) 125, 2373 (1924).

Thorium (IV) Oxide

ThO,

I. Th(NO₃)₄ · 4 H₂O or Th(NO₃)₄ · 5 H₁O or Th(C₁O₄)₁ · 6 H₁O \rightarrow ThO₃ 552.2 570.2 516.3 25%1 \rightarrow

Thorium (IV) oxide is obtained by thermal decomposition of thorium oxide hydrate (which is precipitated with ammonia) or salts of oxygen-containing acids. The nitrate and oxalate are especially suitable as starting materials, while the sulfates give off the last traces of SO_3 only with difficulty.

Pure nitrate is placed in a large evaporation dish and is very carefully heated in an electric furnace. The nitrate swells . °.

Γ.

considerably at 300-400°C and forms a spongy mass, which subsequently collapses and becomes more compact. To prevent the uptake of SlO_2 during calcination of the oxide, the powder obtained on decomposition of the nitrate is placed in a Pt crucible and is then heated for 1-2 hours at 800-850°C.

The oxalate $Th(C_{3}O_{4})_{5}$, $6H_{3}O$ gives off its water of crystallimition at 300°C and is almost entirely decomposed to the oxide (the weight of the final products is <1% greater than the theoretical) at 450°C.

II. According to Brintzinger and Möllers, active oxide is obtained when thorium chloride, nitrate or sulfate is decomposed with steam at 800°C.

III. For the preparation of oxide hydrates and hydroxides, see the references indicated.

PROPERTIES:

White powder, compact or loose depending on the method of preparation. M.p. 3050° C, b.p. 4400° C; d 9.87. Crystal structure: type C1 (fluorite type). Almost insoluble in acids when calcined at high temperatures, although readily decomposed in bisulfate melts or by evaporation with conc. $H_{2}SO_{4}$. In contrast to TiO₂ and ZrO₂, does not form salts with basic oxides and is therefore insoluble in molten NaOH or Na₂CO₃. The oxide prepared by calcination of the oxalate at 500°C may be dissolved by peptization with dilute hydrochloric acid.

REFERENCES:

- L. J. W. Marden and H. C. Rentschler. Ind. Eng. Chem. <u>19</u>, 97 (1927); H. J. Born, Z. phys. Chem. (A) <u>179</u>, 256 (1937).
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Titanium, Zirconium and Thorium Sulfides

TiS, TiS, TiS,

Тб_ь, Тіб_е L

 $TiCl_{*} + 2H_{*}S = TiS_{*} + 4HCl$ $189.7 \quad 68.2 \quad 112.0 \quad 145.9$ $TiS_{*} + S = TiS_{*}$ $112.0 \quad 32.1 \quad 144.1$

Thankern (IV) sulfide TiS_2 is usually prepared by the reaction of a gaseous mixture of $TiCl_4$ and H_2S in a red-hot tube. A chlorine-free product cannot be obtained without an aftertreatment with S in a pressure tube at 600°C. The yield is also unsatisfactory (30-40%, based on the TiCl₄); however, the yield may be increased by repeated passage of the unreacted TiCl₄ from the receivers.

The reaction is carried out in the apparatus shown in Fig. 301; it consists of a Pyrex combustion tube fused at both ends to 100-ml. round-bottom flasks. Flask a is filled with 50 g. of freshly distilled TiCl4 and is then sealed off at c; b is a receiver for unreacted TiCl,, and is cooled with ice-salt. A Stock receiver cooled with Dry Ice and containing about 25 ml, of liquid HaS is connected to the system at d via a small wash bottle filled with glycerol (this is the bubble counter) and two CaCla drying tubes. A fast stream of H2S, generated by gradual removal of the coolant, is passed through the apparatus while the combustion tube is heated to 480-540°C. The TiCl, in a is then heated almost to the boiling point and held at this temperature with a small flame. The TiCl₄-H₂S gas mixture reacts in the tube to form HCl and TiSz; the latter settles on the tube wall. After all the TiCl, is distilled from a, the system is flushed for a short time with H₂ or CO, the HaS line is reconnected at e, and the unreacted TiCl, condensed in b is passed again through the tube, this time into a. After the TiCl, has been used up (3-5 hours), the TiS, produced is treated for two hours at the same temperature in a slow stream of HaS to remove most of the chloride still adhering to the product. The material is allowed to cool in a stream of Ha or CO₂₀ the tube is broken at both ends, and the dark brass-yellow TIS, which crystallizes as leaflets of mosaic gold color, is collected. The yield is about 10 g.



Fig. 301. Preparation of titanium disulfide.

Complete removel of the chloride can be effected only by repeated heating of the product with excess S in a pressure block. Thus, 4 g. of crude TiS₂ and 3 g. of S are placed in a bomb tube of Vycor or similar glass. The sulfur should be completely free of carbon compounds (von Wartenberg method: Z. anerg. allg. Chem. <u>251</u>, 166 (1943); this consists of vacuum distillation, followed by 48-hour heating at 200°C in vacuum or under N₂, followed by another vacuum distillation]. The bomb tube with the TiS_{2} and S is sealed in high vacuum and heated for three days at 600°C. The tube is opened and the volatile compoments are removed in a heated vacuum desiccator (drying pistol) at 100-150°C. The product, which still contains some chloride, is again heated with additional S to about 600°C for two days, and the volatile components are again removed in vacuum. The intermediate product then consists of graphitelike trisulfide and unreacted S. The free sulfur may be removed by vacuum distillation at 400°C; the residual TiS_{3} undergoes thermal decomposition at temperatures above 500°C, yielding pure TiS_{2} .

D.
$$T_i + 2S = T_iS_2$$
; $T_i + 3S = T_iS_3$
47.9 64.1 112.0 47.9 96.2 144.1

Sulfides of any desired composition may be obtained by synthesis from the elements, which is a generally applicable method. This is also the simplest way to prepare chlorine-free products. The starting material consists either of Ti filings made by grinding Ti strips (for the preparation of the strips, see the directions for the lower titanium oxides, p. 1214) or simply Ti powder (which, however, usually has a lower metal content). First 1.5 g. of Ti and 4 g. of S, in a thick-wall Vycor tube, are carefully degassed in high vacuum. The tube is then sealed and heated at 650°C for four days. Metal particles still present in the product are ground separately, added to the sulfide product (total about 3 g.) together with 1.7 g. of S, and again heated in a pressure tube for two days at 600°C. The free sulfur is distilled off at 400°C; the higher sulfides are, if desired, decomposed thermally above 500°C, yielding TiS₂ and TiS₃, as in method I.

PROPERTIES;

 TiS_3 : Formula weight 112.02. Brass-yellow flakes with a metallic luster, d 3.22. Crystal structure: type C6.

Stable in air at normal temperatures; forms TiO_3 on heating, Decomposes in nitric acid and hot conc. H_3SO_4 , releasing S; dissolves in boiling aqueous sodium and potassium hydroxides, forming alkali titanates and alkali sulfides.

TiS₃: Formula weight 144.08. Graphitelike substance. d 3.22. **Except** for its insolubility in boiling NaOH, it is similar to TiS_3 in all chemical properties.

T\$_.

Lower Ti sulfides may be prepared by synthesis from the elements, by treatment of Ti metal with TiS₂, or by reduction of TiS₂ with H_2 .

SYNTHESES STARTING FROM TITANIUM METAL

The procedure is identical to that of method II; in the first stage the S is bound to the Ti, and the resultant product is subsequently homogenized at high temperature. As long as the presence of sulfur is still a possibility, the temperature is raised very slowly, so that it may require as long as two days to reach 800°C in the case of S-rich compounds and 1000°C for S-poor compounds. The above temperatures are then maintained for 2-3 additional days, after which the product is tested for homogeneity by x-ray analysis.

The reaction is carried out in a quartz tube, which undergoes only slight devitrification but no further changes. Titanium metal itself begins to react with quartz at about 850°C. To exclude entirely the possibility of reaction of the titanium with the quartz in the case of the subsulfides ($TiS_{<1}$), the reaction mixture is placed in small ceramic or sintered clay crucibles (8-mm. diameter, 30 mm. long) which are then inserted in suitable quartz tubes and the tubes scaled off. This complication usually results in the necessity of using tubes of lesser wall thickness; hence, greater care must be exercised during heating.

As in other cases where tubes are to be heated to temperatures as high as 800°C, protection against explosion is recommended; this is provided by wrapping the tube in ashestos paper and inserting it into a small cage made of several layers of Ni or Cu wire mesh.

When quartz tubes are cut open with an emery wheel (1 mm. thick), it is not always possible to prevent quartz splinters from getting into the product. If the material is not a mass with a solid, glossy surface affording easy visual separation, the embedded quartz particles should always be removed by shaking with bromoform followed by centrifugation.

REDUCTION OF TiS2 WITH H2

This method permits carrying the reduction as far as the monosulfide stage, provided high temperatures are used. Since all small amounts of Cl present are removed during the reduction, the crude TiS_3 produced by method I can be used as such without further purification. The reaction is carried out in an unglazed porcelain tube, with the boat containing the material placed in the center; a stream of carefully dried H₂ freed of O₂ by contact with Pd) is passed over the boat. Two to three hours suffice for the reduction; the duration of the run depends on the quantity of material and the hydrogen flow rate. The temperature to which the tube is heated is a deciding factor for the degree of reduction (500°C \rightarrow TiS_{1,50}, 900°C \rightarrow TiS_{1,28}, 1200°C \rightarrow TiS_{1,1}). PROPERTIES:

Air stable, colored substances ($TiS_{1,5}$: black; $TiS_{1,13}$: violet; $TiS_{1,0}$: brown; $TiS_{0,5}$: gray). With decreasing sulfur content, the susceptibility to hydrochloric acid attack increases and that by solidic oxidation agents decreases. In contrast to TiS_3 , the lower sulfides are unaffected by sodium hydroxide. The sesquisulfide phase has a wide range of compositions ($TiS_{1,59}$ - $TiS_{1,19}$).

REFERENCES:

W. Biltz and P. Ehrlich. Z. anorg. allg. Chem. <u>234</u>, 97 (1937); see also N. Hahn and B. Harder. Bid. <u>288</u>, 241 (1956) (also contains information on growing of single crystals).

Zirconium Sulfides

Zirconium sulfides can be prepared by exactly parallel methods, i.e., reaction of $2rCl_4$ with H_2S or synthesis from the elements. Orange-red $2rS_8$ may be thermally decomposed to brown $2rS_3$ at 800°C. The lower zirconium sulfides include, in addition to the sesquisulfide and subsulfide phases, an additional compound $2rS_{20.75}$.

REFERENCE:

E. F. Strotzer and W. Biltz, Z. anorg. allg. Chem. <u>242</u>, 249 (1939).

Thorium Sulfides

Synthesis from the elements under pressure yields a deep red polysulfide Th_3S_4 , lilac brown ThS_2 , a sesquisulfide, and a subsulfide $ThS_{0.75}$.

REFERENCE:

E. F. Strotzer. Z. anorg. allg. Chem. 247, 415 (1941).

Titanium (III) Sulfate

Ti₂(SO₄)₂

 $\begin{array}{rl} 2 \operatorname{TiCl}_{\bullet} \rightarrow & \operatorname{Ti}_{t}(\mathrm{SO}_{\bullet})_{\bullet} \\ & 379.5 & 384.0 \end{array}$

Thanhum tetrachloride (100 g.) is carefully decomposed with approximately four times its volume of H_2O . The solution is cooled

and treated with dilute ammonia to precipitate $TiO_3 \cdot aq.$, which is suction-filtered, thoroughly washed with water, and dissolved (vigorous shaking) in 70 ml. of cone. H_2SO_4 . The solution is diluted with water to one liter, the precipitation with ammonia is repeated, and the resultant deposit is reprecipitated two additional times. The $TiO_2 \cdot aq.$ obtained (about 480 g.) is carefully dissolved in 100 ml. of cone. H_3SO_4 . yielding a total liquid volume of about 500 ml.; this is suction-filtered through glass and treated with 300 ml. of cone. H_3SO_4 , yielding about 400 ml. of a solution of Ti (IV) sulfate. This solution is reduced to Ti (III), sulfate by the following electrolytic method.

A low vertical cylinder closed off with a rubber stopper serves as the electrolysis vessel and contains the sulfate solution. The anode is a piece of Pt sheet immersed in a clay cell filled with 20% H₂SO₄. The cell is partially immersed in the Ti (IV) sulfate solution and is surrounded by four amalgamated lead strips, also immersed in the solution. The stopper on the outer electrolysis vessel has holes for the clay cell and for the inlet and outlet gas tubes. The electrolysis is carried out in a constant stream of CO_2 and with efficient water cooling. The current density is 0.06 amp./cm.² at 24 v. for the first six hours, then 0.33 amp./cm.³ at the same voltage for an additional six hours. This reduces all the Ti (IV) sulfate to Ti (III) sulfate; the latter precipitates as an H₂SO₄-containing hydrate (fine, pale light violet crystals).

To obtain the anhydrous Ti (III) sulfate, the product is suctionfiltered in a stream of CO₂, washed with 50% H₂SO₄, and placed (in the absence of air) in a round-bottom flask fitted with a ground joint and filled with CO4. Then 300 ml, of dilute sulfuric acid $(20\% v./v. H_{a}SO_{4})$ is added; the flask is stoppered with a ground stopper fitted with inlet and outlet gas tubes and an opening for the insertion of a thermometer; it is heated in a stream of CO, until the precipitate dissolves. Using gas pressure, the liquid is forced into a filtration apparatus (see Part I, p. 74) and filtered under CO_a through a tubular fritted glass filter fitted with appropriate ground joints. The receiver with the filtrate is in turn closed off with a stopper fitted with a thermometer and gas tubes; CO₂ is passed through, and the temperature is slowly raised by means of an oil bath. This concentrates the liquid to about half its volume. At this point a violet precipitate begins to form; on further beating, this turns to blue and finally, at 190-200°C, to green. The temperature is maintained at 190°C for three hours and is then raised to 210-220°C for 10 minutes. Heating to higher temperatures results in evolution of SO, and oxidation of the Ti (III) sulfate. The material is allowed to cool in a stream of CO₂; it should remain green. If it assumes a blue color, the heating procedure must be repeated. The green precipitate is filtered under COne using the filtration apparatus; the contaminating Ti (IV) sulfate

is removed by washing with conc. H_2SO_4 , followed by glacial acetic acid, anhydrous methanol and ether. The tubular fritted glass filter is removed from the filtration system, covered with a ground cap fitted with a stopcock, and placed horizontally in a short tubular electric furnace; the material is then dried for four hours at 140°C in a constant stream of pure N_{g_2} .

PROPERTIES:

Green crystalline powder. Insoluble in water, alcohol and conc. H_8SO_4 : soluble in dilute H_8SO_4 and in hydrochloric acid, yielding a violet solution.

REFERENCES:

 Schmitz-Dumont, P. Simons and G. Broja, Z. anorg. Chem. <u>258</u>, 307 (1949); W. J. de Haas and B. H. Schultz. Physica [2] <u>6</u>, 481 (1939); A. Stähler and H. Wirthwein. Ber. dtsch. chem. Ges. <u>38</u>, 2619 (1905).

Titanoxy Sulfate

TiOSO,

This compound is produced on evaporation of TiO_2 or $\text{TiO}_2 \cdot \text{aq.}$ with conc. H_2SO_4 ; the dihydrate is obtained under the same conditions but with 70% H_2SO_4 . The material, which is extremely hygroscopic and readily splits off SO_3 , can also be prepared as a white precipitate by dropwise addition of a solution of SO_3 in SO_2Cl_2 to a solution of TiCl_4 in SO_3Cl_2 , followed by refluxing [E. Hayek and W. Engelbrecht, Monatsh. Chemie <u>80</u>, 640 (1949)].

Iron-free titanoxy sulfate is usually not available commercially. When available, it is not completely water soluble. The following procedures are therefore recommended for the preparation of the pure compound.

I. TIOSO,

 $TiCL_{e} + H_{s}SO_{e} + H_{s}O = TiOSO_{e} + 4 HCl$ 189.7 98.1 18.0 160.0 145.8

Pure, multiple-distilled TiCl₄ is added in drops (vigorous stirring) to the stoichiometric quantity of 50% H_3 SO₄. The precipitate formed after each addition should dissolve completely before the next portion of TiCl₄ is added. After the addition of about 3/4 of the TiCl₄, the liquid turns into a viscous, yellowish solution. It

is diluted with 1/5 its volume of water, and the dropwise addition of TiCl₄ is completed.

The resultant solution, which is still highly concentrated in HCl, is evaporated to dryness on a water bath. The residue is pulverized, dried and freed of HCl by heating for several days at 80-100°C in a drying pistol at a pressure of a few mm.

The sulfate obtained in this manner $(TiO_2:SO_3 = 1:1.07)$ is colorless and free of HCl. it is hygroscopic and soluble in water, yielding a clear solution.

Gelatinous or resinous precipitates may appear during the evaporation of the HCl-containing, highly viscous and slightly yellow solutions; the same phenomenon may occur during the vacuum concentration operation. Addition of alcohol or acctone to the concentrated solutions leads to the formation of fibrous precipitates.

IL TIOSO + 2 H2O

 $TiCl_{4} + 2 H_{2}O = TiO_{2} + 4 HCi$ $189.7 \quad 36.0 \quad 79.9 \quad 145.8$ $TiO_{2} + H_{1}SO_{4} + H_{2}O = TiOSO_{4} \cdot 2 H_{2}O$ $79.9 \quad 98.1 \quad 18.0 \qquad 196.0$

A solution of 40 ml. (63 g.) of freshly distilled TiCl₄ (b.p. 134-338 °C) in 130 ml. of water is prepared. Most of this solution is then reduced to a slight extent by means of Zn rods or, better, by electrolysis (light-brown color), while 10 ml. kept separately is reduced to the trivalent titanium ion (deep violet color). The reduction is intended to ensure that all the iron is present in the form of Fe³⁺, to avoid hydrolysis and coprecipitation of Fe³⁺ with the Ti. The reaction is carried out in dilute oxalic acid.

The violet chloride solution is slowly added in drops to a boiling solution of 1 g. of oxalic acid in one liter of water; then the brown chloride solution is added in the same way. The mixture should be maintained at the boiling point for a total of four hours, the volume being kept constant by occasional addition of water. The conditions of precipitation must be closely adhered to, to prevent coprecipitation of unfilterable metatitanic acid. The precipitate is filtered through a large Büchner funnel, washed free of Cl with boiling water and dried by suction. It is then treated with 35 ml. of conc. H_2SO_4 in a beaker. The mixture is gently boiled until precipitation begins. After cooling and addition of 120 ml. of water, the mixture is allowed to stand (with occasional stirring) for several days and, if necessary, is filtered. It is then evaporated, precipitating crystals of TiOSO₄ \cdot H₂O.

III. TROSO, solutions

 $\begin{array}{rll} TiO_t &+& 2\,KHC_tO_t &+& H_tO &=& K_tTiO(C_tO_t)_t \cdot 2\,H_tO\\ \hline 79.9 & 256.3 & 18.0 & 354.2\\ K_tTiO(C_tO_t)_t \cdot 2\,H_tO &+& 2\,H_tSO_t &=&\\ & 354.2 & 196.2\\ & & K_tSO_t &+& TiOSO_t &+& 2\,CO_t &+& 4\,H_tO\\ & & 174.3 & 160.0 & 56.0 & 88.0 & 72.1 \end{array}$

Iron-(res titanium sulfate solutions, used as analytical standards, are readily prepared by repeated recrystallization of $K_{2}TiO(C_{2}O_{4})_{2} \cdot 2H_{2}O$ followed by treatment with conc. $H_{2}SO_{4}$.

A concentrated solution of KHC $_{2}O_{4}$ is saturated at the boiling point with freshly precipitated TiO₂ aq.; the mixture is concentrated, whereupon white needles precipitate out. The double salt is dissolved with heating in an approximately equal weight of water. The solution is filtered and the salt is recrystallized in about 50-90% yield by cooling with ice and stirring. The iron content is reduced in the process from 0.061% to 0.004%, and no further iron can be detected after another repetition of the crystallization. The analytically pure salt has a composition corresponding to $K_{2}TiO(C_{2}O_{4})_{2} \cdot 2H_{2}O$.

To prepare one litter of an approximately 0.1N Ti sulfate solution, 38 g, of the double oxalate is thoroughly mixed with 32 g. of pure $(NH_4)_3SO_4$ (iron-free!) and placed in a 750-ml. Kjeldahi flask. The addition of $(NH_4)_3SO_4$ facilitates the reaction. Then 80 ml. of pure conc. H_3SO_4 is added. The flask is heated carefully with a small flame until cessation of foaming, and the solution is then boiled on a strong flame to decompose the oxalate. The solution is cooled, whereupon it becomes sirupy; it is carefully added, with vigorous stirring, to 500 ml. of distilled water and is then diluted to one liter. If precipitation occurs after standing overnight, the solution is filtered. The solution should give a negative test for oxalate upon addition of 1 drop of 0.1N KMnO₄ to 50 ml. of the liquid.

IV. Alternate method: Pure T1OSO₄ $\cdot 2H_{3}O$ precipitates in the form of long crystal needles from a solution of T1O₂ \cdot aq. in 69-70% H₂SO₄ in which the ratio T1O₂: H₃SO₄ = 1:3 to 1:7. At higher concentrations of acid, the precipitate is powdery and contains less H₂O.

FYRONYAL:

Titanyl culfate.

PROPERTIES:

Anhydrous: highly bygroscopic; dissolves slowly in water to give a clear solution. Dihydrate: readily soluble. Decomposes in hot H_2O with precipitation of TiO₂ aq.

REFERENCES;

- I. Private communication from K. F. Jahr, Berlin.
- H. A. W. Hixson and W. W. Plechner, Ind. Eng. Chem. 25, 262 (1933).
- III. R. Rosemann and W. M. Thornton. J. Amer. Chem. Soc. <u>57</u>, 328 (1935); see also C. Péchard. Comptes Rendus Hebd. Séances Acad. Sci. <u>116</u>, 1513 (1893); A. Rosenheim and O. Schütte, Z. anorg. Chem. <u>26</u>, 239 (1901).
- IV. A. V. Pamfilov and T. A. Chudyakova. Zh. Obschey Khimii <u>19</u>, 1443 (1949).

Zirconium Sulfates

Zr(SO₄)_z · 4 H₂O

Hauser and more recently Falinski have made a thorough study of the system $ZrO_3/SO_3/H_2O$ as a function of the SO_3 concentration. It was found that the tetrahydrate is formed on addition of $ZrOCl_2 \cdot 8H_2O$ to a sulfuric acid containing less than 64% SO₃ (d 1.714). The tetrahydrate solubility is then 2%. The minimum solubility (0.3%) corresponds to 50% SO₃ in the acid (d 1.517).

If the SO₃ content exceeds 64%, acid sulfates precipitate: $Zr(SO_4)_2 \cdot H_2SO_4 \cdot 2H_2O$ at an SO₃ concentration of 64-72%, and $Zr(SO_4)_2 \cdot H_2SO_4 \cdot H_2O$ at 72-79% SO₃.

PROPERTIES:

Formula weight 355.41. Orthorhombic crystals. The basic salt precipitates slowly from neutral, saturated solution, rapidly from dilute solution or above 40°C.

In sulfuric acid solution, the Zr migrates to the anode instead of to the cathode; therefore, the tetrahydrate may actually be present in the form of a disulfate oxozirconic acid $(H_2|OZr(SO_4)_2]$. $3H_2O$.

Zr(SO₄)_z

The anhydrous salt is obtained by evaporation of the tetrahydrate or Zr oxychloride with conc. H₂SO₄. Thus, 100 g. of $ZrOCl_2 \cdot 8H_2O$ is mixed with 50 g. of conc. HaSO₄ and, after termination of the gas evolution, carefully evaporated with stirring on a sand bath. The dihydrate of the sulfate crystallizes out as an intermediate in the process, but decomposes on further heating, giving off additional H_2O . The excess H_2SO_4 is completely evaporated by heating to 350-380 °C. The product is allowed to cool in a desiccator.

PROPERTIES:

Formula weight 283.35. Microcrystalline powder. Very hygroscopic; in air, forms an unstable solution from which the normal tetrahydrate crystallizes after some time. The anhydride dissolves more rapidly in a small than in a large amount of water, since the temperature rise produced by the heat of hydration sharply accelerates the solution process.

REFERENCES:

O. Hauser. Z. anorg. allg. Chem. <u>106</u>, 1 (1919); M. Falinski. Ann. Chimie 16, 237 (1941).

Purification of Zr salts via the tetrahydrate

One volume of conc. H_2SO_4 is added to two volumes of a moderately conc. aqueous solution of Zr sulfate or chloride; the thick, white, crystalline precipitate of Zr $(SO_4)_2 \cdot 4H_3O$ is readily filtered with suction on fritted glass of medium porosity. Since 1 g. of the salt dissolves in 1 ml. of H_3O , the Zr sulfate is easily dissolved; it is reprecipitated by addition of conc. H_2SO_4 . The iron is efficiently removed during the recrystallization provided the solution contains about 10% HCl. After each precipitation, the solid is washed several times with a solution made up of 15 parts by volume of H_2O , eight parts of conc. H_2SO_4 and one part of conc. hydrochloric acid, followed by three washings with acetone. Alcohol should not be used for washing, since it forms complexes during the further precipitations.

Thus, 1135 g. of commercial $2rCl_4$ [equivalent to 1731 g. of $2r(SO_4)_2 \cdot 4H_4O$] was dissolved in 1800 ml. of H_2O and 250 ml. of conc. HCl; then 100 ml. of conc. H_3SO_4 was added, precipitating 1640 g. (94%) of $2r(SO_4)_2 \cdot 4H_2O$; five additional crystallizations of this product (under identical conditions) finally give 1212 g. of pure tetrahydrate. The following table shows the degree of partification achieved:

| Starting material | -0.1% Fe | < 0.1% Mr. Si | % <0.01% | < 0.001% | < 0.0001% | < 0,00001% |
|--------------------|-------------|------------------|----------|----------------|-----------|------------|
| A s receverallized | _ | | | Ca. Cu, Mu | | |
| | | | | Ca, Mg, Na, Si | Ag | Fe,Cu |

A residual Fe content up to 0.01% may be removed by mere recrystallization, without the addition of HCL. The Hf content of 2.7% remains unchanged.

REFERENCE:

W. S. Clabaugh and R. Gilchrist. J. Amer. Chem. Soc. 74, 2104 (1952).

Titanium, Zirconium and Hafnium Nitrides

TiN, ZrN, HfN

Titanium Nitride

A number of procedures are available. The simplest is the industrial process starting from $TiO_a + C + N_B$ described in method I. If metallic Ti is available, synthesis from the elements (method II) is recommended. Very pure nitride in rod or wire form, especially well suited for physical measurements, is obtained by vapor deposition (method III). An additional method of lesser importance consists of the reaction between $TiCl_4$ and NH_3 (method IV).

I. $2 \text{ TiO}_t + 4 \text{ C} + N_t = 2 \text{ TiN} + 4 \text{ CO}$ 159.8 48.0 28.0 123.8 112.0

The industrial process does not yield a pure product. Acetylenederived carbon black is degassed at 1200°C, mixed with TiO₂ (mole ratio 1:2), and the mixture placed in a silicon carbide or molybdenum boat; it is calcined for three hours at 1250°C in a stream of N₂. The product contains 98% nitride; the remainder is lower Ti oxides.

II. $2 \text{ Ti} + N_2 = 2 \text{ TiN}$ $95.8 \quad 28.0 \quad 123.8$

In the first stage of this preparation, the ductile metal absorbs small quantities of N_2 and thus becomes brittle; it can then be pulverized for further treatment with nitrogen.

TREATMENT WITH NITROGEN

Titanium filings ground to pinhead size and treated as described in the directions for the preparation of TiO (p. 1214) are placed in a silicon carbide or molybdenum boat and heated to 1200 °C for 3-3 hours. The operation is carried out in a hard porcelain table in a stream of pure, dry N_2 . The product has the approximate composition $TiN_{0.05}$; it is finely ground and subjected to a second altrogenation. The desired composition is attained in two to three repetitions of the procedure. The quality of the product is adversely and decisively affected by the presence of the slightest traces of O_2 or H_2O during heating.

PRESINTERING

The products prepared in the above manner are ground as finely as possible and compressed under 2000 kg./cm² into rods 3×40 or 5×40 mm. Successful molding usually requires the addition of 2-5% of metal powder. The rods are embedded in nitride powder (to prevent formation of an oxide coating) and presintered in a small tubular tungsten furnace (cf. Part I, p. 40) at about 2300°C in a stream of N₂; the small amount of free metal is converted to nitride in the process. Since the reaction is usually accompanied by considerable shrinkage of the rods and concomitant appearance of porosity, the material must be repulverized, remolded and resintered. This procedure is repeated two to four times, until the presintered rods exhibit some constancy of density.

HIGH-TEMPERATURE SINTERING

When the rods have attained sufficient strength and density in the presintering process, they are fastened with clamps in preparation for direct electrical heating. The operation is carried out in technical-grade Ar containing 12-15% N₂; the equipment used has been described by C. Agte and H. Alterthum, Z. techn. Phys. 11, 182 (1930).

The nitrides are heated to just below their melting points. At these extreme temperatures, all impurities (except some oxides and the carbides) possess higher vapor pressures than the nitrides and therefore evaporate. However, the oxides, even though their melting points are lower, are difficult to remove. The carbides, with higher melting points than the nitrides, remain unchanged.

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The technique used in the vapor deposition process is the same as that described for the proparation of the metals (Ti, Zr and Hi) from the gas phase, except that the gas used here is a TiClasaturated mixture of $H_{2+}N_{2}$ (the reaction at the glowing wire is here successful with N_{2} alone).

A gasometer is filled with a mixture of equal volumes of H_d and N_2 . The gas bubbles through a 36°C wash bottle filled with TiCl₄ (p of TiCl₄ = 17 mm.). The gas flow rate is of no importance, except that it must be low enough to achieve saturation. The optimum reaction pressure is about 30-40 mm., measured with a manometer whose mercury surface is protected by a thin film of butyl phthalate.

The reactor is a round-bottom Pyrex flask with inlet and outlet tubes for the gas fused on the sides. The arc-shaped glow wire (about 8-10 cm, long) is welded to two thick tungsten electrodes; these are sealed into a ground joint inserted through the bottom of the flask. The 0.2-mm. glow wire may be either W or Ta. Wires of Ta can be directly welded to the W rods, whereas the W wires have to be connected via a short Ni bridgepiece.

In the course of the reaction, the glow wire is heated to about 1450 °C; since the depositied TiN is itself a good electrical conductor, the current must be raised from 10 to about 22 amp, within the first 40 minutes. One serious disadvantage of the process is the fact that the temperature cannot be measured with an optical pyrometer because TiCl₃, one of the products of the fast decomposition of TiCl₄, soon coats the flask walls. One must resort, therefore, to indirect estimation of the temperature by measuring it in a blank run with gases containing no TiCl₄. The nitride deposits as a fine crystalline coating of copper to gold luster.

Alternate methods:

IV.

 $\begin{array}{ll} \text{TiCl}_{4} \div \text{NH}_{3} \rightarrow \text{TiN} \\ 189.7 & 17.0 & 61.9 \end{array}$

As we have indicated before, this process is less desirable. Chlorine-containing TiN is formed (in poor yield) on the walls of a porcelain tube in which a gaseous mixture of TiCl₄ and NH₃ is thermally decomposed at 800°C. The same result is obtained when the solid compound TiCl₄.4NH₃ is placed at the front end of the tube, evaporated in a stream of NH₃, and allowed to react at 800°C.

The TiCl₄ ammoniate is prepared by distilling the TiCl₄ into a bomb tube and covering the liquid with excess NH_3 at -60°C; the pale yellow compound is formed after shaking the sealed tube for 12 hours at room temperature.

The "crude nitride" formed at 800°C is heated in a hard porcelain tube at 1500°C for six hours in a stream of NH₃ to obtain a Cl-free product of the composition TiN.

PROPERTIES:

Bronze-colored powder. M.p. 2950°C; d 5.21. Somewhat dissociated at the melting point. Crystal structure: type B1 (NaCl type). This structure holds for a wide range of compositions (TiN₁₋₀-TiN_{0.4}). Very good electrical conductor. **Insoluble in HCl.** HNO_3 and H_2SO_4 , even on boiling; dissolves repidly in hot agus regia. Evolves NH_3 on boiling in potassium hydroxide and on heating in soda lime.

Zirconium Nitride, Hafnium Nitride

These compounds are prepared by the same methods as above.

I. The experimental arrangement is the same as for TiN, except that the reaction temperature is higher (about 1300°C). Since No begins to form a carbide at this temperature, the equipment must be made of tungsten. The products are only about 90% pure; the remainder is mainly the oxide.

II. Yellowish-brown ZrN (m.p. 2980°C) is synthesized from the elements by heating the latter for two hours at 1200°C. The corresponding temperature for HfN is 1400-1500°C.

III. The vapor deposition method: If H_3 (or $H_3 + N_3$, or NH_3) is the carrier gas for $ZrCl_4$ (or $HfCl_4$) the required wire temperatures are 2000-2400°C. With pure N_3 , the temperature must be 2900°C and the rate of deposition is considerably slower.

Nitridation of Zr wire by heating in pure N_3 produces ZrN at very low rates and in a very loose and brittle form, even if the temperature is almost at the melting point of the metal (1860°C).

REFERENCES:

L

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 - I. E. Friederich and L. Sittig. Z. anorg. allg. Chem. 143, 293 (1925).
- II. P. Ehrlich. Z. anorg. Chem. <u>259</u>, 1 (1949); G. L. Humphrey. J. Amer. Chem. Soc. <u>75</u>, 2806 (1953).
- III. A. E. van Arkel and J. H. deBoer. Z. anorg. allg. Chem. <u>148</u>, 345 (1925); F. H. Pollard and P. Woodward, J. Chem. Soc. (London) <u>1948</u>, 1709; Trans. Faraday Soc. <u>46</u>, 190 (1950);
 F. H. Pollard and G. W. A. Fowles. J. Chem. Soc. (London) <u>1952</u>, 2444.
- IV. A. Brager, Acta Physiochim, URSS <u>11</u>, 617 (1939); see also O. Ruff and F. Eisner, Ber. dtsch. chem. Ges. <u>41</u>, 2250 (1908); <u>42</u>, 900 (1909).

Thorium Nitride

Th₁N₄

 $3 \text{ Th} + 2 \text{ N}_2 = \text{Th}_2 \text{N}_4$ 696.4 50.0 752.4

Thorison nitride is usually prepared by heating Th filings in a stream of dry, pure N_2 . The reaction is complete in three

hours at 800°C. The presence of oxide in the metal is detrimental (products lower in N are formed).

a)
$$3 \text{ ThCl}_1 + 2 N_2 + 6 H_2 = Th_3 N_4 + 12 \text{ HCl}$$

ll 2.2 5.6 1.2 75.2 43.8

Since Th₃N₄ is not an electrical conductor, the method of vapor deposition (used in the preparation of pure TiN and ZrN) gives poorer results. Thus, solid ThCl₄ is made to react with N₂ + H₂ in a flask maintained at 800°C. The tungsten glow wire is at < 1000°C. The yield is poor.

b)
$$3 \operatorname{ThO}_{2} + 6 \operatorname{C} + 2 \operatorname{N}_{2} = \operatorname{Th}_{3} \operatorname{N}_{4} + 6 \operatorname{CO}_{792.4}$$

792.4 72.1 56.0 752.4 168.1

A sintered tungsten rod containing $ThO_3 + graphite$ is calcined above 2000°C in a N₂-containing atmosphere; black Th₃N₄ crystals and lighter, oxide-containing products are formed.

PROPERTIES:

Dark-brown, almost black powder. Stable in dry air; readily soluble in acids.

REFERENCES:

- I. B. Neumann, C. Kröger and H. Haebler. Z. anorg. allg. Chem. 207, 145 (1932).
- H. W. Düsing and M. Hüniger. Techn. Wissenschaftl. Abhdig. Osram 2, 357 (1931).

Titanium Tetranitrate

Ti(NO₁).

I. $T_iCl_4 + 4N_4O_5 = T_i(NO_5)_4 + 4NO_5Cl_{169.7} + 432.0 + 296.0 + 325.7$

A solution of 3 ml. (5.1 g.) of TiCl₄ in 10 ml. of CCl₄ is cooled with Dry Ice in a two-neck flask provided with a dropping funnel and a reflux condenser which is protected with a P_2O_5 tube. A solution of 11.6 g, of N_2O_5 in 25 ml. of CCl₄ is then added dropwise. A yellow, flocculent precipitate forms as soon as the CCl₄ melts (-23°C), that is, after removal of the coolant. As the temperature

rises from -23° C to room temperature, the precipitate dissolves with evolution of a gas. If too violent, the bubbling may be slowed down by cooling. Solution of the last fraction of the precipitate is accelerated by mild heating. The volatile components (NO₂Cl and CCl₄) are removed by vacuum distillation, leaving a residue of the white Ti(NO₃)₄, which may be purified by sublimation in high vacuum at 50°C. Part of the product decomposes in the process into N₂O₅ and nonvolatile TiO(NO₃)₂.

| IL. | TiCh H | + 4 CINO ₃ = | Ti(NO _a), + | 4 Ci ₁ |
|-----|--------|-------------------------|-------------------------|-------------------|
| _ | 189.7 | 389.9 | 296.0 | 283.6 |

A large excess of ClNO₃ is condensed at liquid nitrogen temperature onto the surface of 2-3 ml. of TiCl₄, frozen in a cold trap at high vacuum. The trap is connected to a surge vessel and the temperature is raised to -80° C. The reaction, which is accompanied by evolution of chlorine, is complete after a few hours. The volatile components (Cl₃ and excess ClNO₃) are then distilled off in vacuum at room temperature. The Ti(NO₃)₄ residue, in the form of a crystal cake, may be further purified by sublimation at 50°C.

PROPERTES:

After sublimation slightly above the melting point, white needles. M.p. 58,5°C. Decomposes at about 100°C.

REFERENCES:

- I. M. Schmeisser. Angew. Chem. <u>67</u>, 493 (1955); D. Lützow, Thesis, Univ. of Munich, 1955.
- II. W. Fink. Thesis, Univ. of Munich, 1956.

Thorium Nitrate

Th(NO₁)₄ · pH₁O

RECOVERY OF THORIUM SALTS FROM MONAZITE

The mechanical ore-dressing process yields a monazite sand concentrate consisting of a mixture of Th silicate, rare earth phosphates. SiO_2 and usually 4-5% ThO_2 . The material is calcined, finely ground and dissolved by prolonged digestion with conc. H₂SO₄ at 210°C. After cooling, the pasty mass is dissolved in fice water and the undissolved material is filtered off. Further treatment may proceed via the following methods.

I. In this method, Th is quantitatively precipitated as the phosphate, together with a small amount of rare earth phosphates; this is accomplished by neutralization and dilution of the solution. The phosphates are dissolved in cone, hydrochloric acid and precipitated with oxalic acid, and the thoroughly washed precipitate is extracted with warm aqueous Na_3CO_3 . Most of the rare earths stay in the residue, while the thorium dissolves in the form of a carbonate complex, $Na_6Th(CO_3)_5$. The material is freed of the remaining traces of rare earths by repeated crystallization in the form of the sulfate $Th(SO_4)_2 \cdot 8H_3O$. The procedure consists of precipitation of the hydroxide with ammonia and solution of the latter in sulfuric acid to re-form the sulfate. The precipitate from the last purification stage is dissolved in nitric acid to yield the nitrate.

[In an older process, the Th and the rare earths are coprecipitated as oxalates from the initial acidic solution. The Th is extracted as the carbonatothorate by treatment with aqueous Na_2CO_3 solution.]

II. A good yield of ThO₂ may be obtained in another process used primarily for production of the rare earths. The filtered sulfate extract is treated with Na₂SO₄ to precipitate the cerium earths (as double sulfates); the corresponding Th salt Na₂SO₄. Th(SO₄)₂. $6H_3O$ remains in solution. The mixture is filtered and the filtrate is heated to 90°C; it is treated with oxalic acid, yielding a precipitate consisting chiefly of Th oxalate.

Further treatment is the same as in method L.

III. PURIFICATION OF THORIUM NITRATE

Very pure NH_4NO_3 is added to a solution of the crude nitrate; the result is the double nitrate $Th(NO_3)_4 \cdot NH_4NO_3 \cdot 8H_2O$. The product is further purified by dissolving in triple-distilled water, adding redistilled nitric acid, and concentrating in a Pt dish on an electrically heated water bath until crystallization begins. The solution is then cooled with ice and constantly stirred; the resultant crystals are centrifuged off and redissolved. The procedure is repeated five times, yielding about 50% of the initial. Th as the double nitrate.

The product is dissolved in very pure water, filtered and precipitated as the oxalate by addition of a nitric acid solution of purified oxalic acid; the precipitate is suction-filtered, washed with alcohol, and dried. The resultant Th oxalate may be calcined immediately to the oxide, or it may be reconverted to the nitrate. by dissolving in conc. nitric acid. No. No. of Street, Stre

W. PREPARATION OF THE HYDRATES

Depending on the conditions of preparation, $Th(NO_3)_4$ crystallizes from solutions of thorium hydroxide (or from HNO₃ solutions of moderately calcined oxide) with varying contents of water of crystallization. When a not too acid solution is concentrated by evaporation, $Th(NO_3)_4$ crystallizes in the cold with 12 moles of H₂O. A solution evaporated at 15°C yields the pentahydrate, which is stable to 80°C if heated in an atmosphere free of CO₂. At higher temperatures, it converts to the trihydrate, and between 125 and 150°C, to the hemihydrate. Above 150°C the remaining water is split off, together with nitrogen oxides.

V. PREPARATION OF THE ANHYDRIDE

Anhydrous Th(NO₃)₄ is prepared by treatment of the lower bydrates of Th with N₂O₅ condensed at -78°C.

PROPERTIES:

Formula weights: Th(NO₃)₄ 480.15; Th(NO₃)₄.5H₂O 570.23. Very readily soluble in H₃O and alcohol. Due to hydrolysis, the aqueous solution becomes acid and slowly precipitates a basic sait. The commercial product usually contains about four moles of H₃O; it usually also contains some sulfate. Combines very readily with alkali and alkaline earth nitrates to yield double nitrates (very beautiful crystals). The alkali salts corresponding to the formula Alk₂[Tb(NO₃)₆] crystallize in anhydrous form, and the corresponding alkaline earth compounds with eight moles of H₂O. Watercontaining alkali thorates Alk[Th(NO₃)₅] have also been described.

REFERENCES:

- L D. W. Pearce, R. A. Hansen and J. C. Butler in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 38; see also H. and W. Biltz. Ubungsbeispiele aus der unorganischen Experimentalchemis (Laboratory Problems in Experimental Inorganic Chemistry), Leipzig, 1920, p. 226; and L. Vanino. Handbuch der Präparativen Chemie (Handbook of Preparative Chemistry), Vol. I (Inorg. Part), Stuttgart, 1925, p. 759.
- I. E. S. Pilkington and A. W. Wylie. J. Soc. Chem. Ind. <u>66</u>, 387 (1947); this article also lists additional references on the subject.
- III. O. Hönigschmid and S. Horovitz, Sitz.-Ber. Akad. Wissensch. Wien Ha, 120, No. 3 (1916); see also E. H. Archibald. The Preparation of Pure Inorganic Substances, New York, 1932, p. 193.

- IV. E. Chauvenet and Souteyrand-Franck. Bull. Soc. Chim. France [4] 47, 1128 (1930).
 - V. P. Miscialeti. Gazz. Chim. Ital. <u>60</u>, 882 (1930); see also J. R. Ferraro, L. J. Katzin and G. Gibson, J. Amer. Chem. Soc. <u>77</u>, 327 (1955).

Titanium Oxonitrate, Zirconium Oxonitrate

TiO(NO₄)_t, ZrO(NO₄)_t

 $\begin{array}{rcl} {\rm Til}_4[{\rm ZrI}_4] &+ 4\,{\rm N}_2{\rm O}_4 &= {\rm Ti}({\rm NO}_3)_4[{\rm Zr}({\rm NO}_3)_4] &+ 4\,{\rm NO} \,+\, 2\,{\rm I}_2 \\ &\\ 555.6 & 598.9 & 295.9 & 339.3 \\ {\rm Ti}({\rm NO}_3)_4[{\rm Zr}({\rm NO}_3)_4] &= {\rm TiO}({\rm NO}_3)_2[{\rm ZrO}({\rm NO}_3)_2] \,+\, 2\,{\rm NO}_2 \,+\, 1/2\,{\rm O}_2 \\ &\\ 295.9 & 339.3 & 187.9 & 855.3 \end{array}$

A suspension of TiI_4 or ZrI_4 in anhydrous CCI_4 is placed in a three-neck flask and agitated with a magnetic stirrer. Dry dinitrogen tetroxide is then bubbled through; the excess gas and the NC formed in the reaction are allowed to escape through a P_3O_5 tube. On contact with the gas, the liquid assumes a deep violet color due to liberation of iodine. After about one hour, the product is suction-filtered through a sintered glass plate; this operation is carried out in a dry box in flowing nitrogen (see Part 1, p. 71). The product is then washed with anhydrous CCI_4 and the solvent removed in vacuum.

PROPERTIES:

The almost white, powdery oxonitrates are hygroscopic; on heating, they are converted to the dioxides without melting. Soluble in alcohol, insoluble in benzene and CCl₄.

REFERENCE:

V. Gutmann and H. Tannenberger, Monatsh. Chem. 87, 424 (1956).

Titanium Phosphide, Zirconium Phosphides, Thorium Phosphide

TiP, ZrP,, ZrP, Th,P4

Titanium Phosphide

I. The process recommended for the preparation of titanium phose phides is the pressure synthesis from the elements in the "Faradavil

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apparatus (see Part I, p. 76).

Biltz et al. give the following procedure: 2 g. of Ti filings ground to pinhead size (for their preparation see the directions given for the lower titanium oxides, p. 1214) and 4 g. of red P are weighed into a small ceramic or sintered clay cylindrical crucible. The materials are degassed by fanning with a flame in high vacuum and are then sealed (invacuum) into a quartz pressure tube. The colder half of the tube is heated to 450°C, while the Ti side is maintained at 950°C. Two three-day periods are needed for the reaction. After the first period, the tube is slowly cooled for 3-4 hours, and the unreacted P is thus distilled into the cooler section. The product is readily ground in an agate mortar, an indication that the ductile Ti metal has reacted. The grinding is carried out under CS2, which is then removed with alcohol and by drying in vacuum over NaOH at 120-140°C. Microscopic examination of the dark-gray metallic product should show no red phosphorus. The phosphorus quantity used for the second reaction stage should again correspond to an atomic ratio of 3 P:1 Ti. The product treatment after the second three-day heating period is the same as that after the first. The resultant phosphide does not correspond completely to the formula TiP (maximum composition is $TiP_{0.92}$).

П.

$$TiCl_4 + PH_3 \rightarrow TiP$$

189.7 34.0 78.9

The method of Gewecke starts from phosphine generated from yellow P and KOH; the gas is washed with conc. hydrochloric acid to remove spontaneously igniting phosphorus hydrides, followed by NaOH. It is dried in two U tubes filled with $CaCl_2$ pieces (broken up from a solidified melt of the salt) and two P_2O_5 tubes. The gas enters the reaction apparatus proper through a trap (-250°C) designed in such a way that any gaseous TiCl₄ backing up during the reaction will condense out. The PH₃ train is conmected to the reactor via a ground joint, with a two-way stopcock (for venting) inserted in the line.

The reactor consists of a a spherical TiCl₄ vessel followed by a heating tube 40 cm. long. Both the vessel and the tube are Vycor. The gases then flow into an ordinary glass receiving flask for TiCl₄ and absorption tubes for PH_3 (one contains aqueous CuSO₄ and the other copper wire mesh).

The system is first filled with H_p . The reaction tube is heated to 750°C and the PH_3 generator is started (this requires 3-4 hears). The TiCl₄, which is kept cold up to this time, is now heated.

The chloride vapor reacts with the phosphine in the hot reaction tube (reaction time: about three hours). As in the preparation of TiS_2 from $TiCl_4$ and H_2S , the $TiCl_4$ may be cycled back and forth through the tube. The titanium phosphide product is a light-gray, high-polish mirror deposited on the tube walls. However, the product is not free of the chloride even after treatment at $350^{\circ}C$ in high vacuum. Preparations with maximum phosphorus content correspond to $TiP_{0.95}$; the yield is modest.

PROPERTIES:

Black-gray powder with a metallic appearance; attacked only slightly by acids even when heated; thermally very stable; it is assumed that a subphosphide exists, d 3.94.

REFERENCES:

W. Biltz, A. Rink and F. Wiechmann. Z. anorg. allg. Chem. 238, 395 (1938); I. Gewecke. Liebigs Ann. 361, 70 (1908); for data on the system TiCl₄/PH₃, see R. Höltje, Z. anorg. allg. Chem. 190, 246 (1930).

Zirconium Phosphides

The pressure synthesis used for TiP is also employed in the preparation of compounds of the Zr/P system. First stage: treatment in a Faraday tube for 50 hours at a 1000/500°C gradient; atomic ratio 1 Zr:4 P. Second stage: aftertreatment in a quartz pressure tube (wall thickness 4 mm., I.D. 12 mm.) for 50 hours at 800°C. The product is black-gray ZrP_2 ; this may be degraded to ZrP in high vacuum at 820°C. If the desired composition does not exceed $ZrP_{\leq 1}$, the second stage merely increases the homogeneity of the product. Since vapor pressure then ceases to be a factor, ordinary quartz tubes may be used.

The diphosphide ZrP_2 may also be prepared via method II for TiP.

REFERENCE:

E. F. Strotzer and W. Biltz. Z. anorg. alig. Chem. 239, 216 (1988).

Thorium Phosphide

One heating cycle in the Faraday apparatus suffices to prepare Th₃P₄ (a subphosphide ThP _{c-s} also exists). The reactants are heated for 60 hours in a furnace with a 940/450°C gradient **atomic ratio** of Th:P = 1:3). The absorptivity of Th for x-rays is very high, and therefore minute quantities of surface oxide interfere in the x-ray pattern analysis. Therefore, for precision work (particularly when the product is a lower phosphide) an empty cylindrical crucible is first heated for one hour (under high vacuum) in the rear section of the tubular quartz reactor, while the small quarts flask with the raw material at the front end of the reactor remains cold. After cooling of the rear section (in high vacuum), the raw material is transferred to the crucible and the reactor tube is sealed off.

REFERENCE:

E. F. Strotzer and W. Biltz. Z. anorg. allg. Chem. 238, 69 (1938).

Zirconium and Hafnium Phosphates

No unequivocal characterization exists for the phosphates precipitated from Zr salt solutions. The orthophosphate is formulated as either $Zr(HPO_4)_2$ or $ZrO(H_2PO_4)_2$; on prolonged heating above 700°C, it converts to ZrP_3O_7 .

L $ZrOCl_{2} \cdot 8 H_{2}O \rightarrow ZrO(H_{2}PO_{4})_{2} \rightarrow ZrP_{2}O_{7}$ 322.3 801.2 265.2

First, $ZrOCl_2 \cdot 8H_2O$ (2 g.) is dissolved in 1.5 liters of 6N HCl, and then a solution of 2 g. of Na_2HPO_4 in 1.5 liters of 6N HCl is added in drops. The finely divided precipitate is washed by repeated decantation with 6N HCl, filtered and dried at 80°C. The product corresponds to $ZrO(H_2PO_4)_2$.

The hafnium analogue, $HfO(H_2PO_4)_2$, is prepared in exactly the same manner; it is less soluble than the Zr sait.

II. Alternate method: Solutions of Zr sulfate $(2-5\% \text{ ZrO}_3)$ and 2.5% H₃PO₄ in 2N sulfuric acid are added simultaneously in drops to 2N H₂SO₄ at 70-75°C.

PROPERTIES:

Sparingly soluble in conc. mineral acids, except hydrofluoric acid; when freshly precipitated, soluble (with formation of a complex) in a mixture of H_3PO_4 , oxaile acid and cone. H_3SO_4 . An acidsoluble, white peroxy compound is formed when a cold suspension of the phosphate is reacted with an NaOH-Na₂O₂ solution and then digested at 70°C. ZrP_2O_7 crystallizes in the cubic K 6₁ lattice.

REFERENCES:

- I. G. Hevesy and K. Kimura. Angew. Chem. <u>38</u>, 775 (1925); J. Amer. Chem. Soc. <u>47</u>, 2540 (1925); see also J. H. de Boer, Z. anorg. allg. Chem. <u>144</u>, 193 (1925).
- II. E. M. Larsen, W. C. Fernelius and L. L. Quill, Analyt. Chem. 15, 512 (1943).

Titanium, Zirconium and Hafnium Carbides

TiC, ZrC, HfC

Titonium Carbide

Methods I to III, given in detail for the preparation of TiN, are also useful for synthesis of carbides. These are: I) the industrial process $TiO_2 + C$; II) synthesis from the elements; and III) vapor deposition. The last process may be modified by first depositing the metal from a vapor and then converting the deposit (on a glow wire) to the carbide by heating in a hydrocarbon atmosphere (method IV), or by using a glowing carbon wire in an atmosphere of TiCl₄ vapor (method V).

I,

 $T_iO_2 + 3C = T_iC + 2CO$ 79.9 36.0 59.9 56.0

In the method of Agte and Moers, a mixture of pure TiO₂ and acetylene-derived carbon black (the latter degassed at 2000°C) is placed in a graphite boat and heated for half an hour in a tubular graphite furnace to 1700-1800°C. Very pure and dry H_2 is used to flush the apparatus. Since the hydrogen reacts with the bot graphite tube to form hydrocarbons, the carbon content of the raw material mixture should be 15-25% less than the stoichiometric ratio. The products usually still contain some oxygen.

If the $TIO_2 + 3C$ mixture is heated very rapidly (within 20 minutes) to 1900°C in a stream of H₂ or CO, a product containing 19.5% C may be obtained (as demonstrated by Meyerson); further heating reduces the carbon content to 17%, because of decarbonization.

PRESINTERING

The carbide rods, made of powder compressed at 2000 kg./cm², are heated in a graphite boat inside a tubular graphite furnace to temperatures between 2500 and 3000°C and maintained at these temperatures for about 15 minutes. The material is protected against surface absorption of additional carbon by embedding the rods in carbide powder. Due to considerable shrinkage of the rods, the processes of repulverization, recompression and resintering must be repeated >-4 times.

HIGH-TEMPERATURE SINTERING

Since the carbides decompose in vacuum, the high-temperature sintering must be carried out in an atmosphere of technicalgrade argon. The rods are heated to extremely high temperaturesjust short of the melting point (for a description of this procedure, see TiN, p. 1234). Most of the impurities evaporate at these temperatures, leaving a relatively pure product.

I, $T_i + C = T_iC$ 47.9 19.0 59.9

Titantum filings are mixed in the stoichiometric ratio with acetylene-derived carbon black (very thoroughly degassed at 2000°C), and the reaction is started by heating to 1800°C in a BeO boat placed inside a high-vacuum furnace (see Part I, p. 40 for description). The beryllium oxide boats are set up inside the heating element, which consists of tungsten boats (40 mm. long, 10 mm. wide, 8 mm. high) subjected to high-intensity (200 amp.) low-voltage current. The final sintering of the finaly powdered crude product requires 10 minutes at 2400°C.

III. In this process a tungsten wire, which serves only as a substratum for the deposit, is heated to glowing in an atmosphere consisting of a volatile halide of the metal, a carbon compound and H_{a} . Mores recommends the use of hydrocarbons such as toluene, instead of CO; the deposition of free carbon with the carbide is avoided if the partial pressure of the hydrocarbon in the system is low. The hydrogen atmosphere facilitates considerably the reaction at the glow wire by reducing the decomposition temperatures of the halides to a much greater extent than does reduced pressure or even vacuum.

TiCl. + CH. $\stackrel{(+ H_3)}{=}$ TiC + 4 HCl 189.7 16.0 59.9 145.8

A pure hydrogen stream (which must be free of N_2 and O_3 and is therefore most conveniently generated by electrolysis) is divided into two fractions, one of which is passed through a 25°C wash bottle filled with TiCl₄, the other through a similar bottle containing tokens at -15°C; the streams are then recombined and introduced into the reactor. The glow wire is maintained at a temperature of 1600°C, which is kept constant during the experiment by gradually increasing the current. Further details are given by K. Moers.

Alternate methods;

IV. A modification of the method just described consists in heating the metal wire prepared by the vapor deposition process in a hydrocarbon atmosphere. This modification is not, however, very convenient in the case of the lower-melting metals (Ti, Zr) since the wire temperatures must be relatively low and thus very long glow times are required. It may be used successfully with W. Ta and Hf.

V. Another method of avoiding introduction of the tungsten wire (which is used as a substratum in all previously described vapor deposition processes) into the product reverses the above procedure; i.e., a carbon wire is heated to incandescence in the vapor of a volatile halide of the metal (in the presence or in the absence of $H_{\rm p}$).

The method suffers from one disadvantage: the dissociation of the chlorides at the glow wire does not cease when all the carbon originally present in the wire has been consumed. As a result, the products contain varying amounts of the free metal dissolved in the carbide. Carbides of stoichiometric composition are obtained either by calcining the above products in high vacuum (to evaporate the dissolved metal) or in a hydrocarbon atmosphere (to convert the excess metal to carbide). Further details are given in the reference cited below.

PROPERTIES:

Gray powder. Insoluble in hydrochloric acid, soluble in nitric acid. M.p. 3410° C; d 4.92. Very good electrical conductor with a positive temperature coefficient. Crystal structure: type B1 (NaCl type), with a considerable range of phase compositions (TiC₁₀-Ti_{0.3}).

Zirconium Carbide and Hafnium Carbide

These compounds are prepared by the same procedures as titanium carbide. The reaction mixture consists of either ZrO_2 (or HfO_2) + 3 C, or Zr (or Hf) + C; the reaction temperatures Heabove 2000°C. Since both ZrC and HfC are very sensitive to N_{24} the high-temperature sintering stage must be carried out in 99% Ar.

Just like TiC, both ZrC and HfC dissolve carbon when molten. This phenomenon is most detrimental in the case of ZrC, whose melting point is lowered from 3500°C to about 2450°C by the absorption of carbon; the carbon is released on cooling.

The procedures employed for the preparation of TiC by the vapor deposition process must be modified somewhat in the case of ZrC and HfC, since both ZrCl₄ and HfCl₄ are solids. The

• 'r

reactor is filled with a sufficient quantity of the chloride and its lower section is heated with a small furnace to a temperature at which the vapor pressure is about 10-20 mm. (that is, to about 300° C). The same applies in method V.

The industrial preparation of ZrC from ZrSiO₄ and carbon in a graphite crucible using an arc furnace is described by W. Kroll et al. [Trans. Electrochem. Soc. <u>89</u>, 263, 317 (1946); <u>92</u>, 187 (1947); J. Electrochem. Soc. <u>94</u>, 1 (1948)].

REFERENCES:

- General: C. Agte and K. Moers, Z. anorg. allg. Chem. <u>198</u>, 233 (1933).
- G. A. Meyerson and Y. M. Lipkes. Zh. Prikl. Khimii <u>18</u>, 24, 251 (1945); see also E. Friederich and L. Sittig. Z. anorg. allg. Chem. <u>144</u>, 169 (1925).
- II. P. Ehrlich. Z. anorg. Chem. 259, 1 (1949).
- III and IV. A. E. van Arkel and J. H. de Boer. Z. anorg. alig. Chem. 148, 345 (1925).
- V. W. G. Burgers and J. C. Basart. Z. anorg. allg. Chem. 216, 209 (1934).

Thorium Carbides

ThC, ThC₂

| ThO ₂ | + 3C = | ThC + | · 2 CO; | ThO ₂ | +4C = | ThC ₂ + | 2 CO |
|------------------|--------|-------|---------|------------------|-------|--------------------|------|
| 264.L | 36.0 | 244.1 | 56.0 | 264.1 | 48.0 | 256.1 | 56,0 |

Thorium carbides are prepared in an electric arc furnace. The arc is produced in a graphite crucible containing the reaction mixture. About 200 amp, at 110 v. is required to melt the mixture.

A mixture of ThO₂ and calcined carbon black (0.24% ash) or graphite powder (0.33% ash), in quantities corresponding to the above equations, is made into a paste with a small amount of water and starch, and evaporated with stirring (graphite is preferred to carbon black because of its smaller volume). The lumps of dried material are placed in a crucible by means of a porceisin spatula; their large size prevents them from being carried out of the crucible by the CO gas evolved in the process.

PROPERTIES:

The z Opaque. dark-yellow pseudotetragonal crystals with a metallic inster. M.p. 2650°C; d 8.96. Completely miscible with

ThC at high temperature, practically immiscible at room temperature. Forms a sutsettic with graphite (empirical formula $ThC_{2.6}$, m.p. 2500°C). Decomposes slowly in water, rapidly in dilute acids, evolving a mixture of hydrocarbons (chiefly acetylene) and H₂.

ThC: M.p. 2620°C. Crystal structure: NaCl type. For material of empirical formula $ThC_{0.39}$, the miscibility gap begins at a temperature of 1980°C; the gap widens at room temperature to $ThC_{0.05}$ -ThC_{0.79}.

REFERENCES:

M. von Stackelberg, Z. phys. Chem. (B) <u>9</u>, 437 (1930); H. A. Wilhelm and P. Chictti. Trans. Amer. Soc. Metals <u>42</u>, 1295 (1950).

Titanium, Zirconium and Thorium Silicides

TiSir, ZrSiz, ThSir

1. PREPARATION FROM THE ELEMENTS

 $Ti (Zr, Th) + 2Si = TiSi_2 (ZrSi_2, ThSi_2)$ 47.9 91.2 232.1 58.1 104.0 147.3 288.2

The silicides are prepared by fusing or sintering intimate stoichiometric mixtures of the elements (in powder form). The reaction is carried out in sintered clay or ceramic crucibles, placed in a Tammann furnace under a blanket of Ar. In all three cases the reaction takes place at a relatively low temperature and is highly exothermic; therefore, one should work with gram quantitles only.

In the method of Alexander, some advantage is gained by replacing the pure metals with hydride powders. Initial heating takes place in vacuum, which at 400-500 °C is replaced by an atmosphere of the H₂ evolved by the reaction itself. This gives a sintered silicide at temperatures as low as 900 °C.

Brauer and Mitius modified a method developed by Hönigschmid and prepare ThSi₂ by the following procedure. Intimate mixtures of AI, Th and Silumin (13% Si, 87% Al) powders are compressed into tablets 10 mm. long and 5 mm. thick, placed in alumina crucibles and fused at 1100°C in high vacuum. Slow cooling (from 1100°C to 800°C in four hours) produces good crystals of the product within the aluminum ingot. These are freed of excess Al by alternate treatments with dilute hydrochloric acid and potassium hydroxide (moderate heating), followed by washing with water and aloohol. Since most of the silicide particles form cohesive gramles with the Si and SiO₂ contaminants, the crystallites are paiverised in an agate mortar and separated from foreign matter particularly SiO₂, which cannot be removed by chemical means) by flotation with bromoform (d 2.9). The bromoform must be continuously renewed. Evaporation with hydrofluoric acid is not practical, since it destroys the silicide.

Alternate methods:

II. ALUMINOTHERMIC METHOD

Ignition of a mixture of, for example, 200 g, of Al powder, 250 g, of S. 180 g, of SiO₂ and 15 g, of TiO₂ (or 40 g, of K_3TiF_6), covered with a thin layer of Mg, yields an ingot containing, in addition to Si and Al, small, iron-gray tetragonal pyramids of TiSi₂.

III. ELECTROLYTIC PREPARATION

The pure, crystalline silicides are obtained by meltelectrolysis of a mixture of, for example, $10 \text{ K}_2 \text{SiF}_8 + \text{TiO}_2$ at about 900°C , using an iron cathode; alternately, electrolysis of TiO₂ dissolved in a melt of silicate may be used.

IV. REACTION OF THE METAL WITH SILICON TETRACHLORIDE

The silicides are obtained in the form of a coating on the reactor walls when the metals are heated to 1100-1500°C in a hydrogen stream saturated with SiCl₄.

PROPERTIES:

Grayish-white crystals with a metallic luster and good thermal and electrical conductivity. d $(TiSi_2)$ 4.02; $(ZrSi_2)$ 4.88; $(ThSi_2)$ 7.63. TiSi₂ and ZrSi₂ are insoluble in mineral acids (except hydrofluoric acid); ZrSi₂ is also insoluble in 10% KOH. TiSi₂ dissolves slowly in 10% KOH. ThSi₂ is unaffected by alkali, but dissolves in different and conc. hydrogen halides (slowly in the cold and rapidly when heated). Attacked by Cl₂ at temperatures as low as 500°C. TiSi₂ is stable at red heat in air, while ZrSi₂ and ThSi₂ burn.

REFERENCES:

I. O. Hönigschmid, Monatsh. Chemie 28, 1017 (1907); P. P. Alexander. Metals and Alloys 9, 179 (1938); F. Laves and H. J. Wallbaum. Z. Kristallogr. 101, 78 (1939); G. Brauer and A. Mittue. Z. anorg. alig. Chem. 249, 325 (1942); E. L. Jacobson, R. D. Freeman, A. G. Tharp and A. E. Searcy. J. Amer. Chem. Soc. 78, 4850 (1956); see also H. J. Wallbaum. Z. Metallkunde 23, 376 (1941).

- II. O. Hönigschmid. Comptes Rendus Hebd. Séances Acad. Sol. <u>142</u>, 157, 280 (1906); Monatsh. Chem. <u>27</u>, 205, 1069 (1906).
- III. M. Dodero. Comptes Rendus Hebd, Séances Acad. Sol. 208, 799 (1939); J. L. Andrieux, Congr. Chim. Industr. Nancy 14 I, 124 (1938); Rev. Métailurgie 45, 49 (1948).

SECTION 23

Vanadium, Niobium, Tantalum

G. BRAUER

Vanadium

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The preparation of high-purity V metal is difficult because it tends to form very stable occluded phases with nonmetals, particularly with O, N and C. These elements must be removed in advance, because their elimination from the metal phase at a later stage is difficult. Hence only a few of the many proposed methods afford a ductile metal or V powder of a high degree of purity.

I. $V_2O_3 + 5C_2 = 2V + 5C_2O_1$ 181.9 200.4 101.9 280.4

In the method of Marden and Rich, 175 g. of V_2O_5 is mixed with 300 g. of ground Ca and 300 g. of CaCl₂ (dehydrated by preheating at 450°C), and the mixture placed in a small sealable iron bomb. The addition of CaCl₂ as fluxing agent is essential. A small piece of Na or K is also added (to act later as a scavenger for residual O_2 and H_2O), or the bomb is evacuated and then filled with Ar. The bomb is tightly sealed either by screwing down the lid or by welding, heated one hour at 900-950°C, cooled to room temperature and then reopened. The product is chipped out with a chisel, and the chunks are added, slowly and with agitation, to about 20 liters of cold water (avoid local overheating). The product disintegrates and is allowed to settle for about 2 min. The supernatant is decanted; the solid is washed (by decantation) several times with H_2O , then several times with approximately 2 N HCl. The product is ductile, granular V inetal.

According to McKechnie and Seybolt, the reaction between V_2O_5 and Ca is coupled to advantage with the strongly exothermic reaction $Ca + I_2 = Cai_2$. In this case, CaI_2 has the desirable effect of reducing the melting point of the mixture, thus replacing the CaCi₂ used in the previous method.

For example, a mixture of 300 g, of specially purified V_2O_5 (see below), 552 g, of metallic Ca (i.e., about 60% excess) and 150 g, of

 I_2 is placed in a sintered magnesia crucible, which is in turn placed in a 1.5-liter steel bomb; the bomb is then hermetically sealed. With the above quantities, the steel bomb should have a diameter of 100 mm., a height of 280 mm. and a 10-mm.-thick wall; the ltd should be a steel plate held between bolted-down flanges. The magnesia crucible can be closed with a cover of the same material (the cover is formed by pressure-shaping granular magnesia with a steel cover). The bomb is evacuated, filled with Ar, closed and heated to about 425°C to start the reaction. Immediately after ignition, spontaneous heating to a much higher temperature takes place, accompanied by an unusual noise. Granular and powdered V is isolated from the reaction product in 74% yield.

The V_2O_5 , which is normally prepared from NH 4VO₅, must be freed before use of small amounts of N and H still adhering to it. One method of accomplishing this is heating the oxide for 18 hours in a stream of moist O_2 at 400°C.

II. The following reduction affords V as a fine powder:

$$VCl_s + 1\frac{1}{2}H_t = V + 3HCl_{157.3} + 3.81. 51.0 + 109.4$$

A stream of H_2 , thoroughly freed of traces of O_3 , N_3 or H_3O (see p. 112 ff., N_2 removal as for Ar, p. 82 ff.), is passed over a platinum boat located in a Pt tube and containing about 7 g. of VCl₃. The Pt tube forms an insert for a porcelain tube and protects the latter from attack by the subliming VCl₃ and by the V formed from such a sublimate; it also ensures the protection of the boat contents from contamination by Si compounds from the porcelain tube. The V formed during the reaction is further protected against contamination by placing a porcelain boat containing powdered V ahead of the Pt boat. This protective vanadium (which may be less pure) serves to remove the last traces of N₃ and O₂ from the gas stream. The reactor tube is connected to a large, empty U tube which allows observation of the exit gas and is, in turn, connected to a KOH-filled trap.

The porcelain tube is slowly heated to, and then held at, a temperature of 900°C until HCl evolution (which follows the initial formation of a small quantity of brown fumes) is complete. After cooling to room temperature (and not before), the product is removed from the reactor in a stream of H₂. At this point, it consists of vanadium hydride (approximate composition $VH_{1/7}$), which is converted to pure V by heating in high vacuum. It should be borne in mind that finely subdivided vanadium and vanadium hydride are sensitive to atmospheric O₂ even at room temperature.

The Pt sheet absorbs some V during the reaction and turns darker, brittle and fragile. The vanadium can be removed from the Pt in the form of $V_{s}O_{6}$ by heating to red heat in air or, via a more drastic method, by treatment with a molten mixture of 1 part of KNO₃ and 15 parts of NaKCO₃. The Pt is thus completely regenerated. It should be possible to replace the porcelain tube, with no loss of efficiency, by an alumina tube.

Alternale methods: a) Very pure V can be obtained by deposition from the gas phase in the apparatus shown in Fig. 291, p. 1168. In this case the apparatus is made of fused quartz and is heated to 900-1000°C during the reaction. A suitable crude metal starting product is obtained, for example, by reacting a mixture of VCl₃ and Na in a heated iron bomb. Since the transport to the incandescent wire is accomplished via VI₂, whose volatility is relatively low, this process is not as advantageous in the case of V as with metals of Group IV [A. E. van Arkel, Metaliwirtsch. 13, 405 (1934); J. W. Nash, H. R. Ogden, R. E. Durtschi and I. E. Campbell, J. Electrochem. Soc. 100, 272 (1953); H. W. Rathmann and H. R. Grady, Vancoram Rev. 10, 6, 17 (1955)].

b) With Ar as the carrier phase, the reduction of VCl₄ with H_8 (affording pure V powder) can be accomplished at 620°C [G. Jantsch and F. Zenek, Monatsh. Chem. <u>84</u>, 1119 (1953)].

c) According to another proposed method, a stream of dry, high-purity H₂ saturated with VCl₄ vapor is passed over Mg turnings (in a MgO boat) and gradually heated to 700°C over a period of 2.5 hours. After cooling, the product mixture of V, VCl₂ and VCl₃ is thoroughly extracted with H₂O to dissolve out any chlorides present. The residue of V powder (99.3% V) is then vacuum-dried.

d) A mixture of 2 parts of VCl_2 and 1 part of Mg is pressed into pellets and these are heated for 1-2.5 hours at 700°C in a MgO boat inserted in a quartz tube (H₂ or Ar atmosphere). The product metal contains up to 99.5% V [A. Morette, Comptes Rendus Hebd. Séances Acad. Sci. 200, 1110 (1935)].

Solid V metal is comminuted and reduced to a fine powder via the vanadium hydride stage. Thus, vanadium is heated to about 500°C in a stream of high-purity H_2 and is then cooled in the same gas. The hydride is very brittle and can be readily comminuted by pounding or grinding in a volatile organic liquid such as benzene, which protects it against local heating and oxidation. The comminuted material is then dehydrogenated to pure V metal by heating in high vacuum (W. D. Schnell, Thesis, Univ. of Freiburg i. Br., 1960).

The purity of high-grade V can be further increased (to about 99.997%) by long heating (e.g., for 20 hours) in a high vacuum (10^{-5} mm.) at 1650°C (W. D. Schnell, Thesis, Univ. of Freiburg i. Br., 1960).

For information concerning melting V metal in crucibles made of various materials, see T. W. Merril, Vancoram Rev. 11, 11, 16 (1956). PROPERTIES:

Atomic weight 50.95. Light-gray metal, ductile when pure. M.p. 1900°C; d 6.11. Insoluble in hydrochloric and sulfuric acids, soluble in nitric and hydrofluoric acids. High affinity for O, N, C and H. Surface reaction with atmospheric O_2 starts already at 20°C; this can lead, particularly in the case of a fine powder, to considerable contamination. Crystal structure: type A_2 .

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 - J. W. Marden and H. C. Rentschler, Ind. Eng. Chem. 19, 97 (1927); E. D. Gregory, W. C. Lilliendahi and D. M. Wroughton, J. Electrochem. Soc. 98, 395 (1951); A. P. Beard and D. D. Crooks, J. Electrochem. Soc, 101, 597 (1954); R. K. McKechnie and A. U. Seybolt, J. Electrochem. Soc. 97, 311 (1950); J. R. Long. Iowa State Coll. J. Sci. 27, 213 (1953).
- II. Th. Döring and J. Geiler. Z. anorg. allg. Chem. 221, 56 (1934).

Vanadium (II) Chloride VCL

ĩ.

$VCl_s + \frac{1}{2}H_t = VCl_t + HCl_{157.3}$ 11.2 l 121.9 36.5

The reactor is a Pyrex, Vycor or fused quartz tube, and the VCl₃ is placed either directly in the tube or in a porcelain boat (the transfer to the reactor requires great care, because VCl₃ is very hygroscopic). A stream of dry, completely deoxygenated hydrogen is then passed through the tube (the end of the tube is protected against moisture by a CaCl₃ tube), and the system is heated to about 400°C. While HCl is evolved, the temperature is gradually increased to 675°C. Care should be taken not to exceed 760°C (according to Klemm and Hoschek, not even 560°C), otherwise reduction to V metal will occur. The reaction time depends on the quantity of material used; it is about 1 hour for 0.5 g., and about 40 hours for 30 g. At the end of the reaction, the H₂ stream is replaced by a stream of P₂O₅-dried N₂ or CO₂, and the VCl₂ produced is discharged from the reactor under ashydrous conditions. A high yield (~90%) is obtained.

 $\begin{array}{cccc} \text{II.} & 2 \text{ VCl}_{s} = \text{ VCl}_{s} + \text{ VCl}_{s} \\ & 314.6 & 121.9 & 192.8 \end{array}$

Rapid disproportionation of VCi₃ according to the above equation can be achieved at 800°C in a stream of high-purity N_{B} . The VCi₄ is carried away by the N_a stream (4 bubbles/sec.), while the VCl_a remains in the reactor tube. The temperature should not exceed 850°C, to avoid loss of VCl_a by sublimation. The reaction is fairly fast; for example, the reaction of 20 g. of VCl_a takes 2 hours.

PROPERTIES:

Light-green leaflets; m.p. about 1350° C; d. 3.09. Less hygroscopic than VCl₃ and VCl₄; insoluble in alcohol or ether. Crystal structure: Cdl₂ type.

REFERENCES:

- F. Ephraim and E. Ammann. Helv. Chim. Acta <u>16</u>, 1273 (1933);
 W. Klemm and E. Hoschek. Z. anorg. alig. Chem. <u>226</u>, 359 (1936);
 R. C. Young and M. E. Smith in: J. C. Bailar, Inorg. Syntheses, Vol. IV, New York-London-Toronto, 1953, p. 126;
 H. Funk and W. Weiss, Z. anorg. alig. Chem. <u>295</u>, 327 (1958).
- H. O. Rugg and H. Lickfett. Ber. dtsch. chem. Ges. 44, 506 (1911); P. Ehrlich and H. J. Seifert. Z. anorg. allg. Chem. <u>301</u>, 282 (1959).

Vanadium (III) Chloride

VCl₁, VCl₁·6 H₂O

VCI₄

I.

 V_2O_3 + 3 SOCl₂ = 2 VCl₃ + 3 SO₂ 149.9 356.9 314.6 192.2

Vanadium trioxide powder (2.1 g.) and 8.5 ml. of pure SOCl₃ are placed in a bomb tube about 1.5 cm. in diameter, and the sealed tube is heated for 24 hours at 200°C. The tube is cooled to below 0° C (in order to lower the SO₃ vapor pressure) and is then opened to allow SO₂ to escape. Then the tube contents are flushed out, under anhydrous conditions, into a small flask, using some SOCl₃ for this purpose (the SOCl₂ is then removed by vacuum distillation). The VCl₃ residue is washed several times with very pure CS₂ to remove traces of S₃Cl₃, and then thoroughly vacuum-dried at 80°C. Fine crystals of dark-violet VCl₃ are obtained in nearly quantitative yield.

И,

 $\begin{array}{rrrrr} 2 V_2 O_5 &+ 6 S_2 C I_2 &= 4 V C I_3 &+ 5 S O_5 &+ 7 S \\ 363.8 & 810.2 & 629.3 & 320.3 & 224.4 \end{array}$

Pine, pure V_3O_5 powder (18 g.) and 40 ml. of S_3Cl_9 are refluxed under anhydrous conditions for 8 hours (constant stirring). The

excess S_2Cl_2 , containing dissolved S, is decanted and the VCl₃ formed is washed with dry CS₂. Adhering volatiles are removed by heating the material at 120-150°C under vacuum or by extracting it for several hours with CS₃ in a Soxhlet apparatus. After thorough purification, the residual sulfur content of the resulting fine crystals of VCl₃ is about 0.2%. The yield is about 30 g.

Coarse (and hence less hygroscopic) crystals of VCl₃ are obtained by heating the fine crystalline product with a small amount of fresh S_3Cl_3 in a scaled tube at 240°C. Since no gas is evolved in this operation, large amounts can be treated at one time.

The same reaction can also be carried out in a sealed tube at 300° C; however, smaller quantities must be used in this case (6-7 g. of V₂O₅ and 20 ml. of S₂Ci₂).

III. $VCl_4 = VCl_5 + \frac{1}{2}Cl_2$ 192.8 157.3 35.5

A flask containing VCi₄ is connected to a reflux condenser via a ground joint and kept at 160-170°C for 2 days while passing a thoroughly dried and deoxygenated stream of CO₃ or H₃ through the system (to remove the Cl₂ formed in the thermal dissociation). The flask is then arranged for distillation; unreacted VCl₄ and the traces of the VOCl₃ formed are distilled off at 200°C in a H₂ stream. Reduction does not take place under these conditions. The by-products can also be removed by vacuum distillation. All operations are carried out under anhydrous conditions.

Alternate methods: IV. Reaction of VCl₄ with S, removal of the S_3Cl_9 by distillation, then heating of the product at a temperature somewhat below 300°C in a stream of CO₂.

V. If V metal is available as a very fine powder, it can be reacted with excess ICl, according to the equation:

> $2V + 6ICl = 31_{2} + 2VCl_{3}$ 101.9 974.2 761.5 314.6

The mixture is heated under anhydrous conditions in a glass flack equipped with a reflux condenser. The flack is carefully heated with a direct flame until the initially vigorous reaction, which affords iodine vapor, subsides and vapors of the boiling ICI become visible. After cooling, the mixture is extracted with CCI₄ (distilled from P_2O_5), filtered in a N₂ stream through a sintered glass disk, washed with CCI₄ and dried in a vacuum desiccator. The product is very pure provided all of the vanadium has reacted.

PROPERTIES:

Formula weight 157.3. Violet, quite crystalline. Very hygrometropic. Soluble in acidified water. In the absence of air, can be

obtained from solutions as $VCi_3 \cdot 6H_2O$. Soluble in alcohol, insoluble in ethyl ether. d 3.0. Crystal structure: DO_5 (FeCl₃) type.

REFERENCES:

- H. Hecht, G. Jander and H. Schlapmann, Z. anorg. Chem. <u>254</u>, 255 (1947); experiments carried out at the University Laboratory, Freiburg i. Br., 1951.
- H. Funk and C. Müller. Z. anorg. allg. Chem. <u>244</u>, 94 (1940);
 experiments carried out at the University Laboratory, Freiburg
 i. Br., 1951; H. Hartmann and H. L. Schläfer. Z. Naturforsch,
 6a, 754 (1951); H. Funk and W. Weiss. Z. anorg. allg. Chem. 295, 327 (1958).
- H. J. Meyer and R. Backa. Z. anorg. allg. Chem. <u>135</u>, 177 (1924);
 F. Ephraim and E. Ammann. Helv. Chim. Acta <u>16</u>, 1273 (1933);
 R. C. Young and M. E. Smith in: J. C. Bailar, Inorg. Syntheses, Vol. IV, New York-Toronto-London, 1953, p. 128.
- IV. O. Ruff and H. Lickfett, Ber. dtsch. chem. Ges. 44, 506 (1911); F. Ephraim and E. Ammann. Helv. Chim. Acta 16, 1273 (1933).
- V. V. Gutmann. Monatsh. Chem. 81, 1155 (1950).

VCL • 6 H_O

The hexahydrate can be obtained from aqueous, acidic VCl_3 solution by cooling and saturating with HCl. The starting solution is obtained by electrolytic reduction of a solution of V_2O_5 in hydrochloric acid or, more conveniently, by dissolving V_2O_3 in hydrochloric acid.

 $V_{2}O_{3} + 2H_{2} = V_{2}O_{3} + 2H_{2}O$ 181.9 44.8 l. 149.9 $V_{2}O_{3} + 6HCl + 9H_{2}O = 2VCl_{3} \cdot 6H_{2}O$ 149.9 134.4 l. 162.1 265.4

For example, 7.5 g. of V_3O_3 (obtained by reduction of V_3O_5 with H_2 as described on p. 1267) is dissolved in 200 ml. of conc. HCl by allowing the mixture to boil several hours. This solution is concentrated to 50 ml., cooled to -10 to -20° C, and saturated with HCl gas. The precipitate of green VCl₃ · 6 H₃O is suction-filtered on glass frit, dissolved in some H_2O , and reprecipitated with HCl while cooling (see also the preparation of TiCl₃ · 6 H₂O, p. 1193 f.).

PROPERTIES:

Formula weight 265.4. Green, hygroscopic crystals.

REFERENCES:

A. Piccini and M. Brízzi, Z. anorg. Chem. 19, 394 (1899); P. Ehrlich and H. J. Seifert, Z. anorg. allg. Chem. 301, 282 (1959).

Vanadium (IV) Chloride

VCL

1.

 $VCl_{2} + \frac{1}{2}cl_{2} = VCl_{4}$ 157.3 11.2 l. 192.8

In the method of Funk and Weiss VCl₃, which is readily obtained from V_2O_8 and S_2Cl_2 (see p. 1256), is loosely packed in a alightly inclined reactor tube made of high-melting glass. The tube is connected by a ground joint to a receiver, which is protected against moisture. A glass-wool wad is placed at the end of the reactor tube to prevent solid VCl₃ particles from reaching the receiver. Dry Cl_2 is passed through the apparatus to displace the air; the VCl₈ is then heated, starting from the end closest to the receiver. The reaction rate can be controlled by regulating the Cl_3 flow. The orude VCl₄ is collected in the receiver, which is kept at 0°C; it is then distilled from this receiver in a slow stream of Cl_3 (anhydrous conditions), discarding the forerun. Approximately 35 g. of pure VCl₄ is obtained from 30 g. of VCl₃.

11. A process similar to that described in method I may be used to prepare VCl₄ from ferrovanadium and Ci₃. A very long reactor tube is used, and the reaction rate is regulated so as to allow most of the by-product FeCl₃ to settle out. The VCl₄ must be redistilled from the receiver.

Alternate method: Disproportionation of VCl₃ to VCl₃ and VCl₄ by heating in a N₂ stream at 900°C in a porcelain tube [O. Ruff and H. Lickfett, Ber. dtsch. chem. Ges. 44, 506 (1911)].

PROPERTIES:

Dark red-brown liquid. M.p. -109 °C, b.p. 148.5 °C; d 1.87. Fumes in air, and even at normal temperature shows a marked Cl₂ vapor pressure (decomposition). Sealed ampoules containing VCl₄ should be stored in the dark (occasionally they shatter because of high internal pressure). Decomposed by water. Soluble in conc. hydrochloric acid, ethanol and ethyl ether.

REFERENCES:

- I. H. Funk and W. Weiss. Z. anorg. allg. Chem. 295, 327 (1958).
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 Ephraim and E. Ammann. Helv. Chim. Acta 16, 1273 (1933);
 J. H. Simons and M. G. Powell. J. Amer. Chem. Soc. <u>67</u>, 75 (1945).

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Vanadium (II) Bromide

YBr₁

 $VBr_{3} + \frac{1}{2}H_{2} = VBr_{3} + HBr_{290.7}$ 290.7 11.2 l. 210.8 80.9

The starting material is VBr_3 , which is best left in the tube used for its preparation (see below). In this case, the reactor tube is considerably longer than that used merely to prepare VBr_3 .

The zones containing VBr₃ are heated, one after another, to dark-red heat while a H_3 stream is passed through. The heating is best accomplished in a tubular electric furnace, in which heating is more uniform than with open flames; with such a furnace, pronounced local overheating and reaction rate differentials are prevented and the total reduction time is short. The reduction of 2 g. of VBr₃ takes 1-1.5 hours.

PROPERTIES:

Light-brown to reddish; light pink-red when heated. Feltlike to flaky crystal aggregates. More hygroscopic than VCl₂, but not as sensitive as VBr₃. Gives a violet solution with H_2O ; this soon turns brown, evolving H_2 , d 4.58. Crystal structure: C6 (Cdl₂) type.

REFERENCES:

F. Ephraim and E. Ammann. Helv. Chim. Acta <u>16</u>, 1273 (1933);
 W. Klemm and E. Hoschek. Z. anorg. alig. Chem. <u>226</u>, 359 (1936).

Vanadium (III) Bromide VBr,

 $V(+Fe) + \frac{3}{2}B_{T_2}(+\frac{3}{2}B_{T_3}) = VB_{T_3}(+FeB_{T_3})$ 51.6 55.9 239.7 239.7 290.7 295.6

A high-melting glass tube, 10-12 mm, I.D. and 80 cm, long, is charged with 5 g. of very finely powdered high-grade ferrovanadium (no boat is used). A stream of thoroughly dried CO_3 is passed through a small round-bottom flask in which absolutely dry Br_3 , elowly introduced from a dropping funnel, is vaporized by slight heating. The CO_2 and Br_3 vapors then pass through the reactor tube. The other end of the reactor carries (preferably scaled on) containers for the subsequent collection of VBr_3 (e.g., tubes which can be melt-scaled), which are protected from the atmosphere by a P_2O_5 tube. Air and moisture must be rigorously excluded. After filling the reactor with $CO_3 + Br_3$, the Fe-V is heated to red heat. The first product is a small amount of VOBr₃, which is quickly and readily displaced by heating the entire tube length to prevent the deposition of vanadium oxide (the latter cannot be removed). The conversion to VBr₃ and FeBr₃ is then carried out over a period of about 4 hours. Most of the FeBr₃ remains at the exit end of the tube, while the Br₃ sublimes out. It is freed of FeBr₃ by repeated sublimation. Rather low sublimation temperatures and long sublimation tubes are required in this procedure. Finally the system is flushed with pure, Br_3 -free CO_3 .

PROPERTIES:

Black with greenish reflections, crystalline; the vapor is violet. Extremely hygroscopic. d 4.52.

REFERENCES:

J. Meyer and R. Backa. Z. anorg. allg. Chem. <u>135</u>, 177 (1924);
 F. Ephraim and E. Amman. Helv. Chim. Acta <u>16</u>, 1273 (1938);
 W. Klemm and E. Hoschek. Z. anorg. allg. Chem. <u>226</u>, 359 (1936).

Vanadium (II) Iodide

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This compound is prepared by synthesis from the elements.

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V + I_{*} = V_{*}
51.0 253.8 304.8
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I. In the method of Morette, VI_3 is first prepared from V and I_2 (see the following preparation) and then decomposed by heating at 400°C in high vacuum while removing the I_3 split off. The decomposition is virtually complete in 24 hours.

II. In the method of Klemm and Grimm, a stolchiometric mixture of V turnings and I_3 is scaled under vacuum into a short quartz tube, with occasional cooling to reduce the I_3 vapor pressure. The entire tube is then uniformly heated at 160-170°C.

PROPERTIES;

Dark-violet, hexagonal leaflets. Not readily wetted by H_3Q_1 slowly forms a violet solution. Insoluble in absolute ethanol, benzene, CCl₄, CS₂. Partly oxidized in air, turning brown. d 5,44. Crystal structure: C6 (CdI₂) type.

REFERENCES:

A. Morette, Comptes Rendus Hebd. Séances Acad. Sci. 207, 1218 (1938); W. Klemm and L. Grimm, Z. anorg. allg. Chem. 249, 198 (1942).

Vonadium (III) lodide

٧I,

Formed when metallic V and I₂ are heated at 300°C under the vapor pressure generated by the latter.

 $V + \frac{3}{t}I_2 = VI_3$ 51.0 350.7 431.7

Vanadium metal (turnings or powder) and excess I_2 are placed in a hard glass or fused quartz tube, closed at one end; the tube contents are cooled to -80° C; the tube is thoroughly evacuated and then melt-sealed to a short total length. A vigorous reaction sets in on heating. The entire tube is heated for a while at temperatures up to 300°C in order to achieve product uniformity. The excess I_2 is then allowed to distill off into a somewhat cooler zone, and the tube is quickly cooled and opened.

PROPERTIES:

Brown-black, crystalline powder. Very hygroscopic. Readily soluble in water giving a brown solution which turns gradually green in air. Also soluble in absolute ethanol; insoluble in benzene, CCl_4 , CS_2 , d 4.2.

REFERENCE:

A. Morette, Comptes Rendus Hebd. Séances Acad. Sci. 207, 1218 (1938).

Vanadium Oxychloride

VOCI

 $V_2O_8 + VCl_a = 3 VOCl_{149.9} + 157.3 = 307.2$

A quartz tube, about 180 mm. long and 15 mm. in diameter, is charged with 1 g. of V_2O_3 and 2 g. of VCl₃ under anhydrous

conditions. The tube is thoroughly evacuated, melt-sealed and placed horizontally in a furnace providing a temperature gradient such that the raw material is kept at 720°C and the empty half of the tube at 620°C (see Part I, p. 76 f, and preparation of TiOCi, p. 1209). After 1-2 days, VOCI forms as a crystalline deposit in the center of the tube and a dense mass on the 720°C side. In addition, small amounts of VCl₂, VCl₃, VCl₄ and VOCl₃ are also present. The tube is opened indry N₂, and the VCl₄ and VOCl₃ are vaporized in vacuum. The tube contents are then elurried in dimethylformamide, and the VCl₂ and VCl₃ are removed from the VOCl by repeated slurrying and decantation with this solvent. The vOCl, obtained as the residue, is washed with ethanol and ethyl ether and vacuum-dried.

Alternate methods: Vanadium oxychloride can also be obtained a) by heating VCl₃ and CO₃ [O. Ruff and H. Lickfett, Ber. dtsch. chem. Ges. <u>44</u>, 506 (1911); E. Wedekind and C. Horst, Ber. dtsch. chem. Ges. <u>45</u>, 262 (1912)];

b) by heating VCl₃ in an O₂-containing N₂ stream;

c) by heating VOC1₂ in a pure N₂ stream [P. Ehrlich and H. J. Seifert, Z. anorg allg. Chem. <u>301</u>, 282 (1959)].

PROPERTIES:

Formula weight 102.41. Brown crystals, the particle size depending on method of preparation. Decomposes at about 600°C into VCl₃ and the oxide; not attacked by H_3O , hydrochloric acid or alkalies; dissolves in warm conc. HNO₃ and conc. H_2SO_4 . d 3.44; Rhombic crystals, isotypical with FeOCl.

REFERENCES:

H. Schäfer and F. Wartenpfuhl. J. Less-Common Metals 3, 29 (1961); P. Ehrlich and H. J. Seifert. Z. anorg. allg. Chem. 301, 282 (1959).

Vanadium Oxydichloride

voci.

$$V_2O_3 + 3 VCl_3 + VOCl_3 = 6 VOCl_1$$

181.9 472.0 173.3 827.2

A thoroughly ground mixture of 3.6 g. of dry V_2O_5 and 9.4 g. of VCl₃ is placed at the closed end of a 1-m.-long tube, and 0.9 mL of VOCl₃ is then added. The upper part of the tube must be free of traces of these substances. The tube, filled with air, is melt-sealed, and is covered along its entire length with a sheet-metal jacket jits

Nower third, in a slightly inclined position, is then heated to about 600°C with a tubular electric furnace. The sheet-metal jacket **provides a temperature gradient** along which the product $VOCl_3$ **sublimes out of the hot reaction** zone. This procedure requires at **least 4-5 days.** However, the yield can be increased by longer heating time. Green needlelike crystals of $VOCl_3$ are deposited in the cold part of the tube. The tube is opened at a suitable spot; the product is suspended inpetroleum ether, ethyl ether or CCl_4 to dissolve some adhering $VOCl_3$, and then suction-filtered on a coarse fritted-glass filter. The relatively coarse filter separates the $VOCl_2$ crystals from traces of finely divided hydrolysis products. The $VOCl_3$ is freed of adhering solvent and stored under anhydrous conditions.

Alternate method: The older method of reducing VOC1₃ with Zn powder in a scaled tube is less efficient (Gmelin-Kraut, Handb. d. anorg. Chem. [Handbook of Inorg. Chem.], 7th Ed., Heidelberg, 1908, Vol. III/2, p. 120).

SYNONYM:

Vanadyi dichloride.

PROPERTIES:

Formula weight 137.86. Shiny green crystals; hygroscopic. d 2.88. Solutions of VOCl₂ in aqueous hydrochloric acid are obtained by adding VCl₄ to H_2O or by heating V_2O_5 with excess conc. HCl and evaporating most of the excess HCl. The evolution of Cl_2 brought about in this manner can be greatly facilitated by addition of weak reducing agents such as ethanol or H_2S .

REFERENCE:

H. Funk and W. Weiss, Z. anorg. allg. Chem. 295, 327 (1958).

Vanadium Oxytrichloride

VOCI,

I,

$$V_{t}O_{s} + 3 \text{ SOC}_{t} = 2 \text{ VOC}_{s} + 3 \text{ SO}_{t}$$

181.9 356.9 348.6

A flask connected to a reflux condenser via a ground joint is charged with 20 g. of V_2O_6 and 24 ml. of SOCl₂ (equivalent quantities) and heated for 6-8 hours on a water bath under rigorously abydrous conditions. After rearranging the apparatus for forward distillation, the reaction product is distilled directly from the flask. This method yields pure VOCl₂ provided no excess of SOCl₂ is used. п.

 $V_zO_3 + 3 Cl_z = 2 VOCl_s + 1/z O_z$ 149.9 67.2 *l*. 348.6

Pellets, obtained by compressing a mixture of $V_{\rm g}O_3$ and coal powder, are heated at 500-600°C in a Cl₂ stream. The red-brown reaction product, containing VOCl₃ as well as considerable amounts of VCl₄ and Cl₂, is repeatedly redistilled over Na metal until it is yellow. The product should not be distilled to drypess because it is likely to ignite. Rigorously anhydrous conditions are required.

Alternate method: The VCl₃ is heated in a stream of O₂, using the apparatus described for the preparation of VCl₄ from VCl₃ and Cl₂, p. 1259 [H. Funk and W. Weiss, Z. anorg. allg. Chem. <u>295</u>, 327 (1958)].

SYNONYM:

Vanadyl trichloride.

PROPERTIES:

Formula weight 173.32. Light-yellow liquid. M.p. -79.5 °C, b.p. 127 °C; vapor pressure (0 °C) 4.4 mm., (80 °C) 175 mm.; d (0 °C) 1.85. (32 °C) 1.81. Instantly hydrolyzed by H₂O; quickly attacked even by atmospheric moisture; violent reaction with Na above 180 °C. Soluble in ethanol, ethyl ether and glacial acetic acid.

REFERENCES:

- I. H. Hecht, G. Jander and H. Schlapmann, Z. anorg. Chem. <u>254</u>, 255 (1947).
- H. W. Prandtl and B. Bleyer, Z. anorg. Chem. <u>65</u>, 153 (1909); L. Vanino, Hando, d. präp, Chemie, Anorg. Teil [Handbook of Preparative Chemistry, Inorganic Section], 3rd Ed., Stuttgart, 1925, p. 675; F. E. Brown and F. A. Griffits in: H. S. Booth, Inorg. Syntheses, Vol. I, New York-London, 1939, p. 106 and J. C. Bailar, Inorg. Syntheses, Vol. IV, New York-London-Toronto, 1953, p. 80; A. Morette. Comptes Rendus Hebd. Séances Acad. Sci. <u>202</u>,1846 (1936).

Vanadium Dioxychloride

VO₂CI

 $VOCl_3 + Cl_2O = VO_4Cl + 2Cl_2$ 173.3 86.9 118.4

A 250-ml., two-neck flask equipped with a large-diameter inititube, with all joints and stopcocks made gas-tight with Hestalish

1203

- H17.14

(Farbworke Hoechst) or Teflon grease, is purged with dry N_3 , Then pure VOCl₃ (100 ml.) is distilled in, and Cl₂O gas diluted with O₃ is introduced at room temperature. The Cl₃O gas mixture is obtained by passing O₂ and Cl₃(both dried over P₃O₅) over HgO. It is advantageous to keep the HgO in a rotatable glass tube surrounded by a cooling jacket (Liebig condenser).

After a while an orange-colored, microcrystalline mass is formed, while the temperature of the reaction mixture increases slightly. The O_3 - Cl_3O feed is continued until the quantity of the crystals formed makes further feeding impossible. The material is filtered under rigorously anhydrous conditions and then vacuumdried. The product must not be washed with CCl₄, becaused this solvent slowly reacts with VO₂Cl even at room temperature, affording phosgene.

The yield, based on $Cl_{2}O$, is nearly quantitative; based on VOCl₃, it is not higher than 60%.

PROPERTIES:

Orange-red, microcrystalline, very hygroscopic powder. At 150°C, disproportionates into V_2O_5 and $VOCl_3$. Sparingly soluble in nonpolar solvents, moderately soluble in ethyl ether, soluble in H_2O with decomposition. d 2,29.

REFERENCE:

K. Dehnicke. Personal communications, 1960.

V_tO₁₃

a) A stoichiometric mixture of V_3O_5 and V_2O_3 is heated for 48 hours at not less than 600°C, preferably at 750-800°C, in an evacuated, sealed quartz tube.

b) Or, the V_2O_5 surface is reduced in an SO₂ stream at a temperature somewhat higher than 700°C, and the unreacted V_2O_6 is extracted from the reaction product with conc. ammonia.

PROPERTIES:

Bine-black, crystalline powder. Readily soluble in conc. HNOs. sparingly soluble in conc. ammonia and 2 N NaOH. The independent phase with a monoclinic crystal structure is stable only below about 700°C.

VO2

Since the direct reduction of V_2O_5 does not give a well-defined product, this compound is best prepared by synthesis from V_2O_5 and V_3O_3 , suggested a long time ago by Berzelius;

> $V_2O_3 + V_2O_3 = 4 VO_4$ 181.9 149.9 331.8

An intimate mixture of V_3O_5 and V_3O_3 , in the exact proportion, required by the equation, is heated for 40-60 hours at 750-800°C in a small evacuated, sealed quartz tube.

Alternate methods: The V_3O_5 is fused with an excess of crystalline oxalic acid until a greenish-blue, completely water-soluble mass of vanadyl oxalate is obtained. This mass is then calcined to complete decomposition in the absence of air. The VO_3 is obtained as the residue.

PROPERTIES:

Blue-black powder. M.p. 1650°C; d 4.34. Deformed C 4 (rutile) type crystal structure.

 V_nO_{2n-1}

According to G. Anderson, several lower vanadium oxides have very similar compositions which are intermediate between those of VO₃ and of V₂O₃ and correspond to the formula V_nO_{2n-1} (where n = 3, 4, 5, 6, 7 or 8). These oxides have very narrow regions of homogeneity and are obtained by vacuum heating corresponding. mixtures of V₂O₅, V₂O₅ and V for 2-20 days at 650-1000*C.

V₂O₂

$$V_{2}O_{3} + 2H_{3} = V_{2}O_{3} + 2H_{2}O_{3}$$

181.9 44.81. 149.9 36.0

The V_3O_5 is reduced in a stream of very pure H_3 in two steps: first, for 2 hours at 600°C (the 658°C m.p. of V_3O_5 should not be exceeded), then for 6 additional hours at 900-1000°C.

For information on the formation of V₂O₃ single crystals, see H. Hahn and C. de Laurent, Angew. Chem. <u>69</u>, 529 (1956). PROPERTIES:

Dull, black powder. M.p. 1970°C; d 4.87. Crystal structure: alumina type.

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 $V_{p}O_{4} + V = S VO_{149.9} = 51.0 = 200.9$

Synthesized from V_2O_3 and V metal powder under vacuum or Ar. The reactants are kept in Al₂O₃ crucibles which, in turn, are inserted into small, evacuated quartz tubes. Or. the apparatus described by Ehrlich for the preparation of TiO (p. 1214) may be used. The optimum reaction temperatures lie between 1200 and 1600°C. A product of greater uniformity is obtained by occasionally interrupting the heating and repulverizing the material. A reaction time of the order of 24 hours at 1200-1300°C is needed, whereas 1 hour is sufficient at 1600°C.

Alternate method: Electrolysis of phosphate melts containing dissolved V_2O_5 [H. Hartmann and W. Mässing, Z. anorg. allg. Chem. <u>266</u>, 98 (1951)].

PROPERTIES:

Gray powder. The region of homogeneity is $VO_{0.75}$ - $VO_{1,20}$. Crystal structure: B 1 (NaCl) type.

REFERENCES:

H. Fendius. Thesis, Univ. of Hannover, 1930; W. Klemm and L. Grimm. Z. anorg. allg. Chem. <u>226</u>, 359 (1936); W. Klemm and E. Hoschek. Z. anorg. allg. Chem. <u>242</u>, 63 (1939); W. Klemm and L. Grimm. Z. anorg. allg. Chem. <u>250</u>, 42 (1942); W. Klemm and P. Pirscher. Optik <u>3</u>, 75 (1948); F. Aebi. Heiv. Chim. Acta <u>31</u>. 8 (1948); S. S. Todd and K. R. Bonnickson, J. Amer. Chem. Soc. <u>73</u>, 3894 (1951); M. Frandsen, J. Amer. Chem. Soc. <u>74</u>, 5046 (1952); N. Schönberg. Acta Chem. Scand. <u>8</u>, 221 (1954); G. Anderson, Acta Chem. Scand. <u>8</u>, 1509 (1954).

Vanadium (III) Hydroxide

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A sentral Na 3VO 4 solution is reduced electrolytically at a mer-

A) PREPARATION OF THE VANADATE SOLUTION

 $V_2O_3 + 6N_aOH = 2Na_3VO_4 + 3H_2O_181.9$ 181.9 240.0 367.9 54.9

Concentrated NaOH is prepared from equal weights of NaOH and H_2O , and the solution is filtered in the absence of CO_3 to remove the Na₂CO₃ contaminant. The strength of the solution is then

determined by analysis. The amount of V_3O_5 required by the above equation is then dissolved in this solution, and 1 M Na₃VO₄ is prepared by dilution with water.

B) ELECTROLYSIS

An electrolysis cell of the type shown in Fig. 302 is filled with very pure Hg and the Na₃VO₄ solution. The cell is closed off with rubber stopper C, and the anode space within the clay disphragm Disfilled with 1 M Na SO solution. Very pure Na is bubbled (via inlet tube R) through the electrolyte solution for the first 15 minutes, and is passed over the liquid surface for the remainder of the electrolysis. Electrolysis is carried out with a current of 0.1 amp, at a cathode potential of -1.70 v. (checked by means of the standard cell N). Brown-green V(OH)a precipitates, and the electrolyte assumes a brownred color. The electrolysis is discontinued after 5-10 hours, and V(OH)3 isolated in

the absence of air. This is accomplished by first draining the Hg through the stopcock, then suction-filtering the $V(OH)_3$ suspension under a N_3 atmosphere and thoroughly washing the precipitate with descrated H_9O . Finally the $V(OH)_3$ is dried in high vacuum.

PROPERTIES:

Formula weight 101,97. Brass-colored, crystalline; readily oxidized by O₂.

REFERENCE:

N. Konopik and A. Neckel, Monatsh. Chem. 88, 917 (1957).

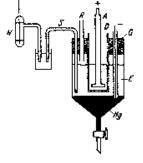


Fig. 302. Preparation of vanadium (III) hydroxide. A) carbon anode; D) clay diaphragm; E) electrolyte solution; C) rubber stopper; N) standard cell; R) N_2 inlet type; S) electrolyte bridge.

1 N 190

Vanadium (V) Oxide

V_zO₅

Highest grade V_2O_5 is obtained by calcining NH VO₃ at 500-550°C. Traces of N usually contaminating the product thus obtained can be virtually eliminated by heating for 18 hours at 530-570°C in a moist O₂ stream.

PROPERTIES:

Formula weight 181.9. Red to orange-yellow powder. M.p. 674°C. Slightly soluble in water: 0.07 g./100 g. H_2O ; d 3.36. Readily soluble in alkali hydroxide solutions, acids and ethanol. Crystal structure: orthorhombic.

Supported V: Os (V: Os catalysts)

I. ON ASBESTOS

A solution of 5g. of NH₄VO₃ in 100 ml. of boiling H₂O is reduced with NH₄HSO₃ and treated with sulfuric acid until the solution turns a pure blue-violet. Asbestos (20 g.) is added; the mixture is allowed to boil for 10-15 minutes and is then cooled to 40-50°C; it is then rendered strongly alkaline by addition of conc. NH₃, whereby the V(OH)₃ precipitates onto the asbestos. The latter is dried and again treated with unreduced NH₄VO₃, whereupon the asbestos and the flask wall become violet-blue. The asbestos mass is then pulled apart into small clumps, dried and calcined at 500-600°C; its V₃O₅ content may be as high as 50%.

11. ON CERAMIC MATERIALS

To produce a homogeneous deposit of V_2O_5 on ceramic materials (e.g., firebrick), 2-3 equivalents of a mineral acid is added to a NH₄VO₃ solution. The resulting dark-yellow solution, which contains colloidal $V_2O_5 \cdot aq$, is boiled in the presence of the ceramic material (heating on the water bath is insufficient), thereby causing precipitation onto the carrier of a yellow-red, strongly adhering layer of V_2O_5 . Glass (not porcelain) reaction vessels should be used in this process.

REFEBENCES:

 N. Yefremov and A. Rozenberg. Khim. Prom. 4, 129; Chem. Zentr. 1927. II, 1994; I. Adadurov and G. Boreskov. Khim. Prom. 6, 732; Chem. Zentr. 1929, II, 2926.

Colloidal V2O3

1. METHOD OF BILTZ

a) A mortar is used to grind 1 g, of NH_4VO_3 with some H_3O_3 and 10 ml. of 2 N HCl is added while stirring with the pestle. The red precipitate formed and the supernatant are transferred onto a filter, the liquid is filtered off, and the solid is washed with H_3O_3 . After a while, the initially clear filtrate becomes reddish and turbid. The precipitate is then transferred from the filter to an Erlenmeyer flask (using water from a wash bottle), and the volume is adjusted to 100 ml. The quantities of material used may be increased up to 200-fold, provided the proportions are kept the same. After a few hours the conversion of the precipitate to a clear orange-red V_2O_5 sol is complete. Fibrillar birefringence becomes evident only after prolonged standing.

b) In the modification of Humphry, 0.5 g. of NH₄VO₃ and 2 ml. of nitric acid (1 vol. of conc. HNO₃ + 10 vol. of H₂O) are ground together and then an additional 2 ml. of HNO₃ is added. The mixture is filtered, and the V₂O₅ formed is washed until it starts passing through the filter; it is then shaken with 200 ml. of H₂O and allowed to stand for 14 days.

PROPERTIES:

Because of the fibrillar structure of the particles, the sol exhibits strong streaming birefringence and on aging shows an increase in fibril length. Part of the V_3O_5 is always molecularly dissolved, in an amount increasing symbatically with the total concentration. The sol absorbs electrolytes strongly, and always contains some vanadium (IV).

IL METHOD OF PRANDTL AND HESS: SAPONIFICATION OF TERT-BUTYL ORTHOVANADATE

 $2(C_{4}H_{0})_{5}VO_{4} + 3H_{2}O = V_{2}O_{5} + 6C_{4}H_{0}OH_{572,8}$ 54.0 181.9 444.7

a) tert-Butyl alcohol and V_3O_5 are refluxed for several hours, affording a light-yellow solution of tert-butyl orthovanadate containing 5.3 g. of V_3O_5 per 100 g. The solution is filtered and subjected to fractional vacuum distillation in an Anshütz flask. This ester is sometimes repurified by a second vacuum distillation.⁴ Ester properties: b.p. 117°C (15 mm.), 132°C (32 mm.); m.p.⁶. 45-47°C.

b) H_3O is added to the ester; this produces a very loose (swollen) orange-colored precipitate. On boiling with a large quantity of H_3O , a clear, colloidal V_3O_5 solution is obtained. The alcohol (b.p. 82°C) is completely eliminated by the boiling. PROPERTIES:

Electrolyte-free, virtually monodisperse sol; does not age

Alternate methods: a) Pouring molten V_3O_5 into H_3O gives a fairly polydisperse sol, which is electrolyte-free and undergoes little or no aging [E. Müller, Kolloid-Z. 8, 302 (1911)].

b) Dissolving V_3O_5 in dilute H_3O_3 and boiling the solution affords a strongly polydisperse sol, which is electrolyte-free and does not age appreciably [W. Ostermann, Jahrb. d. philos. Fak. Göttingen II, 265 (1921)].

REFERENCES:

General: H. Gessner. Kolloid-Beih. 19, 213 (1924).

- I. W. Biltz, Ber. dtsch. chem. Ges. <u>37</u>, 1095 (1904); E. Sauer. Kolloidchem, Praktikum [Lab. Manual of Colloid Chemistry], Berlin, 1935; R. H. Humphry. Proc. Phys. Soc. (London) <u>35</u>, 217 (1923).
- II. W. Prandtl and L. Hess. Z. anorg. allg. Chem. 82, 102 (1913).

Ammonium Metavanadate

NH₄VO₄

Ammonium metavanadate is a common commercial product, but its purity usually leaves something to be desired. Since it is easily prepared from V_3O_5 (see method II) and in turn readily yields V_2O_5 on calcination, it plays an important role in the preparation and purification of vanadium compounds. Only the purification of NH₄VO₃ is treated here.

I. A saturated NH_4VO_3 solution is prepared in boiling, weakly ammoniacal H_3O . About 500 ml. of H_3O is required for 25 g. of NH_4VO_3 but, to avoid excessive hydrolysis, it is better to use more water than to prolong the boiling. The solution is filtered hot through a fine-pore fritted glass filter, 10% of its weight of solid NH_4Cl is added to the filtrate, and the mixture is cooled to $0^{\circ}C$. The precipitating NH_4VO_3 is allowed to stand at $0^{\circ}C$ (1 hour); it is then suction-filtered and washed with a small amount of icecold, ammoniacal H_2O and finally with some ice-cold pure water.

If necessary, this recrystallization may be repeated several times. Complete removal of alkali ions and traces of $V_3O_5 \cdot xH_3O$ (formed on slight hydrolysis) is extremely difficult.

H. If a smaller volume of liquid is desired, V_3O_5 is dissolved in Na₂CO₃ as NaVO₃, and NH₄VO₃ is precipitated from this solution by addition of NH₄Cl.

Thus 25 g. of V_2O_5 is added, in small portions and with stirring, to a boiling solution of 17.5 g. of anhydrous Na $_2CO_3$ in 125 ml. of H₂O. After the CO₂ evolution has subsided, saturated KMnO₄ solution is added to the reaction mixture in an amount just sufficient to discharge the green-blue color stemming from partial reduction of the vanadium. Undissolved V_2O_5 and MnO₂ are carefully suctionfiltered on a fine-pore fritted glass filter until the filtrate is completely clear. The residue is washed with H₂O until H₂O₂ no longer gives a positive reaction for vanadium. The filtrate, which amounts to about 125-150 ml., is heated to 60°C and then poured all at once into a hot solution of 75 g. of NH₄Cl in 125 ml. of H₂O. Precipitation of NH₄VO₃ starts immediately and is complete after a few hours. Some of the salt adheres fairly tenaciously to the glass walls. The salt is suction-filtered and washed with small portions of H₂O until the washings are free of chloride ion. It is then dried in air at a temperature below 40°C. An almost purewhite salt, still containing some Na (about 0.3% NaCl) is obtained in 80% yield.

The NH₄VO₃ can be recrystallized under similar conditions. For example, 25 g, of the salt is dissolved in a solution of 16 g, of Na₂CO₃ in 125 ml, of H₂O with mild heating (to 30-40°C). The mixture is then carefully filtered and precipitated at once with NH₄Cl as described above.

PROPERTIES:

White, crystalline salt, often yellowish due to slight traces of V_2O_5 . Solubility: (15°C) 0.62 g., (32°C) 1.0 g., (50°C) 1.6 g. per 100 g. of H_2O . d 2.33. Liberates NH₂ above 50°C. Readily converted to V_2O_5 when heated dry.

REFERENCES:

- I. L. Vanino, Handb. d. präp. Chem., Anorg. Teil [Handbook of Preparative Chemistry, Inorg. Part], 3rd Ed., Stuttgart, 1925, p. 672; M. Lachartre, Bull. Soc. Chim. France [4] 35, 321 (1924).
- H. R. H. Baker, H. Zimmermann and R. N. Maxson in: L. F. Audrieth, Inorg. Syntheses, Vol. III, New York-Toronto-London, 1950, p. 117; experimental data and personal communications from several laboratories.

Alkali Vanadates

Among the alkali vanadates, only NaVO₃ is commercially available. However, the number of existing defined alkali vanadates is rather large. Only the system $K_2O-V_2O_5$ has been subjected to a systematic preparative study. It may be assumed that the other systems have similar structures.

A stoichiometric mixture of K_3CO_3 and V_3O_5 (for example, a total of 5-6 g.) is heated in an open crucible. The crucible material

is Pt or, if the mixtures are rich in alkali, an 80% Au-20% Pd alkoy. The temperature should not be increased at a rate faster than 10°C/min., in order to prevent a too vigorous reaction which would result in loss by spattering. At low alkall contents, the maximum required temperature is about 500°C, while 1000°C is needed when the alkali content is high. Several hours (8-24) of heating are required at these temperatures. The product is cooled to below 350°C in a desiccator to prevent moisture absorption. The preparation must be modified somewhat, depending on raw material composition (see the original literature).

The phase diagram of the $K_2O-V_3O_5$ system shows the existence of the following potassium vanadates: $K_2O \cdot 4 V_2O_5$ (m.p. 520°C, incongruent); $K_2O \cdot V_2O_6$ (m.p. 520°C); 16 $K_2O \cdot 9 V_2O_5$ (m.p. 696°C, incongruent); 2 $K_2O \cdot V_2O_5$ (m.p. 910°C); 3 $K_3O \cdot V_2O_5$ (m.p. ~ 1300°C).

REFERENCE:

F. Holtzberg, A. Reisman, M. Berry and M. Berkenblit, J. Amer. Chem. Soc. <u>78</u>, 1536 (1956).

Vanadium Sulfides

All vanadium sulfides can be synthesized from the elements. An intimate mixture of the finely pulverized components, in the proper proportions, is placed in sintered clay tubular crucibles; these are inserted in quartz tubes, which are then evacuated and melt-sealed. The tubes are then slowly heated and finally maintained for a long time at a maximum temperature of 1000-1300°C. Contact between the vanadium metal and the quartz must definitely be avoided.

This procedure yields V₃S, VS and V₂S₃.

 $3V + S = V_3S;$ V + S = VS; $2V + 3S = V_2S_3$ 152.9 32.1 185.0 60.0 32.1 92.1 101.9 96.2 198.1

All the sulfides, as phases of the V-S system, have more or less wide regions of homogeneity.

Other preparative methods can also be used to obtain particular sulfide phases.

٧s

$$V_t S_k = 2 V S_i + S_i$$

198.1 100.0 32.1

Thermal decomposition of V_2S_3 at 1000°C in a H₂ stream yields a product of composition VS_{1,03} in 20 hours.

23. VANADIUM, NIOBIUM, TANTALUM

Pure VS can also be prepared by prolonged calcination of $V_{9}O_{8}$ in a stream of $H_{9}S$.

PROPERTIES:

VS exists, as a phase of the V-S system, between VS_{1.00} and VS_{1.16}. d 4.51. It has a B8 (NiAs) type crystal structure with voids.

V.S.

 $V_2O_3 + 3H_2S = V_2S_1 + 3H_2O$ 149.9 102.2 198.1 54.0

A thin layer of about 0.5 g. of V_3O_3 is spread in a porcelain boat, which is then inserted into a suitable tube and heated for 10 hours at 750°C in a moderately fast H_2S stream, predried over silica gel. At the end of this heating period, the tube is cooled in an H_2S stream and the V_2S_3 removed from the boat. A uniform and thin layer of V_2O_3 is essential to achieve a reasonable reaction time. Under the same conditions, 2-3 g. of V_2O_3 requires 2 days for complete conversion to the sulfide. Increasing the temperature to 850°C reduces the reaction time to a few hours, but the end product contains somewhat less S than required by the formula V_2S_3 (e.g., $VS_{1.47}$).

In addition, V_2O_5 can also be used as the starting material, by heating it at 700°C in a stream of CS₂ vapor. For data concerning the formation of V_2S_3 single crystals, see H. Hahn and C. de Laurent, Angew. Chem. 68, 523 (1956).

PROPERTIES:

Homogeneous between $VS_{1,17}$ and $V_{1,53}$. Dark-gray powders: Quite resistant to dil. acids; in contrast to VS_4 , insoluble in dilute sodium hydroxide. d 3.7.

VS₄

A mixture of V_3S_3 and excess S, corresponding to the approximate formula VS_{20} , is heated for 15 hours at 400°C in a scaled tube, followed by a 12-hour annealing period at 90°C (to convert the excess S into the soluble α -form). The reaction product is then exhaustively extracted in a Soxhlet apparatus, with the VS3 remaining as the residue. Extending the heating period (to several months) affords larger crystals.

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PROPERTIES:

Formula weight 179.19. Black powder. Composition sometimes does not correspond exactly to the formula. Unstable above 500°C, decomposing into V_3S_3 and S. Quite resistant to dilute acids; readily and completely soluble in sodium hydroxide, yielding a red solution. $VS_{3,65}$: d 2.8.

REFERENCES (all sulfides):

W. Biltz and A. Köcher. Z. anorg. allg. Chem. <u>241</u>, 324 (1939); E. Hoschek and W. Klemm. Z. anorg. allg. Chem. <u>242</u>, 49 (1939);
W. Klemm and E. Hoschek. Z. anorg. allg. Chem. <u>226</u>, 362 (1936); B. Pedersen and F. Grønvold. Acta Crystallogr. <u>12</u>, 1022 (1959); B. Pedersen. Acta Chem. Scand. <u>13</u>, 1050 (1959);
G. M. Loginov. Zh. Neorg. Khimii <u>5</u>, 221 (1960).

Vanadium Selenides

I.

 $V_2O_3 + 3H_2 + 3Se = V_2Se_3 + 3H_2O_149.9$ 67.2 l, 236.9 338.8 54.0

About 0.5 g. of V_2O_3 , which during its preparation has been heated not higher than 500-600°C so that is an active product capable of fast reaction, is placed in a small porcelain boat, which is inserted into a quartz tube. A larger boat containing Se is placed ahead of the one containing V_2O_3 , and a stream of very pure H_2 is passed through the tube. The V_2O_3 zone is first heated to 600°C, and then gradually to 900°C, using a small tubular electric furnace; simultaneously, the Se is vaporized by heating with a gas burner. The section of the quartz tube extending beyond the furnace is cooled with a cooling coil. After passing over the reaction product, most of the Se condenses in this section. After the reaction, the tube is allowed to cool and the product is repulverized; the selenation is repeated twice.

The composition of the products thus obtained varies markedly: when prepared at 800°C, the end product is $\sim VSe_{1.9}$, at 1000°C $\sim VSe_{1.4}$.

11. Heating the above products with a suitable excess of Se in a short sealed quartz tube at a temperature which, depending on the Se content, should be between 600 and 800°C affords products with a higher Se content.

III. Thermal degradation of the products of the first selenation, by heating in a high vacuum at 1000-1100 °C for several days, affords $VSe_{1.0}$.

1276

PROPERTIES:

The V-Se system has 3 stable phases with very broad homogeneity regions.

 α -Phase (VSe), from VSe_{1.0} to VSe_{1.26}. Dull-gray powder. d 5.94. B8 (NIAs) type crystal structure, with voids.

 β -Phase (V₂Se₃), from VSe_{1.25} to VSe_{1.60}. Gray powder with metallic luster. d 5.87.

 γ -Phase (VSe₂), from VSe_{1.62} to VSe_{1.67}. Gray, small, leaflike crystals with metallic luster. d 5.79. Crystal structure: C6 (CdI₂) type.

REFERENCE:

E. Hoschek and W. Klemm. Z. anorg, allg. Chem. 242, 49 (1939).

Vanadium (II) Sulfate

VSO4 · 6 H₄O

Produced by electrolytic reduction of VOSO $_{4}$ followed by ethenol precipitation of VOSO $_{4} \cdot 6$ H₂O from the resulting vanadium (II) solution.

 $VOSO_4 \cdot 3 H_2O \rightarrow VSO_4 \cdot 6 H_2O$ 217.1 255.1

A) ELECTROLYTIC REDUCTION

The electrolysis vessel consists of a glass cylinder, 5 cm. in diameter and 10 cm. high, such as, for example, a small Pyrex pressure vessel. This vessel is closed with a five-hole rubber stopper to accommodate the cathode stem, thermometer, diaphragm, and N_2 inlet and outlet tubes. A suitable outlet tube is a small fermentation tube, which serves as protection against air and should, if possible, be drawn out into an outward-pointing capillary.

The cathode is made by bending a lead strip $(3 \times 25 \times 80 \text{ mm.})$ into a cylinder so that it encloses the diaphragm. A hole is then drilled near one end of the Pb strip, and a lead rod (serving as a bus bar) is attached to it by hammering in place. The anode also consists of a lead rod, which can be prepared by pouring molten Pb into a glass tube, while cautiously fanning the latter with a flame, and then cooling and breaking the tube. Prior to electrolytic reduction, the cathode is pretreated, according to the method of Tafel, by using the cathode as an anode in 2N H₂SO₄, until it is uniformly coated with brown PbO₂. The disphragm consists of a glass tube, about 16 cm. long and 2 cm. LD., with a fine fritted-glass disk sealed to its lower end. A 2M VOSO₄ solution, which is also 2N in H_2SO_4 , is prepared by dissolving 66 g. of VOSO₄ · 3 H_2O (for preparation, see p. 1285) in H_2O , adding 8.5 ml. (15 g.) of conc. H_2SO_4 , and diluting to 150 ml, with H_2O .

The diaphragm is filled with 6N H_2SO_4 to the level of the VOSO₄ solution in the cathode space. This is best done by pouring both solutions in at the same time. Electrolysis is started at 0.3 amp. and about 5 v. Cooling is unnecessary, since the temperature does not exceed 30°C. If the current should exceed 0.3 amp, during the first few hours, it must be readjusted to this value. During the intermediate reduction period, the current drops to 0.2 amp., while the voltage increases. The current should, however, not be raised to 0.3 amp. During reduction, the dark-blue VOSO₄ solution first turns dark blue-green, then later dark and opaque. In the final reduction period the current again rises while the voltage drops. Reduction is complete when the solution is red-violet. Reduction time: 55-60 hours. During electrolysis, a slow stream of O_2 -free N₂ or CO₂ is passed through the electrolyte at the cathode.

If only the reduced vanadium (II) solution is needed and precipitation of crystalline VSO₄ is not desired, the electrolyte solution can be protected from atmospheric O_2 in a simpler fashion, by covering it with a xylene layer about 2 cm, deep.

If desired, the electrolysis may be continued at 0.01-0.02 amp, and 3 v. for several months; a completely reduced VSO₄ solution is thus always available for use. To remove solution as needed, the gas outlet tube is pulled out of the rubber stopper and a pipette inserted in its place. Virtually no oxidation takes place if the VSO₄ solution aspirated into the pipette is immediately allowed to run out into another vessel under an inert gas blanket.

A low current density is necessary in order to obtain a relatively concentrated VSO_4 solution with a minimum H_2SO_4 content, as required for the precipitation with ethanol described below.

B) PRECIPITATION WITH ABSOLUTE ETHANOL

The glass apparatus shown in Fig. 303 is suitable for the isolation of crystalline VSO₄. Its main section is adapter k, bent at an angle of about 100°. The ends of k are connected via standard taper joints to the other parts of the apparatus. The joints are lightly lubricated with stopcock grease. The entire apparatus is fastened to a cross-shaped supporting rack of iron bars by means of two common clamps (not shown in the drawing), one holding the meck of the round-bottom flask p and the other the receiver m. The rack can be rotated, with moderate resistance, about its axis (which is perpendicular to the plane of the drawing).

The gas inlet tube e is connected via a pressure hose to a twoway stopcock which connects the system either to an oil-type vacuum pump or to a source of pure, P_2O_5 -dried N_2 . The N_2 must be very pure; it is pressurized to 0.2 atm. gauge by means of a Hg or H_2O leveling device (2-m. water column), and then introduced into the apparatus. A two-liter flask, serving as a N_2 surge vessel, is inserted between the N_2 purifier and the P_2O_5 drying train.

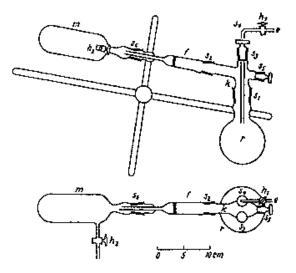


Fig. 303. Preparation of vanadium (II) sulfate. k) bent adapter; s_1) 29/25 joint; s_2) 24/25 joint; s_3 and s_4) 12/18 joints; e) gas inlet tube with stopcock h_1 ; r) 250-ml. round-bottom flask; f) tubular adapter with fritted-glass disk; m) receiver; h_1 and h_2) stopcocks.

The apparatus is completely purged of air by alternate evacuation and flushing with nitrogen. Then 20 ml. of 2 M VSO₄ solution is removed from the electrolysis vessel with a pipette, the stopper ϵ_{3} is removed, the pipette is immediately inserted through this opening until it almost touches the bottom of flask τ , and the solution is allowed to flow out. With stopcock h_1 open, the filling operation is carried out in a countercurrent nitrogen stream.

In the same manner 40 ml. of absolute ethanol, previously deaerated by boiling while passing through pure dry nitrogen, is added to flask r. Stopper s_3 is immediately closed, and the entire apparatus vigorously shaken for 5 minutes by a back-and-forthe movement of the cross arm. Solid, granular VSO₄ · 6 H₂O begins to precipitate within a few seconds. Stoppoock h_2 is now connected

via a rubber hose to a wash bottle containing some water and also serving as a bubble counter and liquid seal. With stopcocks h_1 and As open, the pale-purple mother liquor is decanted by carefully tilting the cross arm. The salt precipitate in r is washed by vigorous shaking with the liquid quantities indicated below and decanting the used liquid before each new addition. The wash liquid is introduced, as indicated above in the case of the VSO4 solution, in a countercurrent N_2 stream by means of a pipette inserted through s3. The wash liquids are introduced in the following order: 2 × 15 ml. of deaerated absolute ethanol; 25 ml. of the same ethanol plus 10 ml. of absolute ether; 10 ml. of ethanol plus 25 ml, of ether; 5 ml, of ethanol plus 15 ml, of ether; 3 ml, of ethanol plus 25 ml, of ether. Finally the salt is transferred onto the fritted-glass filter f with an additional 25 ml. of absolute ethyl ether. The ether adhering to the substance is removed by continuing the N₂ purge stream (about one hour). Flask m is replaced with the Ng-filled drying vessel t shown in Fig. 304 while continuing the Na stream via ha. Vessel t is charged to one third of its capacity with a P2O5-pumice drying mixture, and any oxygen present in the latter is removed by alternate evacuation and purging with N₂. Then the drying vessel and the tube / are detached from adapter k at joint s_2 , f is immediately closed off with a ground stopper, and the system is connected to the oil vacuum pump by way of h_3 (resetting the two-way stopcock). After evacuation, stopcock h₃ is closed and the drying vessel with the product is allowed to stand for 5 days at 25 °C (drying can also be accomplished, without the PaOs-pumice mixture, by immersing the evacuated drying vessel in liquid nitrogen). The light red-violet product is stored in container n, shown in Fig. 304, which provides protection from oxygen and enables one to remove the product when desired. To transfer the product to n, the latter is evacuated, then filled with N2; the drying vessel is also filled with N₃ through h_3 , the glass stopper is removed from f, and the storage container n (which carries a male joint), from which the two-joint adapter and bent tube p have just been removed, is inserted in its place. During this operation, the Na stream is introduced via stopcock h₄ of the storage container, as well as via h_3 . The substance is transferred to n from the fritted-glass tube i by turning the tube upside down. The storage container is then detached from the tube and closed off with the two-joint adapter and bent tube p. To remove any O2 entrained during the transfer, container n is immediately evacuated and filled with N₂; these two operations are then repeated twice. Approximately 10 g. of VSO4 · 6 H₃O is obtained (90% yield, based on the 20 ml. of 2 M VSO4 solution used).

Short exposure of the product to air does not affect its storage stability provided the last traces of O_3 are removed by repeated purging of the system with N_2 . The product is stable for several months, even if frequently sampled.

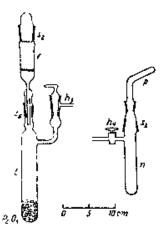


Fig. 304. Drying tube and storage container for vanadium (II) sulfate. f) fritted-glass tube as in Fig. 303; t) drying tube containing the P₂O₅-pumice mixture; n) storage tube p) bent tube for filling operations involving small amounts of substance; s_2 and s_6) standard taper joints, as in Fig. 303.

To remove some product from the storage container, the estimated amount is transferred to the bent tube p by inclining and tapping n (Fig. 304). Nitrogen is introduced via h_4 , and tube p containing the product is quickly replaced by an identical empty tube. The closed-off storage container is then evacuated twice and filled with Na; at the same time, the open, previously tared bent tube p containing the VSO . . 6 HaO is quickly weighed (to ascertain the weight of sample in it), and is then quickly connected to the Nnfilled apparatus (Fig. 303) by inserting its male joint into joint s3. By quickly turning the cross arm, the sait is poured from the bent tube p into the flask r, whereupon the system (of Fig. 303) is reevacuated via h_1 and refilled with N₂. The VSO₄ · 6 H₂O can then again be dissolved in Og-free H2O, added from a pipette in a countercurrent stream of Ng. In this manner, an HaSO -free solution of VSO, is obtained; this can be used to prepare other vanadium (II) compounds in the same apparatus while retaining the certainty that air is completely absent.

Alternate method: A solution of VO in H₂SO₄ is prepared in the absence of air, and is then evaporated in vacuum [C. M. French and J. P. Howard, Trans. Faraday Soc. 52, 712 (1956)]. PROPERTIES:

Light red-violet, fine crystalline powder, oxidized to brown even in dry air. Readily soluble in descrated H_3O , yielding a red-violet solution.

A heptahydrate $VSO_4 - 7 H_2O$ may also be formed under other conditions.

REFERENCES:

J. Dehnert. Thesis, Univ. of Jena, 1952 S. Herzog. Z. anorg. allg. Chem. <u>294</u>, 155 (1958); L. Malatesta. Gazz. Chim. Ital. <u>71</u>, 615 (1941); J. Meyer and M. Aulich. Z. anorg. allg. Chem. <u>194</u>, 278 (1930); A. Piccini and L. Marino. Z. anorg. Chem. <u>50</u>, 49 (1906).

Hydrogen Disulfatovanadate (III)

HV(SO₄), · 4 H₂O

A paste obtained by stirring 10 g. of V_2O_5 and 36 g. of conc. H₂SO₄ is heated for a while on a water bath and allowed to stand until the next day. The mixture is then treated with 80 ml. of H₂O and reduced on the water bath by bubbling through it a stream of SO₂. Reduction to VOSO₄ is complete in a few minutes. Excess SO₂ is bolled off and the product electrolytically reduced to the trivalent state, using the apparatus described for ammonium vanadium (III) alum (p. 1284). The resulting green solution is filtered on a fine-pore fritted-glass disk and allowed to stand in a vacuum desiccator over H₂SO₄. After a few days, a green crystalline powder separates out; it is stirred with a large quantity of ethanol, suction-filtered and then thoroughly washed with ethanol. The product is dried over H₂SO₄ in a CO₂-filled desiccator.

SYNONYM:

Disulfatovanadic (III) acid.

PROPERTIES:

Formula weight 316.14. Green crystalline powder; can be stored for extended periods of time in closed bottles even in the presence of air.

Other compounds: The above procedure yields $NH_4V(SO_4)_2$ 4 H_2O when 12 g, of NH_4VO_3 is used in place of 10 g, of V_2O_5 .

The hexahydrate, $HV(SO_4)_3 \cdot 6 H_3O$, is formed if 150 g. of H₂SO₄ is used; the salt $NH_4V(SO_4)_3 \cdot 6 H_3O$ results when NH_4VO_3 is reacted with the stoichiometric amount of H_3SO_4 .

Sulfates of trivalent vanadium can be obtained using hydrazine as the reducing agent and glacial acetic acid as the reaction medium. An intermediate, $V(CH_3 COO)_3$, is formed under these conditions. Hydrates of $V_2(SO_4)_3$, for example, $V_2(SO_4)_3 \cdot 9 H_2O$, can be prepared in this manner.

The anhydrous compounds $HV(SO_4)_2$ and $V_3(SO_4)_3$ can be prepared by using conc. H_2SO_4 , or by thermal dehydration. See Meyer and Markowicz.

REFERENCES:

J. Meyer and E. Markowicz, Z. anorg. alig. Chem. <u>157</u>, 211 (1926); J. T. Brierley, J. Chem. Soc. <u>49</u>, 823 (1886); A. Stähler and H. Wirthwein, Ber. dtsch. chem. Ges. <u>38</u>, 3970 (1905); J. Dehnert, Personal communication, 1951.

Ammonium and Potassium Disulfatovanadate (III)

NH₄V(SO₄)_b KV(SO₄)_b

NH4V(SO4):

A paste prepared by stirring 12 g, of NH_4VO_3 with some H_2O is slowly added to 300 ml, of 2 NH_2SO_4 . The resulting pure yellow solution is mixed with 200 ml. of saturated SO_2 solution and 40 g, of $(NH_4)_2SO_4$. The blue solution obtained is evaporated, first on a water bath, then over an open flame, until a blue sait begins to precipitate. Concentrated H_2SO_4 (30-50 ml.) is added and the heating, during which fumes are evolved, continued for a while. The mixture is allowed to cool overnight and is then taken up in H_2O . The residue is suction-filtered, triturated with H_3O , reboiled with H_2O , thoroughly washed, and then dried over H_3SO_4 in a vacuum desiccator. Yield: 4.7 g, of $NH_4V(SO_4)_2$.

KV(SO₄)₂

The K salt is prepared similarly, by evaporating a mixture of 200 ml. of 2 N H₂SO₄, 10 g. of vanadyl sulfate, 21.1 g. of K₂SO₄ and 10 ml. of sulfurous acid on a water bath, then adding 10 ml. of conc. H₂SO₄ and heating for a while, while fumes are evolved. After cooling, 400 ml. of H₂O is added and the mixture boiled for a short time. The green product is washed with H₂O, suction₃, filtered and vacuum-dried over H₂SO₄.

PROPERTIES:

Green, crystalline powder. Insoluble in H_2O and acids; attacked and decomposed by alkali. REFERENCES:

A. Sievers and E. L. Müller, Z. anorg. alig. Chem. <u>173</u>, 313 (1928);
 A. Rosenheim and H. Y. Mong. Z. anorg. alig. Chem. <u>148</u>, 25 (1925);
 V. Auger. Comptes Rendus Hebd. Séances Acad. Sci. <u>173</u>, 306 (1921).

NHAV(SO.): - 12 H2O (Alum)

A mixture of 25 g. of NH₄VO₃, 180 ml. of H₂O and a g. of cone. H-SO, (see below) is prepared with stirring. The hot mixture is treated with SO2 until a clear, dark-blue VOSO solution is formed. Excess SO₂ is boiled off; the mixture is evaporated to 120 ml. and filtered. A porous clay cylinder 5 cm. in diameter and 10 cm. high, serving as diaphragm, is placed in a Pt cup (12 cm. in diameter and 6 cm. high). The vanadium salt solution is poured into the annular space; then, 25 ml. of 10% H_SO4 and a Pt coil serving as anode are placed in the inner space, and the mixture is subjected to electrolysis for 45-50 min, at 3-4 v. and 6-7 amp. The electrolysis is continued until a pure green solution is obtained. The end-point of the reduction can be determined accurately by comparison with the color of a known vanadium (III) solution or by a control titration with KMnO4. The reduced solution is allowed to stand in a closed vessel. Crystallization of the alum is complete within 2-3 days the yield is 30-50%.

The H₂SO₄ quantity a used initially determines whether the red or the blue alum form will be obtained. When a = 20 g., pure red crystals result, whereas when a = 40 g., the crystals are pure blue.

PROPERTIES:

Red or blue crystals; effloresce slowly in air with loss of water and oxidation. At 40-50°C, the alum melts in its water of crystallization, affording a green mass. Solubility (20°C): 40 g./100 g. $H_2O.$ d 1.687.

K, RE AND Cs VANADIUM (III) ALUMS

The preparation of these compounds is similar to that of the NH₄ alum. The starting material is either V_3O_5 , which is converted to a VOSO₄ solution by treatment with H_3SO_4 and SO_3 , or a VOSO₄ compound. The stoichiometric quantity of K_3SO_4 , Rb_3SO_4 or Cs_3SO_4 is added and the mixture is then electrolytically reduced. The ease and completeness of precipitation of these alums from their green solutions increase (and their solubility decreases) is the order $K \rightarrow Rb \rightarrow Cs$.

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REFERENCES:

A. Piccini. Z. anorg. Chem. <u>11</u>, 106(1896); <u>13</u>, 441 (1897); A. Bilitemann. Z. Elektrochem. <u>10</u>, 141 (1904); J. Meyer and E. Markowicz. Z. anorg. alig. Chem. <u>157</u>, 211 (1926); H. Hartmann and H. L. Schäfer. Z. Naturforsch. <u>6a</u>, 754 (1951).

Vanadium (IV) Oxysulfate

(Vanadyl Sulfate)

VOSO4

VOSO4 · 3 H2O

A solution of V_2O_5 in pure sulfuric actid is reduced, preferably with SO_2 (which is easier to work with than oxalic actid and ethanol because its excess may be readily removed).

> $V_2O_3 + H_2SO_4 + SO_2 + 5H_4O = 2 VOSO_4 \cdot 3H_4O$ 181.9 98.1 21.9 l 90.1 434.1

Thus a stiff paste is prepared by stirring 190 g. of mildly calcined VaOs with 110 ml, of conc. HaSO, and 50 ml, of HaO; considerable heat is evolved during this operation. On the next day, 100 ml. of H₂O is added and SO₂ introduced while heating the mixture on a water bath, until nearly all of the V₂O₅ is dissolved. The dark-blue filtered solution is concentrated on a slowly boiling water (or steam) bath until a thick crystal mass is formed; the crystals are then suction-filtered and washed acid-free with 96% ethanol. The undesirable formation of a thick, blue sirup or a hard crystal cake, mentioned in the literature, seems to be due to impurities or to reaction conditions which differ from those given here; no such inconveniences are encountered when V_2O_5 , prepared from thrice-recrystallized NH4VO3, and SO3 as the reducing agent are used according to the above procedure. The bright, light-blue crystalline powder is dried over P_3O_5 in a vacuum desiccator. Yield: 235 g. of VOSO4 · 3 H2O. Evaporation of the mother liquor affords another crop of less pure vanedyl sulfate. S. Come S.

PROPERTIES:

Sky-blue crystalline powder. Readily soluble in H_2O , sparingly in ethanol. Hygroscopic; indefinitely stable in a closed bottle provided oxygen is absent.

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REFERENCES

L. Vanino. Handb. d. präp. Chemie, Anorg. Teil [Handbook of Preparative Chemistry, Inorg. Part], 3rd ed., Stuttgart, 1925, p. 677; J. Dehnert. Thesis, Univ, of Jena, 1952, and a personal communication.

VOSO, anhydrous

 $V_{z}O_{z} + 2H_{z}SO_{4} = 2VOSO_{4} + 2H_{z}O_{2} + \frac{1}{4}O_{z}$ 181.9 196.2 326.0 36.0

Analytical grade conc. $H_{3}SO_{4}$ (100 ml.) and 3 g. of $V_{3}O_{5}$ are boiled for several hours in a long-neck, round-bottom flask. The product is cooled (first in air, then in ice), and poured into 500-700 ml. of $H_{3}O$. The solid is suction-filtered until dry and washed with a large quantity of water. Since the product is still heterogeneous (yellow-brown particles, in addition to green ones), it is again subjected to the same treatment and, after suctionfiltration, dried with ethanol and ether, or over $H_{3}SO_{4}$ in a desiccator.

PROPERTIES:

Green, loose, granular to finely crystalline powder; virtually insoluble in H_2O .

REFERENCES:

A. Sieverts and E. L. Müller, Z. anorg. allg. Chem. <u>173</u>, 313 (1928); V. Auger, Comptes Rendus Hebd, Séances Acad. Sci. <u>173</u>, 306 (1921).

Vanadium Nitrides

٧N

I. If pure V metal is available, it is best to proceed via the syntheses:

 $\frac{V + \frac{1}{2}N_2}{11.2 \text{ i}} \approx \frac{VN}{51.0}; \quad \frac{V + NH_2}{11.2 \text{ i}} \approx \frac{VN}{55.0} \approx \frac{3}{51.0} = \frac{VN}{23.4 \text{ i}} \approx \frac{3}{65.0}$

which give the purest products. Depending on the metal particle size, a reaction temperature between 900 and 1300°C is required. The starting material is placed in a boat (or crucible) made of Al_2O_2 or Mo metal (see also the preparation of TiN, p. 1233, and of MoN, p. 1328). When other preparative methods are used, particularly those employing oxygenated starting materials (as in the method described below), the nitride product inevitably contains

Alternate methods:

II. Very pure NH₄VO₃ is heated for several hours at 900-1090*C in a very dry NH₃ stream.

III. VOCl₃ or V₂O₃ is heated in an NH₃ stream,

IV. $V_2O_3 + 3C + N_2 = 2VN + 3CO$.

V. Deposition from gas phase on an incandescent wire; the gas contains VCl₄, H₂ and N₃, (see also TiN, p. 1233).

V.N

I. Vanadium nitride, VN, is intimately mixed with the stoichiometric quantity of V metal powder; either the loose or the compacted mixture is then heated at 1100-1400°C in an Al₃O₃ or Mo crucible under Ar.

PROPERTIES:

Dark, submetallic materials.

VN: M.p. 2050°C; d 6.04. Homogeneity region: VN₂₋₀₀⁻⁻ VN_{0.71}. Crystal structure: B1 (NaCl) type.

 $V_{a}N$: Homogeneity region: $VN_{0.60}$ - $VN_{0.37}$. Crystal structure: L 3 type.

REFERENCES:

- I, II. H. Hahn. Z. anorg. Chem. <u>258</u>, 58 (1949); V. E. Epelbaum and A. Brager. Acta Physicochim. URSS <u>13</u>, 595 (1940); W. D. Schnell. Thesis, Univ. of Freiburg i. Br., 1960.
- HI. H. W. Roscoe, Ann. Pharm. Suppl. <u>6</u>, 114(1868); <u>7</u>, 191 (1870); N. W. Whitehouse, J. Soc. Chem. Ind. <u>27</u>, 738 (1907).
- IV. E. Friederich and L. Sittig. Z. anorg. allg. Chem. 143, 293 (1925).
- V. A. E. van Arkel and J. H. de Boer. Z. anorg. allg. Chem. 148, 345 (1925); K. Moers. Z. anorg, allg. Chem. 198, 243 (1931).

Vanadium Phosphides

VP, VP, VP

Vanadium phosphides are synthesized from the purest V metal available and P.

 $V \div 2P = VP_{t}$; $V + P = VP_{t}$ 51.0 62.0 113.0 51.0 81.0 82.0

Phosphorus and vanadium, the latter contained in an Al_29 ; crucible, are placed in a quartz tube of the type used for the "Faraday synthesis" (see p. 76 f.). The tube is thereughly evacuated, melt-scaled and then beated for 24-48 hours in such a

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way that the average temperature of the metal is 700-1000°C and that of the P is 480-550°C. To achieve homogeneous products and high P contents, the reaction must be carried out in stages, with intermediate grinding of the materials. Atmospheric oxygen must be carefully excluded during the grinding, to avoid appreciable absorption by the products.

The V-P system contains the phases VP₂ and VP, as well as several phases in which the P content is low.

In the preparation of VP_3 , an excess of P must be used from the very start because VP, once formed, reacts extremely slowly with additional phosphorus.

The vanadium phosphide VP can be obtained not only via the above synthesis, but also by thermal degradation of VP_3 at 700-900°C (vacuum).

Lower phosphides (including V_3P) are obtained by synthesis from the elements or from VP and V.

Alternate method: Electrolysis of V_2O_5 -containing phosphate melts, with cathodic reduction to vanadium phosphides [M. Chène, Comptes Rendus Hebd. Séances Acad. Sci. 208, 1144 (1939); Ann. chimie [11], 15, 272 (1941)].

PROPERTIES:

Dark-gray substances; the lower phosphides have a submetallic luster. Not attacked by dilute H_3SO_4 . Attacked by conc. H_3SO_4 the more readily, the lower the phosphorus content. Incompletely soluble in nitric acid and aqua regia. Can be analyzed after decomposition by fusion with sodium carbonate-sodium nitrate.

VP: d 4.7; VPo. 35: d 5.4.

REFERENCE:

M. Zumbusch and W. Biltz, Z. anorg. allg. Chem. 249, 1 (1942).

Vanadium Carbides

VC, V_tC

I. It is probable that pure products can be obtained only by synthesis from the elements:

> V + C = VC; $2V + C = V_{s}C$ 51.0 12.0 63.0 101.9 12.0 113.9

The reactants, preferably in finely subdivided form, are intimately mixed and, if needed, also compressed into peliets. The reaction is then carried out in a high vacuum. At a temperature of 1300°C, approximately 24 hours, or at 2000°C about 15 minutes, are required for homogenization of the product. The reaction is best carried out in a graphite crucible. Alternate methods: a) The elements are combined by heating in a carbon are [A. Morette and M. G. Urbain, Comptes Rendue Hebd. Séances Acad. Sci. 202, 572 (1936)].

b) Vanadium oxides are mixed with carbon and heated in a B₂ stream or in high vacuum. Carbides of an increased degree of purity are obtained if the final temperatures are allowed to reach 1700-2100°C (see the corresponding preparation of TiC, p. 1245 ff.) [C. Agte and K. Moers, Z. anorg. allg. Chem. <u>198</u>, 233 (1931); E. Friederich and L. Sittig, Z. anorg. alig. Chem. <u>144</u>, 169 (1925); A. Morette, Bull. Soc. Chim. France [5], <u>5</u>, 1063 (1938); W. Dawihl and W. Rix, Z. anorg. Chem. <u>244</u>, 191 (1940)].

c) Vapor deposition method (see TiC, p. 1246). An H₂ stream containing VCl₄ and toluene vapors is passed over an incandescent W wire [K. Moers, Z. anorg. allg. Chem. <u>198</u>, 243 (1931)].

PROPERTIES:

Dark, very hard, chemically resistant submetallic substances. The V-C system has two phases:

VC: Homogeneity region VC_{0.92} VC_{0.74}; m.p. 2800°C. Crystal structure: B 1 (NaCl) type.

 V_9C : Homogeneity region $VC_{0.4}$ - $VC_{0.5}$. Crystal structure: L 3 type.

REFERENCES:

 A. Osawa and M. Oya. Sci. Rep. Tohoku Imp. Univ. 19, 95 (1930); Chem. Zentr. 1930, II, 298; W. Rostoker and A. Yamamoto. Trans. Amer. Soc. Metals 46, 1136 (1954); N. Schönberg. Acta Chem. Scand. 8, 624 (1954); M. A. Gurevich and B. F. Ormont. Zh. Neorg. Khimii 2, 1566 (1957); W. D. Schnell. Thesis, Univ. of Freiburg i. Br., 1960.

Dibenzenevanadium (0)

V(C₄H₆)₂

 $\begin{array}{rcl} & & & & & & \\ & & & & \\ VCl_{s} + Al + 2 C_{s}H_{s} = V(C_{s}H_{s})_{2} AlCl_{s} \\ & & & & \\ 192.8 & 27.0 & 156.2 & & 576.0 \end{array}$

 $5 V(C_{8}H_{4})_{8}^{+} + 8 OH^{-} = 4 V(C_{8}H_{4})_{8} + VO_{4}^{+} + 4 H_{8}O + 2 C_{8}H_{8}$

The reactor is a 250-ml., three-neck flack equipped with an agitator, a reflux condenser and a mercury safety valve. A mixing

1289

5 . Acti

Ser Line and

of 10 g. (0.37 moles) of dry Al powder and 4 g. (0.03 moles) of finely subdivided AlCl, and 150 ml. of absolute benzene (an excess) is added. The system is purged by introducing N₂ via the reflux condenser. The flask is equipped with a pressure-equalizing dropping funnel containing a solution of 9 g. (5 ml., 0.047 moles) of freshly distilled VCl. in 50 ml. of benzene. The flask contents are heated to a boil while stirring under a blanket of N2. The VCl. solution is then added dropwise (slowly) over a period of one hour, and the mixture is agitated and boiled for an additional 20 hours. It assumes a golden yellow color. It is allowed to cool, and the dropping funnel, the agitator and the reflux condenser are replaced (under a N₃ stream) with stoppers and a vacuum adapter. The benzene is then removed in vacuum, with heating toward the end of the distillation. The dry residue is reduced to small pieces (in the same flask and under N2). While protecting it from air. a part of the residue is then transferred to a 500-ml. separatory funnel kept under Na (which is introduced through a side tube), and covered with 200 ml. of N2-saturated petroleum ether. This is followed by repeated additions, with vigorous shaking, of 100-ml. portions of N2-saturated 1 N NaOH. After complete hydrolysis, the mixture is allowed to stand, the aqueous layer is separated, and the brown-red petroleum ether solution is washed three times (in the absence of air) with 20-ml. portions of N_2 -saturated H_2O . Hydrolysis of the remainder of the solid reaction product is carried out similarly, in 2-3 operations. The combined petroleum ether extracts are dried for 15 minutes over solid KOH and the solvent is evaporated in vacuum. The residue is sublimed at 120-150°C in high vacuum, placed in a V-shaped washing tube, washed three times with 5-10 ml, of air-free, absolute petroleum ether to remove organic impurities, and finally resublimed. Yield: 1.3-2.5 g. (13-25%, based on VCL).

PROPERTIES:

Formula weight 207.18. Brown-red to black crystalline substance. M.p. (in N₂) 277°C. Sublimes in high vacuum at 120-150°C, decomposes above 300°C. Instantly oxidized by air (decomposition). Soluble in benzene, ether, pyridine, petroleum ether and acetone; the solutions are brown-red and stable in the absence of air. Insoluble or only sparingly soluble in CCi₄ and methanol. Not dissolved or attacked by H_2O in the absence of O_2 , but decomposed in the presence of air.

REFERENCE:

E. O. Flecher and H. P. Kögler. Chem. Ber. 90, 250 (1957).

Potassium Hexathiocyanatovanadate (III)

K₁V(SCN)₁

A vanadium (III) solution is obtained from V_2O_B by reduction of the latter with SO_2 , followed by electrolysis. This solution is then reacted with KSCN:

$$V_{2}O_{3} + 5H_{2}SO_{4} + 12KSCN + 4e^{-1}$$

$$IS1.9 + 490.4 + 1166.2$$

$$= 2K_{3}V(SCN)_{5} + 3K_{5}SO_{4} + 5H_{5}O_{7} + 2SO_{7}^{2}$$

$$I033.5 + 522.3 + 90.1$$

Fine V_2O_8 powder (91 g., 0.5 moles) is stirred with 250 ml, of 4 N H₂SO₄, the suspension heated, and SO₂ introduced until a clear, pure blue solution is obtained. The mixture is heated to a boil to remove the excess SO₂ and is then concentrated to 2/3 of its previous volume.

This solution is subjected to electrolytic reduction in a cell containing a clay cylinder diaphragm; the current is 2-3 amp. at 10 v. (the procedures are those described on pp. 1277 and 1284). The electrolysis is continued until the electrolyte at the cathode shows the pure green color of vanadium (UI). The best electrodes are those made of platinum sheet.

The theoretical quantity of KSCN used depends on the volume of the cathode electrolyte and is calculated on the assumption that 6 moles (or 583 g. of KSCN) corresponds to 1 g.-atom of vanadium. This quantity of KSCN, in the form of a concentrated aqueous solution, is then added to the above electrolyte. The resulting red liquid is concentrated on a water bath; the residue is dissolved in the minimum amount of ethanol and treated with ether until K₂SO₄ no longer precipitates. The K₂SO₄ is filtered off, the filtrate is evaporated on a water bath, and the precipitation operation is repeated. The residue thus obtained (it is completely free of K₂SO₄) is recrystallized from a small amount of H₂O. Wellformed crystals of the dihydrate, K₃V(SCN)₅ · 2 H₂O, are obtained.

The anhydrous salt is obtained by drying the dihydrate over H_2SO_4 in a vacuum desicoator, finely pulverizing it, and then completely dehydrating it under vacuum (drying pistol) at 95°C until constant weight is reached.

PROPERTIES:

 $K_3V(SCN)_8 \cdot 2 H_3O$: Formula weight 552.79. Brown-red, leaflike crystals.

K₃V(SCN)e: Formula weight 516.76. Very hygroscopic.

REFERENCE:

O. Schmitz-Dumont and G. Broja. Z. anorg. Chem. 255, 299 (1348).

Niobium Metal, Tantalum Metal

Because of the tendency of Nb and Ta metal to form very stable oxides, nitrides and carbides, the difficulties in the preparation of these metals are similar to those encountered in the preparation of Ti and Zr (see pp. 1161 and 1172).

Three methods are available for industrial preparation of the pure metals. The first involves electrolysis of fluoride melts containing K_2NbOF_5 (or K_2TaF_7), as well as a certain amount of the corresponding oxides. Nb_2O_5 or Ta_2O_5 . An iron fusion pot serves as the cathode and graphite rods as the anodes. The resulting metal is a fine powder which may be separated from the admixed salt melt by a variety of processes. In the second method an oxide and a carbide, for instance $Nb_2O_5 + 5$ NbC, are mixed, compressed into pellets and heated in high vacuum to temperatures exceeding 1600°C. In the third method, a double fluoride is reduced either with liquid sodium or sodium vapor. In each case, the material is processed further via powder-metallurgical methods, by subjecting it to repeated and alternating procedures which increase density and hot degassing treatments.

I. REDUCTION WITH SODRUM OR CALCIUM

The laboratory preparation of the metal powder proceeds via reduction of the halides with sodium, calcium or CaH_2 .

Thus, for example, 50 g. of high-purity, dry K_3TaF_7 and 18 g. of Na (precut into small pieces under benzene) are placed in a heavy-wall steel vessel, tightly closed off with a well-fitting conical lid, which is fastened on with screws. The system is heated for one hour at red heat, allowed to cool completely, and reopened; the reaction mixture, which still contains some free Na, is carefully introduced, in small portions and with agitation, into 500 mJ. of H₂O. The lumps disintegrate, and the resulting metal powder is treated several times with H₂O, then hot nitric acid (d 1.2), strong hydrochloric acid (1:1) and, finally, again and thoroughly with water. It is then dried.

According to Kroll, the oxides can be reduced with calcium metal in the presence of $CaCl_2$ as the fluxing agent

| Nb ₂ O ₅ 265.8 | + | 5 Ca 200.4 | 2 Nb 185.8 | + | 5 CaO 280.4 |
|---|---|---------------|---------------|---|----------------|
| TesO5 441.9 | ÷ | 5 Ca 200.4 | 2 Ta 351.9 | ÷ | 5 CaO 280.4 |

Bedistilled Ca turnings of the best grade are used in approximately 30% excess. The presence of $CaCl_2$ is essential. For example, in a preparation of a small amount of metal, 8 g. of Mb_2O_6 (or 13 g. of Ta_2O_6), 8 g. of Ca and 15 g. of CaCl₂ are placed in a heavy-wall tubular iron crucible (25 mm, in diameter,

80 mm. long) which is filled with Ar and made gas-tight by closing it off with a welded-on (oxygen-acetylene flame) iron plug. This orucible is then heated for half and hour at about 1000-1100°C, allowed to cool completely, and sawed open. The contents are treated with water and acids, as described above. The metal powder contains some very fine particles which are best separated by decantation and discarded.

The above two methods are equally applicable to Nb and to Ta. Various modifications of these methods are possible; in particular, the reduction with Ca may be replaced by one with CaH₂ [see the corresponding procedures for Ti, methods I and II, pp. 1161-1165, as well as G. Tourné, Ann. Chim. [13], 4, 949 (1959)].

The metal powders thus obtained are not particularly pure and often contain not more than 97% of the metal, which is accompanied by hydrogen, some oxygen, and sometimes also small amounts of nitrogen, carbon and iron. The purity can be increased by repeating the treatment with the reducing metal or with CaH₃ and, also, by increasing the batch size. At any rate, it is of advantage to purify these powders further by heating them at a high temperature under vacuum, for example, via procedure II. However, the further conversion of Nb or Ta powder to the corresponding halides is not affected by the impurities, provided they are not metallic.

II. PURIFICATION BY CALCINATION

Low-purity Nb or Ta can be freed of most of its contaminants by heating to red heat in a vacuum. Both Nb and Ta have very high melting points, and thus the contaminants can simply be evaporated. In this procedure, the metal powder, pressed into oblong rods and clamped between water-cooled molybdenum jaws, is resistanceheated with a high current, or the loose or compressed metal powder is heated to red heat on a support of ThO2. W or Ta sheet. placed in a tungsten electrical heating element. The best type of heater is the furnance shown in Part I, p. 40 f., wherein a tungsten tube or a tungsten trough is used as the heat conductor. Highfrequency induction heating can also be used. in each case, a very high vacuum of at least 10⁻⁵ mm. is of controlling importance, if the purification is to be efficient. The material is first degassed by preheating it for about 1 hour at 1200°C. The temperature is then slowly increased and then maintained at 2000-2200°@. for some time (one to several hours). If this temperature is reached too quickly or if the vacuum is not good, no purification will be achieved; in addition, in the case of Nb, there will also be undesirable melting, among other things (formation of a subscitis) between metal and impurities).

III. CRYSTAL-GROWING (OR VAPOR-DEPOSITION) PROCESS

High-purity Nb or Ta can be obtained by deposition on an incandescent wire from gaseous NbCl₅ and TaCl₅, either in the presence or the absence of hydrogen. This crystal-growing process corresponds closely to that described for titanium on p. 1168 ff., particularly as far as the apparatus is concerned. Since tungsten and Nb or Ta readily form brittle alloys, a tungsten nucleating (substratum) wire cannot be used in this case; instead, one uses an approximately 0.1-mm. ϕ wire of the metal to be deposited. In addition, Ni (and not W) terminals are used, and the system is degassed by heating to red heat in vacuum before the start of the run. The chloride (NbCl₅ or TaCl₅) is introduced into the side tube and vacuum-sublimed in situ; the entire reactor system is heated and thoroughly degassed prior to sublimation, because the absence of gas is essential to the quality of the deposited metals. The reactor remains connected to the vacuum pump throughout the entire process. Vapor deposition takes place by heating the chloride and the entire vessel to about 100°C; the substratum wire is heated to 1800°C in the case of Nb, and to 2000°C in the case of Ta. The deposited metals are of very high purity.

The thickness of the incandescent wire changes continuously during the reaction, so that careful supervision of the process and good electrical control are imperative. This disadvantage is circumvented in Rolsten's modification of the process, whereby the volatile iodide of the metal is decomposed at 750-1100°C in an indirectly heated fused quartz (or Vycor) tube.

Alternate methods: a) Reaction of the chlorides with Mg [J. Prieto, A. J. Shaler and J. Wulff, Metals Technol. <u>14</u>, No. 6 (1947)].

b) Reduction of the oxides with Si while volatilizing the nascent SiO [E. Zintl et al., Z. anorg. allg. Chem. 245, 1 (1940)].

IV. COMMINUTION OF THE SOLID METAL

Commercially available solid Nb and Ta (sheet, wire, etc.) are usually far purer than the powdered material. When metal powder of very highest purity is required for the preparation of a Nb or Ta compound, solid waste pieces may be used to advantage. They are pulverized by hydrogenation at 500-600 °C (see hydrides) and cooling under H₂. The resulting hydrides are very brittle and are readily pulverized to the desired size. The powder thus obtained is then dehydrogenated at 1000 °C in an extremely high vacuum. The decrease in purity occurring during these operations is negligibly small provided very pure H₂ is used, the pulverization of the hydrides is carried out in an inert gas atmosphere, and the heating and degassing of the material is always carried out so slowly that no appreciably loss of vacuum occurs in the system (which is permanently connected to a vacuum pump).

PROPERTIES;

Nb: Atomic weight 92,91. M.p. 2468°C; d 8.58.

Te: Atomic weight 180.95, M.p. 2030°C; d 16.6.

These two metals are not attacked by mineral acids (with the exception of hydrofluoric); they are readily soluble in a mixture of concentrated hydrofluoric and nitric acids. Crystal structure: A 2 (W) type.

REFERENCES;

- General: A. E. van Arkel, Reine Metalle [Pure Metals], Berlin, 1939; H. Funk. Die Darstellung der Metalle in Laboratorium [Laboratory Preparation of Metals], Stuttgart, 1938; Ullmans Enzyklopádie d. tech. Chemie [Ullman's Encyclopedia of Industrial Chemistry], <u>12</u>, Munich-Berlin, 1960, Niobium, p. 736 ff.; G. L. Miller. Tantalum and Niobium, London, 1959.
 - K. R. Krishnaswami, J. Chem. Soc. (London) <u>1930</u>, 1277; W. Kroll. Z. anorg. allg. Chem. <u>234</u>, 42 (1937); J. W. Marden and M. N. Rich. U. S. Patent 1,728,941 (1927/29); G. Brauer. Unpublished experiments, Darmstadt, 1942; W. E. Dennis and A. F. Adamson, U.K.A.E.A. Techn. Note No. 92 (1954); E. F. Block, U.S. Bureau of Mines, paper given at the Achema meeting, Frankfurt, 1958.
 - II. H. Bückle, Z. Metallkunde <u>37</u> (Metallforschg. <u>1</u>), 53 (1946); R. H. Myers. Metallurgia (Manchester) <u>38</u>, 307 (1948); Symposium on the Metallurgy of Niobium, J. Inst. Metals <u>86</u> (1956-57); B. W. Gonser and E. M. Sherwood. The Technology of Columbium, New York-London, 1958.
- III. W. G. Burgers and J. C. M. Basart. Z. anorg. alig. Chem. 216, 223 (1934); see also the literature cited in section on Ti, method V; R. F. Rolsten. Trans. A.I.M.E. 215, 472 (1959); J. Electrochem. Soc. 106, 975 (1959); Z. anorg. alig. Chem. 305, 25 (1960).

Vanadium, Niobium and Tantalum Hydrides

After thorough degassing at red heat in vacuum, the metals are heated in an atmosphere of extremely pure H_3 . The rate of hydrogen absorption depends strongly on the particle size of the metals, the metal purity and the pretreatment method. Above 460°C, even solid Nb and Ta (sheet, wire, etc.) react fairly rapidly. The rate of the reaction increases with the metal purity and is particularly high if the metal history includes a previous hydrogenation and dehydrogenation. In that case, hydrogen is sometimes absorbed even at room temperature. Both the NbH and the TaH systems may exist in two stable phases; the transitions from one to another, however, are not clearly reflected in the isotherms and isobars of the H₂ equilibrium pressure. Hence, depending on the temperature and equilibrium H₂ pressure, the hydrogenated material may contain hydrogen in all ratios up to the limiting composition, which is approximately NbH_{0.93} and TaH_{0.9} (corresponding to 112 ml, of H₂/g, of Nb and 56 ml, of H₂, corresponding to the limiting formula VH_{0.94}.

The deuterides of Nb and Ta are analogous to the hydrides prepared under the same conditions.

PROPERTIES:

Lustrous metallic or metallic gray appearance, much like that of the free metals. The lower hydrides (up to approximately $MH_{0,1}$) are quite hard but are still ductile, increasing in brittleness with increasing H content and becoming extremely brittle at high hydrogen ratios. The hydrogen can be removed in a high vacuum at temperatures exceeding 400°C, and rapidly between 800 and 1000°C.

REFERENCES:

General: D. P. Smith. Hydrogen in Metals, Chicago, 1948,

- V-H: L. Kirschfeld and A. Sieverts, Z. Elektrochem. <u>36</u>, 123 (1930); H. Huber, L. Kirschfeld and A. Sieverts. Ber. dtsch. chem. Ges. <u>59</u>, 2891 (1926); M. J. Trzeciak, D. F. Dilthey and M. W. Mallett. Batelle Mem, Inst. Rep. 1112 (1956).
- Nb-H: A. Sieverts and H. Moritz, Z. anorg. allg. Chem. 247, 124 (1941); W. M. Albrecht, M. W. Mallett and W. D. Goode. J. Electrochem. Soc. 105, 219 (1958); 106, 981 (1959);
 S. Komjathy. J. Less Common Metals 2, 465 (1960).
- Ta-H: A. Sieverts and H. Brüning. Z. phys. Chem. (A) <u>174</u>, 365 (1935); A. Sieverts and E. Bergner, Ber, dtsch. chem. Ges. <u>44</u>, 2394 (1911).

Niobium [II] Chloride

NbCl₂

 $Nb \div 2 NbCl_{3} = 3 NbCl_{4}$ 92,9 398.6 491.5

Stoichiometric quantities of Nb metal powder and NbCl₃ are weighed under anhydrous conditions, triturated and placed in a quartz tube which is closed at one end. Constrictions b and d(Fig. 305) are then made in the end of the tube and it is connected to a high-vacuum source. (It should be remembered in calculating the amount of NbCl₃ that this compound exhibits a considerable phase width and can, therefore, be of varying composition. The use of NbCl_{3.57} is particularly convenient.)

To degas the contents, the reactor is heated for 12 hours in high vacuum at 200°C and is then melt-sealed at constriction d. The reaction is completed by heating the entire tube at 800°C for two to three days. The tube is then chilled in water and the fairly volatile by-products (NbCl₅, NbOCl₃) are distilled forward into tube section c by establishing a 200/20°C temperature gradient. The NbCl₂ remains in a.

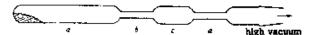


Fig. 305. Preparation of niobium (II) chloride. The quartz reactor is 8 mm. I.D. Length: a = 50 mm., c = 20 mm.

PROPERTIES:

Formula weight 163.82. Black-brown crystals. Stable in air, insoluble in H_2O and organic solvents. When heated in an evacuated tube, the NbCl₂ decomposes at a temperature gradient of 800/550°C via the equilibrium reaction: 4 NbCl₂ = Nb + 3 NbCl_{2, 87}; at a temperature gradient greater than 800/20°C, the reaction is: 2 NbCl₂ = Nb + NbCl₄. Heating in air produces NbOCl₃ and Nb₃O₅.

REFERENCES:

H. Schäfer and K. D. Dohmann. Z. anorg. allg. Chem. 300, 1 (1959); H. Schäfer and F. Kahlenberg. Z. anorg. allg. Chem. 305, 291 (1960).

Niobium (III) Chloride

NbCl₂

I.

 $NbCl_{s} + H_{s} = NbCl_{s} + 2 HCl_{270.2} + 22.4 i. 199.3 + 72.9$

High purity, oxygen-free hydrogen is passed through a vessel containing NbCl₅ heated to 150-190°C. The gas stream then passes through a Pyrex or Vycor tube heated to 400-530°C and solid precipitate of green-black NbCl₃ deposits on the walls-Complete conversion of NbCl₅ to NbCl₃ may be achieved, provided the gas rate is low. The lower partial pressures of NbCl₅ (at a saturation temperature of 160°C) and the higher temperature of the reaction zone (that is, 530°C) lead to a limiting composition which is low in chlorine (NbCl_{2,67}). Brubaker and Young prepared NbCl₅ from Nb metal and Cl₂ in the apparatus shown in Fig. 310; they then allowed it to sublime in an H₂ stream through constriction c into the right-hand tube, which was beated to 500°C and equipped with a cold finger. The NbCl₃ separated both as a dark crust on the tube wall and as a coneshaped deposit on the cold finger. The product may be pyrophoric when prepared by this procedure; it should, therefore, be handled only under a protective N₃ blanket.

II. $3 \text{ NbCl}_{s} + 2 \text{ Nb} \neq 5 \text{ NbCl}_{s}$ 3 Si0.6 185.8 396.4

High-surface No metal (e.g., foll) and a slight excess of NbCl. are placed in an evacuated reactor tube which is then sealed. (The NbCis can be prepared in the reactor itself before introducing the No metal: this can be accomplished by reacting weighed amounts of Nb 205 and CCl4-see preparation of NbCl5, method III.) The sealed borizontal reactor is heated for three days in a temperature gradient such that the end of the tube containing Nb is at 390°C. while the remainder of the tube is at 355°C. The contents are thus converted to NbCla, which, as a result of the reversible equilibrium NbCl_a (solid) + NbCl₅ (gas) = 2NbCl₄ (gas), is transported into the 355°C zone where it deposits as crystals. It can then be resublimed by reversing the temperature gradient. At the end of the procedure, only the part of the tube containing the NbCla is heated for a few minutes to 390°C while keeping the other end at 20°C, thus driving the NbCl₅ to the cold end. The tube is allowed to cool and is then opened under anhydrous conditions.

The partial pressure of NbCl₅ and, hence, the composition of the NbCl₅ phase can be varied in this synthesis by varying the ratio of the NbCl₅ to the volume of the sealed tube (saturation pressure of NbCl₅ at 355°C is 8 atm.).

III. $3 \text{ NbCl}_{s} + 2 \text{ Al} = 3 \text{ NbCl}_{s} + 2 \text{ AlCl}_{s}$ $810.6 \quad 53.9 \quad 597.8 \quad 266.7$

Sublimed NbCl₅ is heated with a less than stolchiometric quantity of Al powder in an evacuated, sealed tubular reactor. For example, 1.2 g, of NbCl₅ and 0.08 g, of Al may be used. The entire length of the tube is heated to 275°C for about 40 hours. It is then placed in a temperature gradient, with the main section encased in an aluminum block at 300°C and the protruding end at room temperature. The partially formed NbCl₄ decomposes into NbCl₅ and NbCl₅, the excess NbCl₅ and AlCl₃ sublime into the tube end, while the green-black NbCl₃ remains in the main (lower) section of the tube. It is recovered by opening the tube; no special precautions against air are needed. The product of this process usually contains a small amount of Al₂O₃ (about 0.7%) which is introduced with the Al powder.

1296

Alternate methods: a) Reduction of NbCl₅ with activated (excitation) H_2 at 200°C [V. Gatmann and H. Tannenberger, Monatsh. Chem. <u>87</u>, 769 (1956)].

b) Preparation from Nb metal in an HCl stream at 300°C. A mixture of NbCl₃ and NbCl₅ is obtained [V. Y. Spitsyn and N. A. Preobrazhenskiy, Zh. Obshch. Khimii 10, 785 (1940); C. H. Brubaker and R. C. Young (1951)].

PROPERTIES:

Green-black: crystallizes in crusts, rods, or plates. Under sufficiently high NbCl₅ pressure and in the absence of air, NbCl₅ is stable at 800°C. It disproportionates to NbCl₆ and Nb in a temperature gradient. Only slightly air-sensitive at room temperature. Insoluble in H_3O , dilute acids and dilute alkali. Attacked by oxidizing agents at varying rates depending on the concentration and the temperature. Insoluble in organic solvents, even in ethanol.

Exhibits a rather wide homogeneity region (between NbCl_{3.18} and NbCl_{3.47}), d 3.75.

REFERENCES:

- P. Süe, Bull. Soc. Chim. France [5] <u>6</u>, 630 (1939); H. Schäfer and C. Pietruck. Z. anorg. alig. Chem. <u>266</u>, 151 (1951); C. H. Brubaker and R. C. Young, J. Amer. Chem. Soc. <u>73</u>, 4179 (1951); H. Schäfer and K. D. Dohmann (1959).
- H. H. Schäfer and K. D. Dohmann, Z. anorg. alig. Chem. <u>300</u>, 1 (1959).
- III. H. Schäfer, G. Göser and L. Bayer. Z. anorg. allg. Chem. 265, 258 (1951).

Niobium (IV) Chloride

NЬСЦ

Prepared by reduction of NbCls.

I. $2 \text{ NbCl}_{s} + \text{Fe} = 2 \text{ NbCl}_{s} + \text{FeCl}_{s}$ 540.4 55.9 469.5 126.8

The reaction is carried out in a sealed tube divided into two sections by a constriction, as shown in Fig. 306. The NbCl₂ (3 g.) is introduced into the closed tube end a by connecting the tube via its still open end b to the apparatus used for isolation of NbCl₅ (Fig. 309). Pure iron (0.24 g., e.g., Armoo iron turniage or reduced iron) is placed in section b, the tube is drawn out to a

<u>,</u>:-

point, high vacuum is applied, and the tube is sealed at the point. The borisontal sealed tube is encased in two closely spaced aluminum blocks which are electrically heated to two different temperatures. The section containing NbCl₅ is heated to 195° C, and that with Fe to 400° C. The reaction time is at least 40 hours. The gaseous NbCl₅ is reduced and NbCl₄ separates as well-formed crystals in a transition region between the two temperature zones. The FeCl₂ (which at 400° C is still not very volatile) and unreacted NbCl₅ are found in the other sections of the tube.

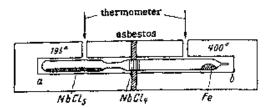


Fig. 306. Preparation of niobium (IV) chloride,

To prevent scattering of the reaction products by a rapid influx of gas (dry air, CO_2 or N_2) while opening the evacuated tube, the tip of the tube should be scratched, placed in a slightly larger vacuum hose, and broken off under vacuum. The tube may then be gradually filled with gas through the vacuum hose. To isolate the NbCl₄, the tube is then broken at an appropriate spot.

II. The NbCl₅ can also be reduced with Nb metal.

 $4 \text{ NbCl}_{s} + \text{ Nb} = 5 \text{ NbCl}_{4}$ 1080.8 92.9 1173.7

Thus, NbCl₅ and an excess of Nb metal are sealed into a tube described in method I and heated in the same temperature gradient; the reaction is complete in about 16 hours.

Alternate methods: a) Reduction of NbCl_s with Al metal; requires a subsequent distillation of excess NbCl_s and AlCl₃.

b) Reduction of NbCl₅ with H_2 at 2 atm. (generated when the tube is filled at STP, sealed and then heated). The reaction does not go to completion and NbCl₅ and NbCl₄ must be separated by sublimation.

c) Reaction of NbCl₅ and NbCl₃; as in most methods, an excess of NbCl₅ is usually required to depress the decomposition of NbCl₄.

PROPERTIES;

Brown-black crystal needles; pure brown in transmitted light. Sublimable at about 275°C, provided decomposition into NbCl5 and

1300

NbCl₃ is prevented by a sufficiently high NbCl₅ pressure. Decomposes on exposure to air and moisture (color change first to black, then to white). Dissolves in a small amount of H_3O and in dilute hydrochloric acid, giving a dark-blue solution.

REFERENCES:

I.

H. Schäfer, C. Göser and L. Bayer, Z. anorg. allg. Chem. <u>265</u>, 258 (1951); data from the Chemical Laboratory of the University, Freiburg i. Br., 1952; H. Schäfer, L. Bayer and H. Lehmann. Z. anorg. allg. Chem. <u>268</u>, 268 (1952).

Tantalum (IV) Chlorida TaCk

 $4 \text{ TaCl}_{0} + \text{ Ta} = 5 \text{ TaCl}_{0}$ 1433.0 181.0 1814.0

A quartz reactor tube with a narrow hooked constriction, shown in Fig. 307 (I), is thoroughly degassed by heating in a high vacuum; then, 4 g. of Ta metal (preferably foil) and 10-15 g. of TaCl₅ are introduced into the tube on opposite sides of the constriction, and the tube is sealed under high vacuum. It is then heated in a slanted position in a temperature gradient so that the liquid TaCl₆ (in the higher end of the tube) is at 280°C and the Ta at 630°C. The nascent

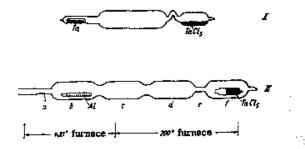


Fig. 307. Preparation of tantalum (IV) chloride, b) aluminum foil; f) TaCl₅.

TaCl, deposits in the 280° zone (large crystals) but is separate from the TaCl₅. A six-day runyields 8-10 g.; there is also a residue, of unreacted starting materials. Before opening the tube, the reactor is cooled, and the section containing TaCl₄ is reheated to 200°C to separate any admixed TaCl₅ by sublimation. The opening of the tube and handling of TaCl₄ should be carried out in the absence of moisture. Ľ,

 $ST_{a}Cl_{a} + Al = ST_{a}Cl_{a} + AlCl_{a}$ 1074.7 27.0 968.3 183.4

The reaction is carried out in a sealed reactor tube (Fig. 307, II) in a high vacuum. Aluminum foil (for example, 50 mg.) is introduced at b, while TaCl₅ (4-5 g.) in an ampoule is at f; both are introduced under anhydrous conditions. The TaCl₅ is made to sublime (in high vacuum) toward tube section d, and the tube is sealed off at constrictions a and c. The sealed tube is heated for TO hours in a temperature gradient (see Fig. 306) such that b is at 400°C and the remainder of the tube at 200°C. The TaCl₄ deposits at c as large orystals. The tube is allowed to cool and only section c is reheated to 200°C to remove any TaCl₅ present in it.

III. $TaCl_{s} + H = TaCl_{s} + HCl_{358,2} = 322.8$

Whereas TaCl₃ reacts with molecular H_2 only at temperatures exceeding 500°C (to form Ta metal), the reduction of TaCl₄ with H_2 activated by a high-frequency electrical discharge can be carried out at 200°C. The apparatus is the same as that for the preparation of TaBr₄ (Fig. 311) and the process is the same in all its details. A two-hour run completely reduces 1 g. of TaCl₅.

PROPERTIES:

Brown-black crystals. Moisture-sensitive; decomposes with oxidation on exposure to air. On heating in vacuum, disproportionates to $TaCl_5$ and a lower chloride; on heating in air forms Ta_2O_5 and volatile $TaCl_5$. Partly soluble in H_3O and dilute acids, yielding coffee-brown solutions; an insoluble dark material is also formed.

REFERENCES:

- I. H. Schäfer and F. Kahlenberg. Z. anorg. allg. Chem. <u>305</u>, 178 (1960).
- **II.** H. Schäfer and L. Grau. Z. anorg. allg. Chem. 275, 198 (1954).
- III. V. Gutmann and H. Tannenberger. Monatsh. Chem. 87, 769 (1957).

Niobium (V) and Tantalum (V) Chlorides

NbCl_s, TaCl_s

NI-CL

L

Nb + $\frac{\delta}{t}$ Cl₂ = NbCl₆ 92.9 S6 l, 270.2

Nichtum metal, either as a powder or as a solid, can be readily chloringted in a Cl₂ stream. The reaction is best carried out in a tube similar to that shown in Fig. 312 (preparation of NbBrs); how 4 ever, the saturation tube is replaced by a T connector through which the sealed tube can be evacuated or dry N2 or Cl2 introduced. The end arrangement of the apparatus varies depending on the expected amount of NbCl₅. Air must be carefully displaced by evacuation or purging with N_2 . The reaction with Cl₂ starts at 125-240°C; at 240°C, it takes only a few fours regardless of the No particle size. The absorption of Cl₂ is usually quite rapid. The NbCl₅ product is taken out under anhydrous conditions and resublimed in an appropriate manner (the apparatus of Fig. 308 can be used).

И.

$$Nb_{3}O_{5} + 5 SOCl_{2} = 2 NbCl_{5} + 5 SO_{2}$$

265.6 594.9 540.4 320.3

A common, carefully dried bomb tube is charged with 2.7 g. of Nb₂O₅ and 10 ml. of SOCl₂. Care should be taken in the preparation of Nb₂O₅ (from precipitated hydrated oxide) not to exceed 400°C, since excessively calcined oxide is inactive and reacts incompletely.

vacuum

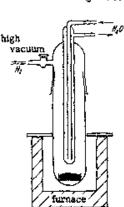
Fig. 308. Resublimation of ntobium and tantalum pentahalides under aphydrous conditions.

Thus, if the oxide is excessively caloined, it is fused with KHSO 4. the melt hydrolyzed, the hydrated oxide precipitated with ammonia and then dried for a long time at about 400°C. Before use, the SOCl₂ is purified by first refluxing it for 4 hours in the presence of S and then fractionally distilling it in a column [D. L. Cottlet, J. Amer. Chem. Soc. 68, 1380 (1946)).

The filled and sealed tube is heated for 3 hours at 200°C. On slow cooling, NbCis crystallizes in needles. The tube is cooled to -10°C, opened, and the SOg dise charged by heating to room temperature; the excess SOCl, is removed by further slight heating in vacuum. To achieve this, as well'as for the further handling of NbClist

the apparatus shown in Fig. 309 is attached to the open bounds: Because of the high sensitivity to moisture exhibited by NoCla, ites absolutely necessary to equip the apparatus with devices which permit handling of the product in such a way that even traces of moisture will be excluded. The NoCl5 remaining at a is first moved to b by subliming it under vacuum; it is then transferred to g (under nitrogen) for further handling. This is achieved his removing the ground cap c, stretching a thin perforated rubbers

1362



oup over the tube and introducing through this cap a small spatula with a long handle. Tube g of Fig. 309 is used for storing the product; it is closed at f with a ground glass stopper and permits partial removal of the chloride. Protection from moisture is provided by N₂, which is introduced through h. Naturally, other types of containers can be used instead of g, for example, a simple ampoule which is sealed off.

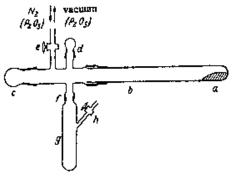


Fig. 309. Purification by sublimation and filling of a vessel with niobium (V) chloride. *a*, *b*) bomb tube; *c*,*d*) openings for introducing spatulas and long-handle hooks; g)storage vessel.

III. The oxide can also be chlorinated with CCl_4 in a similar fashion:

 $Nb_2O_3 + 5 CCl_4 = 2 NbCl_5 + 5 COCl_2$ 265.8 1269.2 540.4 494.6

In this method (which was originally developed for analytical purposes) 1 g. of oxide and 4 ml. of CCl₄ are heated for 5-10 hours at 270-300°C in a sealed tube. It is not absolutely necessary to remove the air from the tube before the reaction. After opening the tube, which should be done with the usual precautions, the reactants are distilled off. The NbCl₈ is resublimed under vacuum and isolated as described in method II. Because of the high pressures developed in the sealed tube, this method is limited to small quantities of reactants [E. R. Epperson et al., Inorg. Syntheses 7, 163 (1963)].

Alternate methods:

 $Nb_2O_5 + 5C + 10Cl_2 = 2NbCl_5 + 5COCl_2$

In this very old method, the oxide is mixed with purified sugar charcoal in a 1:4 molar ratio. The granular mixture is placed (without a boat) in a tube of high-melting (Pyrex or Vycor) glass.

1304

Beyond the mixture (in the direction of gas flow) there is a fairly long bed of pure charcoal. Before starting the chlorination, both layers are dehydrated by heating to 500°C in a stream of very pure N₂. Very pure, O₂-free Cl₂ is then passed through while heating the mixture to 280-350°C and the adjacent charcoal layer to 750°C. The NbCl₅ receiver is sealed directly onto the reactor via a constriction. During the reaction (3 hours for 8 g. of Nb₂O₅ and 32 g. of C) the constriction must be checked to make sure that it does not become plugged with NbCl₅. The formation of the byproduct NbOCl₃, which is usually difficult to avoid in this reaction, is almost completely prevented under these conditions. In spite of this, separation of the NbCl₅ from the NbOCl₃ by careful fractional sublimation is recommended. [P. Süe, Bull. Soc. Chim. France [5] <u>6</u>, 830 (1939); R. F. Rolsten, J. Amer. Chem. Soc. <u>80</u>, 2952 (1958)].

$$Nb_{s}O_{s} + 5 CCl_{s} \stackrel{(Cl_{s})}{=} 2 NbCl_{s} + 5 COCl_{s}$$

A chlorine stream containing CCl₄vapor (the stream is saturated by bubbling through a CCl₄-containing wash bottle) is reacted with the oxide held in a boat which is inserted into a tube of high-melting glass or, better, a quartz tube. The reaction temperature is 300-400°C. Quite often, NbOCl₃ is also formed as a by-product [Gmelin-Kraut, Handbuch anorg. Chem. [Handbook of Inorganic Chemistry], 7th ed., Vol. IV/1, Heidelberg, 1928, p. 236].

VI.
$$NbS_{t} + V_{r}Cl_{r} = NbCl_{s} + S_{r}Cl_{r}$$

[O. Hönigschmid and K. Wintersberger, Z. anorg. allg. Chem. 219, 161 (1934).]

PROPERTIES:

Yellow, granular to needle-shaped crystals; dark-red when contaminated with 1 mole 5 of WCl₅. M.p. 204.5°C, b.p. 254°C; d 2.75. The melt is orange.

Extremely sensitive to moisture, which rapidly converts it to the white NbOCl₃ and then to Nb₂O₅ \cdot xH₂O; hence it cannot be handled in air without marked decomposition. Reacts vigorously with water (dec.); dissolves without decomposition in ethanol, ether and, by an unknown mechanism, also in very concentrated hydrochloric and oxalic acid solutions.

TaCl,

I.

 $T_A + 4_* CI_s = T_A CI_s$ 181.0 561, 358.2

The preparation from the elements is exactly the same as in method I for NbCl₅. When Ta powder is used, the reaction starts at 170°C and is complete in a few hours at 250°C.

G. BRAUER

1306

U.

 $Ta_2O_3 + 5 SOCl_2 = 2 TaCl_3 + 5 SO_2$ 716.5 594.9 441.9

A mixture of 2.6 g. of Ta₂O₅ and 5.5 ml. of SOCI₂ (threefold excess) is heated for 6 hours in a bomb tube at 230-240°C. The preparation of the starting materials and the procedure are exactly the same as for NbCl5, method Il. The reaction yields a liquid solution of TaCl₅ in SOCl₂ from which SOCl₂ is removed by distillation in the apparatus shown in Fig. 309, while the TaCls is resublimed.

320.3

Ш.

 $T_{a_2}O_s + 5 CCl_s = 2 T_aCl_s + 5 COCl_s$ 716.5 494.6 769.2441.9

The reaction is carried out exactly as for NbCl₅, method III. the mixture being heated to 300-320°C.

Alternate methods: a) Methods IV and V for the preparation of NbCls can be applied to TaCls in exactly the same manner. Since (in contrast to NbOCIs) no tantalum oxychloride is formed, the products are fairly pure.

b) From Ta and HCi at about 400°C [R. C. Young and C. H. Brubaker, J. Amer. Chem. Soc. 74, 4967 (1952)].

c) According to Chaigneau, the reaction between Ta₂O₅ and AICL, reported by Ruff and Thomas is nearly quantitative when the reactants are used in the following proportions:

> $3 \operatorname{Ta}_{t}O_{s} + 10 \operatorname{AlCl}_{s} = 6 \operatorname{TaCl}_{s} + 5 \operatorname{Al}_{t}O_{s}$ 2149.4 1325.71333.5509.8

Before use, the AlCl₃ should be purified by vacuum sublimation. The reactants are sealed under vacuum into a tube of high-melting glass. After heating for 48 hours at 400°C, the TaCl5 product can be separated from the Al₂O₂ by vacuum sublimation at 200°C. According to Schäfer, Göser and Bayer, reaction mixtures with a different composition (2 $Ta_2O_5 + 5 AlCl_3$) yield AlOCl as the residue. Mixtures of Nb₂O5 and AlCl3 usually yield only mixtures of NoCls and NoOCl₃ [O. Ruff and F. Thomas, Z. anorg. allg. Chem. 148, 1 (1925); H. Schäfer, C. Göser and L. Bayer, Z. anorg. allg. Chem. 263, 87 (1950); M. Chaigneau, Comptes Rendus Hebd. Séances Acad. Sci. 243, 957 (1956)).

PROPERTIES-

Coloriess crystalline needles; yellow when contaminated by NbCls (even 1% NbCls imparts a definite yellow color) or tungsten chlorides. M.p. 216.2°C, b.p. 239°C; d 3.68. Very sensitive to moisture; decomposed by H2O and even by concentrated HCl, separating tantalic acid. Soluble in absolute ethanol,

ţ. Z, REFERENCE:

- I. K. R. Krishnaswami, J. Chem. Soc. (London) <u>1930</u>, 1277; K. M. Alexander and F. Fairbrother. J. Chem. Soc. (London) <u>1949</u>, 223; W. Littke. Thesis, Univ. of Freiburg i. Br., 1961.
- II. H. Hecht, G. Jander and H. Schlapmann, Z. anorg. Chem. 254, 255 (1947); J. Wernet. Z. anorg. allg. Chem. 267, 213 (1952); experiments carried out in the Chemical Laboratory of the University, Freiburg i. Br., 1951.
- III. O. Ruff and F. Thomas. Z. anorg. allg. Chem. <u>156</u>, 213 (1926); H. Schäfer. Z. Naturforsch. <u>3b</u>, 376 (1948); H. Schäfer and C. Pietruck. Z. anorg. allg. Chem. <u>264</u>, 1 (1951); <u>267</u>, 174 (1951).

Niobium Oxytrichloride

NbOCl,

1.

 $NbCl_{2} + \frac{1}{2}O_{2} = NbOCl_{2} + Cl_{2}$ 270.2 11.2 l. 215.3

About 2 g. of NbCl₅ is allowed to sublime from a side arm into a reactor tube which is approximately 20 mm. I.D. To promote good distribution of the NbCl₅, the tube contains a small amount of washed and dried glass wool. A slow stream of dry O_{3} (1=2 liters/hour) is passed through while the tube which is heated to 150°C by means of a tubular electric furnace. About 80% of the NbCl₅ reacts in 2 hours. The remainder sublimes unchanged into the cold section of the tube, from which it is driven back (vacuum) and then again treated with O_{2} . In this manner, nearly complete conversion is achieved; the nascent NbOCl₃ is sublimed in an O_{3} stream at 200°C to that section of the tube which is kept at 100°C. It deposits there as a dense crystal rosette. The material is discharged from the tube and handled under completely anhydrous conditions.

II. Prepared in a sealed tube according to the reaction:

 $Nb_{2}O_{3} + 3 SOCl_{2} = 2 NbOCl_{3} + 3 SO_{2}$ 265.8 356.9 430.6 192.2

The reaction proceeds exactly according to the stolchiometry shown by the equation. The method used for preparing the reactants is the same as that described for the preparation of NbCl₅ (p. 1303). A recommended charge for a normal bomb consists of 13.3 g. of Nb₃O₅ (1/20 mole) and 10.9 ml. of SOCl₂, prestirred into a paste.

1307

ŗ.

It is important that the reactants be intimately mixed before they are beated, because otherwise the $SOCl_3$ will react preferentially with the outer part of the oxide mass to form NbCl₅, while a large portion of the oxides will remain unreacted. The mixture is beated for about 6 hours at 200°C. After cooling, well-formed crystals of NbOCl₃ (fine needles) are found in the lower part of the tube. Purification (by sublimation) and isolation of the NbOCl₃ must be done carefully: temperatures should be held below 350°C to prevent decomposition into Nb₂O₅ and NbCl₅. This operation is best carried out in the apparatus of Fig. 309.

III.
$$Nb_2O_3 + 3 NbCl_5 = 5 NbOCl_5$$

285.8 810.6 1076.5

A glass tube is filled under vacuum with 0.3 g, of Nb₂O₅ and 3 g, of NbCl₅ (a very large excess), with the two compounds placed at opposite ends of the tube. The inclined tube is then heated in a temperature gradient (Nb₂O₅ 350°C/liquid NbCl₅ 210°C). After 12 hours, white crystalline needles of NbOCl₃ deposit in the center of the tube. Unreacted NbCl₅ is then removed by heating the tube in a 200/20°C temperature gradient. The NbOCl₃ is isolated under a blanket of dry, inert gas.

Alternate methods: a) The NbOCl₃ is often a by-product of preparative reactions for NbCl₅ [e.g., Nb₂O₅ + CCl₄, D. E. Sands, A. Zalkin and R. F. Elson, Acta Crystallogr. 12, 21 (1959)]. The separation from NbCl₅ can be achieved by repeated fractional sublimation under vacuum or in an O₂ stream at temperatures below 350°C.

b) The product can also be prepared by thermal decomposition of $NbCl_5$ etherate at 90°C. {F. Fairbrother, A. H. Cowley and N. Scott (1959)}.

PROPERTIES:

Colorless, often crystallizes in very fine needles. Vapor pressure: 10 mm. (234°C); 760 mm. (335°C). Disproportionates into Nb₂O₅ (or Nb₂O₇Cl) and NbCl₅ above 350°C. Best purified by vacuum sublimation at 200°C. Very sensitive to moisture; decomposed by H₂O. Tetragonal crystals.

REFERENCE:

- P. Süe, Bull. Soc. Chim. France [5] 6, 830 (1939); F. Fairbrother, A. H. Cowley and N. Scott. J. Less-Common Metals 1, 206 (1959).
- II. H. Hecht, G. Jander and H. Schlapmann. Z. anorg. Chem. 254, 260 (1947); J. Wernet. Z. anorg. alig. Chem. 276, 213 (1952).
- III. H. Schäfer and F. Kahlenberg. Z. anorg. allg. Chem. <u>305</u>, 327 (1960).

, J

Niobium (III) Bromide

NbBr₂

NbBr₃ + H₂ = NbBr₃ + 2 HBr 492.5 22.4 l. 932.7 161.8

The apparatus of Fig. 310, containing boat s with the niobium metal, is dried in a stream of very pure N_3 at 200°C. Furnace o_1 is then heated to 450°C and dry Br₂ vapor is introduced in an N₂ stream. The nascent NbBr₅ condenses at a.

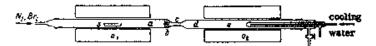


Fig. 310. Preparation of nicbium (III) bromide. s) boat containing niobium metal; b) asbestos wool; o_1, o_3) electric furnaces.

After complete bromination, the bromide is sublimed in a pure N_2 stream at 270°C, passing through glass wool plug b and the constriction c into section d. Then, a stream of high-purity H_2 is introduced and NbBr₅ is allowed to sublime slowly into tube section c, kept at 500° by means of furnace o_2 . It deposits on the tube wall as a shiny black crust and as a black cone on the cold finger. The tube is opened and the product is removed under a protective N_2 blanket. The outer crusts are not air-sensitive and are insoluble in H_2O . On the other hand, the cones deposited in the inner part of the apparatus decompose rapidly in the presence of moist air.

PROPERTIES:

Black, with varying air sensitivity, depending on preparative conditions. Almost completely resistant to H_{sO} and dilute acids. Decomposed by concentrated H_{sO4} and HNO3. Insoluble in organic solvents. Can be sublimed in a high vacuum (10^{-4} mm.) at about 400°C. Thermal decomposition into NbBr₅ and Nb begins at 900°C.

The TaBr₃ and the TaBr₃ can be obtained in the same manner as NbBr₃, starting from TaBr₅ and H₃ at 700°C; however, the purity and the yield are lower [R. C. Young and T. J. Hastings, J. Amer. Chem. Soc. 64, 1740 (1942)].

The NbBr₂ can be prepared from NbBr₃ and activated H₂ at 200°C; see preparation of TaBr₄, p. 1310 [V., Gutmann and H Tannenberger, Monatsh. Chem. <u>87</u>, 769 (1956)].

REFERENCE:

G. H. Brubaker and R. C. Young. J. Amer. Chem. Soc. <u>73</u>, 4179 (1951).

Tantalum (IV) Bromide

TaBr₄

 $T_{2}Br_{5} + H = T_{2}Br_{4} + HBr_{580.5}$ 580.5 500.8

The horizontal reaction tube of high-melting glass (about 3 cm. I.D. and 50 cm. long) shown in Fig. 311 is heated in vacuum, and a boat containing TaBr₅ is introduced under anhydrous conditions. High-purity, dry H_2 is passed through the tube at a rate of about one liter per hour.

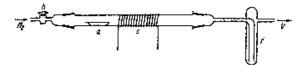


Fig. 311. Preparation of tantalum (IV) bromide. a) boat containing TaBr₅; f) cold trap; h) grooved stopcock for fine flow regulation; s) induction coll; *) vacuum.

A pressure of 4-6 mm. is maintained in the tube by means of the grooved stopcock h, which regulates the vacuum v. A glow discharge is produced by coll s, which consists of 16 turns of copper wire (2 mm. O.D.) on the outside of the tube; a highfrequency current of 4000 kilocycles/second is applied to the coll, which consumes about 20 watts. The glass wall temperature at the coil is about $180-200^{\circ}$ C. The tube section containing TaBr₆ is heated; the TaBr₅ is slowly vaporized and reacts with the H₂ activated in the glow discharge zone. The nascent TaBr₄ is deposited on the tube wall in this zone. Unreacted TaBr₅, which condenses on the cooler portions of the tube, can be driven back into the reaction zone and reduced by moving the induction coil to mother spot. The reaction of 0.8 g. of TaBr₅ is complete within 3 hours. The tube is allowed to cool and the product is soraped off the tube wall under anhydrous conditions.

PROPERTIES:

Black powder with steel-blue tinge. Slightly bygroscopic. Disproportionates to TaBr₅ and TaBr₅ at 300°C under vacuum, yields a brown solution and an insoluble residue with H_2O .

REFERENCE:

V. Gutmann and H. Tannenberger. Monatsh. Chem. 87, 769 (1956).

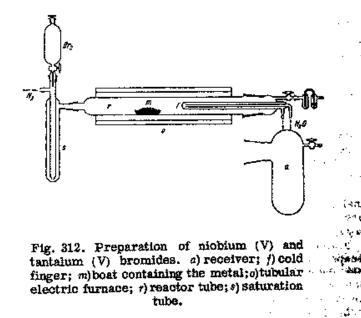
Niobium (V) and Tantalum (V) Bromides

NbBrs, TaBrs

Ι.

| Nb | ÷ | ∕₂ Br₂ | - | NbBr _s ; | Ta + | */, Br, | | TaBr, |
|------|---|--------|---|---------------------|-------|---------|-------------|-------|
| 92,0 | | 399.6 | | | 181.0 | | | 380.5 |

Pure, dry N_2 is saturated with Br_2 in a washing bottle or a saturation tube *s* (Fig. 312); the gas mixture is then passed over Nb or Ta metal contained in the horizontal reactor tube *r* made of quartz or high-melting glass. The metal may be either powder or solid.



First, the air is completely removed from the reactor. These the section of the tube containing the metal is heated by scole wound directly on the reactor, or by a tubular electric furnace o. If ND powder is used, then bromide formation begins at 90°C; with solid ND, it starts at 195°C and with Ta powder at 155°C; it is complete in a few hours at 230-256°C. The nascent bromide sublimes onto cold finger f. When larger quantities are desired, large-diameter receiver a is attached to the end of the reactor. The extremely hygroscopic bromide should be removed from the apparatus while the latter is in a dry box (Part I, p. 71).

II. $S Nb_{2}O_{3} (S Ta_{2}O_{3}) + 10 AlBr_{3} = 6 NbBr_{3} (6 TaBr_{3}) + 5 Al_{2}O_{3}$ 797.5 1325.7 2667.3 2954.9 3483.2 509.8

In the method of Chaigneau, the mixture of pentoxide and AlBr₃, in proportions indicated by the above equation, is sealed under vacuum into a Pyrex glass tube (before use, the AlBr₃ is purified by vacuum sublimation). The tube is heated for 24 hours at 200°C, and allowed to cool; the small amounts of Br₃ formed in the process and residual AlBr₃ are vacuum-sublimed at 140°C. The pure pentabalide is then separated from the Al₂O₃ by vacuum sublimation at 240°C, yielding large crystals.

III.
$$Nb_{2}O_{5}(Ta_{2}O_{5}) + 3C = 6Br_{2} = 2NbBr_{5}(2TaBr_{5}) + COBr_{2} + 2CO_{5}$$

265.8 441.9 36.0 959.0 985.0 1163.1 187.8 58.0

The bromides are prepared by a method similar to that presented for NbCl₅ (or TaCl₅) (method IV). An intimate mixture of the pentoxide with very pure charcoal (preferably sugar charcoal) is heated in a stream of inert gas (CO_2, N_2) carefully prepurified to remove traces of O_3 and H_3O and saturated with dry Br_3 in a wash bottle. There is a possibility of a side reaction leading to the oxybromide in the case of Nb₂O₅; however, this does not happen with Ta₃O₅. Wiseman and Gregory report a reaction temperature of 700-860°C in the case of Ta₂O₅. The final product is resublimed under an inert gas or, better, in a high vacuum (190-200°C); because of its high sensitivity to moisture, it should be handled only under anhydrous conditions.

Alternate methods: a) Reaction of the pentoxide with CBr₄ (analogous to that with CCl₄, see p. 1306) in a sealed tube yields pure TaBr₅ (in the case of Ta₃O₈) according to the equation: Ta₃O₅ + 5 CBr₄ = 2 TaBr₅ + 5 CO + 5 Br₃. The reactant mixture is heated for 7 days at 200°C, the gases formed are allowed to escape and TaBr₅ is vacuum-sublimed at 300°C. The yield is only about 70%. The corresponding reaction with Nb₂O₈ does not yield pure NbBr₆; instead, mixtures are formed [M. Chaigneau, Comptes Rendus Hebd, Séances Acad, Sci. <u>248</u>, 3173 (1959)].

b) The TaBrs can also be obtained from Ta and HBr at 375°C [R. C. Young and C. H. Brubaker, J. Amer. Chem. Soc. <u>74</u>, 4967 (1982)].

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PROPERTIES:

NbBrs: red crystals; m.p. 265.2°C, b.p. 361.6°C.

TaBr₅: yellow crystals; m.p. 265.8°C, b.p. 348.8°C, d 5.0.

Both compounds are very sensitive to hydrolysis, very soluble in ethanol (with a chemical reaction), and somewhat soluble in CCl₄.

REFERENCES:

- M. Alexander and F. Fairbrother, J. Chem. Soc. (London) <u>1949</u>, 223; D. H. Nowicky and I. E. Campbelli in: H. S. Booth, Inorg. Syntheses, Vol. IV, New York~London-Toronto, 1953, p. 130; R. F. Rolsten, J. Phys. Chem. <u>62</u>, 126 (1958); K. R. Krishnaswami, J. Chem. Soc. (London) <u>1930</u>, 1277; C. H. Brubaker and R. C. Young, J. Amer. Chem. Soc. <u>73</u>, 4179 (1951); W. Littke, Thesis, Univ. of Freiburg 1. Br., 1961.
- II. M. Chaigneau. Comptes Rendus Hebd. Séances Acad. Sci. 243, 957 (1956).
- III. W. K. van Haagen. J. Amer. Chem. Soc. <u>32</u>, 729 (1910); W. H. Chapin and E. F. Smith. J. Amer. Chem. Soc. <u>33</u>, 1499 (1911); E. L. Wiseman and N. W. Gregory. J. Amer. Chem. Soc. <u>71</u>, 2344 (1949).

Niobium Oxytribromide

NbOBr₁

í.

 $Nb_2O_5 + 3 CBr_6 = 2 NbOBr_3 + 3 CO + 3 Br_9$ 265.8 995.0 897.3 67.2 l. 67.2 l.

A stoichiometric mixture of Nb₃O₅ and CBr₄ is heated for 24 hours at 200°C in an evacuated, scaled tube. The tube is opened at its thin, drawn-out end, and the gases present are allowed to escape. The NbOBr₃ is then purified by vacuum-sublimation at 300°C. The yield is nearly quantitative.

II. NbBr₅ +
$$\frac{1}{2}O_{e}$$
 = NbOBr₅ + Br₂
492.5 11.21. 348.7

The apparatus is similar to that used for preparation of NbOGl₃ (method I); the NbBr₅ is heated in an O₃ stream at 150°C. About I hour is necessary for 1 g, of NbBr₈. The NbOBr₃ product is then vacuum-sublimed at 180°C into another section of the reactor and kept there at 90°C. A dense crystal deposit is obtained. The final NbOBr₃ must be isolated and handled under completely anhydrous conditions.

Alternate methods: a) Reaction of Nb₂O₅ with C and Br₃ at 540°C.

Decomposition of NbBrs etherate at 112°C [F. Fairbrother, A. H. Cowley and N. Scott (1959)].

TaOBr₃ can be prepared from TaBr₆ and O₂ at 200°C via method **II**, but cannot be sublimed without decomposition.

PROPERTIES:

Yellow-brown; moisture sensitive, fumes in moist air. Thermal decomposition into ND_3O_5 and $NDBr_5$ begins above 320°C.

REFERENCES:

- I. M. Chaigneau. Comptes Rendus Hebd. Séances Acad. Sci. <u>248</u>, 3173 (1959).
- II. F. Fairbrother, A. H. Cowley and N. Scott. J. Less-Common Metals 1, 206 (1959).

Nobium (IV), Nobium (III) and Nobium (III) ladides

NbI₄, NbI₁, NbI₂

Nhle

A tube, dried by fanning with a flame and prepared for evacuation and melt-sealing, is charged with a small amount of NbI_5 under completely anhydrous conditions.

The tube is then sealed in a high vacuum and the end containing Nbl₅ is heated to 270°C while the reactor is in a horizontal position. The liberated iodine collects at the other end, which is kept at a temperature of about 35°C ($p[I_2] = 0.8 \text{ mm.}$). The reaction time is about 48 hours. A residue of Nbl₄ remains on the spot where the starting Nbl₅ was placed; it can be sublimed at about 300°C under the above-indicated I_2 pressure.

MM,

Either Nbl₅ or Nbl₄ is heated under vacuum in a horizontal scaled tube, as described in the preparation of Nbl₄. The higher iodide is heated to 425-430 °C and the tube end in which the liberated l_{3} collects is kept at 40 °C. Reaction time is 48 hours. The Nbl₃ formed can be resublimed in the tube at 450-500 °C (partial decomposition). NbI:

A boat containing NbI₃ is heated in a stream of pure H_2 . The reaction begins at 300°C and is complete in a few hours at 400°C. Higher temperatures should be avoided to prevent reduction to Nb metal or Nb hydride (these reactions start above 400°C).

PROPERTIES:

Nbl₄: dark-gray crystalline oblong leaflets or thin needles; metallic luster. Soluble in H_2O and dilute hydrochloric acid.

NbIs: insoluble in HaO or cone. HCi.

Nb1₂: gray-black. Insoluble in organic solvents; slowly hydrolyzed by H_2O . d 5.18.

REFERENCE:

M. Chaigneau. Comptes Rendus Hebd. Séances Acad. Sol. <u>242</u>, 263 (1956); <u>245</u>, 1805 (1957); J. D. Corbett and P. X. Seabaugh. J. Inorg. Nuclear Chem. <u>6</u>, 207 (1958).

Niobium (V) Iodide

NbI,

 $Nb + \frac{5}{2}I_2 = NbI_3$ 92.9 634.6 737.5

A vertical tube of Vycor or Pyrex glass (I.D. approximately 23 mm., wall thickness 2.5 mm.) is charged with 4-12 g. of Nb metal (either solid or powder). A dense glass wool plug is placed over the charge and approximately 20 cm. from the closed tube end, followed by a 20% excess of pure, resublimed I₂ powder. The tube and its contents are thoroughly degassed in a high vacuum and melt-sealed under vacuum. Then the reactor is placed in a slightly inclined position (with the Nb metal at the higher and the I₂ at the lower end) and heated by means of two separate tubular electric furnaces (these meet at the center of the tube). The nichium is heated to 300°C and the I₂ first to 180°C and then to 250°C. The reaction is nearly quantitative after 10-15 hours and NbI₅ crystals collect in the transition zone between the two temperature regions. The yields are lower with Nb powder than with solid Nb. The reactor is broken at the center, the NbI₆48

removed under anhydrous conditions (e.g., in a dry box, see Part I, p. 71), and repeatedly rinsed with dry petroleum ether (under N_{a}) until the adhering I_{a} is removed and the petroleum ether stays coloriess. The traces of petroleum ether are evaporated in vacuum.

According to Corbett and Seabaugh, this synthesis can also be carried out in a V-shaped, closed reactor tube.

The method of reacting a pentoxide with AlI₃, used successfully for the preparation of TaI₅, yields only impure NbI₅ when Nb₂O₅ is the starting material [M. Chaigneau, Comptes Rendus Hebd. Séances Acad. Sci. <u>242</u>, 263 (1956)].

Alternate method: Repeated distillation of NbBr₅ in an HI stream (a pure product is not readily obtained, however) [W. M. Barr, J. Amer. Chem. Soc. <u>30</u>, 1568 (1908); W. K. van Haagen, J. Amer. Chem. Soc. <u>32</u>, 729 (1910)].

PROPERTIES:

Yellow leaflets or needle-shaped crystals with a brass luster. Sublimes without decomposition only under considerable I_3 pressure. Very sensitive to moisture; decomposed by H_2O , forming HI.

REFERENCE:

 F. Körösy. J. Amer. Chem. Soc. <u>61</u>, 838 (1939); K. M. Alexander and F. Fairbrother. J. Chem. Soc. (London) <u>1949</u>, 2472; R. F. Rolsten. J. Amer. Chem. Soc. <u>79</u>, 5409 (1957); J. D. Corbett and P. X. Seabaugh. J. Inorg. Nuclear Chem. <u>6</u>, 207 (1958); W. Littke, Thesis, Univ. of Freiburg 1, Br., 1961.

Tantalum (V) lodide

Tai,

1.

$$Ta + \frac{3}{2}I_{t} = TaI_{t}$$

180.9 634.8 815.5

The procedure corresponds exactly to that described for NbI₅. The tube end containing the Ta metal is heated to 300°C and that containing the I₂ first to 180, then to 250°C. The reaction is complete in 10-15 hours.

Π.

 $3 Ta_2O_5 + 10 All_5 = 6 Tal_5 + 5 Al_2O_3$ 1325.7 4077.1 4893.0 509.8

is this method of Chaigneau, a stoichiometric mixture of Ta_3O_6 and All₂, in a Pyrex glass tube, is heated in vacuum for 24 hours

23, VANADIUM, NICHIUM, TANTALUM

at 230°C. The tube section containing the reaction mixture (which by then is black) is heated further to 350°C and finally to 520°C. The Tal₅ sublimes (nearly theoretical yield) into the colder end of the tube, where it deposits as crystals.

PROPERTIES:

Shiny black rhombic crystals, subliming at 543°C. Vapor pressure: 7.6 mm. (320°C); 96 mm. (420°C); 421 mm. (500°C). d 5.80. Very sensitive to moisture.

REFERENCE;

- F. Körösy. J. Amer. Chem. Soc. <u>61</u>, 838 (1939); K. M. Alexander and F. Fairbrother. J. Chem. Soc. (London) <u>1949</u>, 2472; R. F. Rolsten. J. Amer. Chem. Soc. <u>80</u>, 2952 (1958); W. Littke. Thesis, Univ. of Freiburg i. Br., 1961.
- M. Chaigneau. Comptes Rendus Hebd. Séances Acad. Sci. <u>242</u>, 263 (1956).

Niobium (II) Oxide

NbO

I.

$NbO_1 + Nb = 2 NbO_{124.9} 92.9 217.8$

A mixture of NbO₃ and Nb metal is pulverized to as small a size as possible and then compressed into small pellets which are heated for 10-20 minutes at 1600-1700 °C in an atmosphere of very pure Ar or in a high vacuum. The best support for these pellets is Nb sheet; however, the pellets should touch this sheet only at a very few points.

II. NbO can also be prepared via a prolonged reduction of higher niobium oxides with H_2 . An especially thorough prepurification and predrying of the hydrogen is essential. The reaction is carried out at 1300-1750°C. The reduction of 0.5 g. of NbO₂ to NbO takes about 60 hours at 1350° and about 15 hours at 1700°C. It is important to follow the progress of the reduction via a periodic check on the weight of the reactants; this is because the reaction also readily yields Nb metal in addition to NbO. The metal may start to accumulate after the run is in progress for some time and, in the presence of the unavoidable trace impurities in H_{30} may be converted into Nb₂N and Nb₃C.

PROPERTIES:

Formula weight 108.91. Gray, submetallic. d 7.30. Crystal structure: special type similar to B 1 (NaCl) type.

REFERENCE:

G. Grube, O. Kubaschewski and K. Zwiauer. Z. Elektrochem. <u>45</u>, 885 (1939); O. Kubaschewski. Z. Elektrochem. <u>46</u>, 284 (1940);
 G. Brauer. Z. anorg. allg. Chem. <u>248</u>, 1 (1941).

Niobium (IV) Oxide

NbO₂

In this procedure, pure Nb_2O_5 is reduced in an H₂ stream at 1000-1200°C.

 $Nb_2O_3 + H_2 = 2 NbO_3 + H_2O_285.8 22.4 I 249.8 18.0$

The reduction time for 1 g. of oxide (contained in a boat) is 1-2 bours. Weight control is necessary, since prolonged heating at high temperatures produces some further reduction to NbO.

PROPERTIES:

Formula weight 124.91. Black powder. d 5.9. Crystal structure: C 4 (rutile) type.

REFERENCE:

P. Klinger. Techn. Mitteil. Krupp, Forschungsber. <u>1939</u>, p. 171; G. Grube, O. Kubaschewski and K. Zwiauer. Z. Elektrochem. <u>45</u>, 885 (1939); G. Brauer. Z. anorg. allg. Chem. <u>248</u>, 1 (1941).

Niobium (V) and Tantalum (V) Oxides

Commercial Nb₂O₅ and Ta₂O₅ are usually low-purity products; in particular, Nb₂O₅ often contains Ta₃O₅. They are frequently contaminated with Fe, Ti and Sp since these elements accompany Nb and Ta in the original minerals. The following methods for purifying the pentoxides are based on the assumption that the content of these impurities does not exceed a few percent.

I. PURIFICATION VIA THE CHLORIDE

a) The tantalum and the tin can be removed from commercial Nb_3O_5 (or Ta_3O_3) by converting the oxide into a chloride, followed by extraction or distillation. This method is limited to small quantities of reactants.

As we have shown in the preparation of NbCl₅ (or TaCl₆) (p. 1304) 1 g. of the oxide and 4 mi. of CCl₄ are placed in a common tubular bomb (which need not be evacuated), and chlorination is carried out while heating to $250-300^{\circ}$ C. The sealed tube is then opened, and the solid pentachloride product is extracted five times by shaking with 5-ml. portions of CCl₄, followed by phase separation. This may be done in air provided the operation is carried out quickly. The TiCl₄ and SnCl₄ are very readily soluble in CCl₄, whereas the pentachlorides dissolve less readily and leas rapidly (less than 10 mg. of chloride/1 ml. of CCl₄) and therefore remain as residues. The residues are then converted to the oxides with H_2O . Assuming complete chlorination prior to the extraction, the Ti and Sn content of the product oxides should be $\ge 0.05\%$.

b) Instead of leaching the TiCl₄ and SnCl₄ out of the chlorination product, the latter can be removed by vacuum sublimation at 0.1 mm. and 200°C (after the sealed tube is opened). In this procedure the subliming pentachlorides travel only a short distance within the tube before depositing in a cooler zone; however, the TiCl₄ and SnCl₄ are volatilized so completely that the pentoxides obtained by this procedure contain less than 0.05% of TiO₂ and SnO₂.

c) The following method, which can be used to purify Nb_2O_s (but not Ta_2O_5), has the advantage over the previously described one that it can be used with larger quantities of reactants.

The following preliminary treatments may be used:

a) Nb_2O_3 is fused with KHSO₄; the melt is allowed to cool and, after the grinding, is treated with dilute H_2SO_4 and H_2O_3 . The hydrated oxide is precipitated from the peroxide solution with SO_2 at the boiling point, the mixture is decanted, the supermatant is discarded and the aqueous slurry of the precipitate is used in further reactions.

b) Freshly precipitated hydrated oxide (or the Nb_2O_5 -KHSO₄ melt) is directly dissolved in ammonium oxalate or tartaric acid and the resulting solution of the complex is used in further reactions.

c) A hydrochloric acid solution or suspension of the ohlorination products (NbCl₅, NbOCl₃) may be the starting material.

Next, the solution (or suspension) is adjusted to a volume corresponding to a maximum concentration of 4 g. (or, even better, 2-3 g.) of Nb₂O₅/100 ml and the solution is saturated, while ice-cooling and agitating, with HCl gas as described in detail in the preparation of (NH₄)₂TiCl₆, p. 1199 ff. The suspension, as well as

the hydrated oxide precipitated during the treatment with HCL. eventually becomes clear when the solution is saturated with HCl; sometimes, however, the HCl treatment and the agitation must be quite long. Approximately three hours are required per 100 ml. Then 4 g. of solid NH₄Cl per 100 ml. is added and the mixture is agitated for approximately half an hour. The (NH4) TiCl6 and (NH4) SnCl6 precipitate up to their respective solubility limits (0.5 mg. of Ti and 0.4 mg. of Sn/100 ml.). The mixture is filtered through a small-pore fritted-glass filter (it is best to cool the filter externally with ice); the filtrate is diluted with four to five times its volume of H2O and then hydrolyzed at the boiling point. The readily filtered hydrated oxide is then calcined to the oxide. A 70-80% yield of purified Nb₂Os. containing less than 0.1% of TiO 2 or SnO 2, is obtained. The losses are due to the isomorphous occlusion of (NH4) NbOC15 by the precipitated (NH4) TiCla.

II. SEPARATION VIA THE OXALATE

Very pure niobium oxide can be obtained either from crude niobium oxide or from concentrated niobium oxide mixtures, provided the $Ta_2O_5:Nb_2O_5$ ratio is not greater than 1:4. The following method is used: Precipitated, moist hydrated oxide (equivalent to about 20 g. of anhydrous oxide) is repeatedly treated with fresh 200-ml, portions of a solution which is 2N in HCl and 5% in oxalic acid dihydrate. Each treatment involves heating the mixture for several hours on a bath at 60-70°C with stirring, followed by decantation. Most of the Ta remains in the insoluble residue, which also becomes concentrated in Ti and W; the nearly pure Nb goes into solution, always accompanied by Sa. The combined solutions are evaporated to dryness, and the residue calcined to decompose the oxalic acid. The calcination residue is rather pure Nb₂O₅, containing only about 1% Ta₂O₅ plus some alkali stemming from the starting material.

This fairly pure Nb₂ O_5 , in the form of precipitated hydrated oxide, may again be subjected to the same leaching operation, which gives a virtually Ta-free oxide.

III. SEPARATION BY EXTRACTION

The extraction of squeous hydrofluoric solutions of the pentoxides with immiscible ketones can be used with very impure starting materials. In this case there is no restriction on the permissible Nb: Ta ratio. In this extraction, the aqueous phase contains HF and either HC1, HNO_3 or H_2SO_4 ; the best purification efficiency is obtained with HNO_3 and H_2SO_4 . The coefficients for partition of Nb and Ta between the two phases depend to a large

extent on the acid concentration. The extracting agents may be methyl isobutyl ketone (MIBK) or cyclohexanone. All equipment must be made of an HF-resistant material (polyethylene or polyvinyl chloride).

The pentoxide (or a mixture of pentoxides) is dissolved in strong hydrofluoric acid and the resulting solution adjusted, by addition of H_2SO_4 , to a concentration of 100 g. of pentoxide/liter, 5.6 N HF and 9 N H_2SO_4 . This solution is extracted twice with half its volume of MIBK. The combined ketone extracts contain virtually all of the Nb and Ta originally present and are free of other metals. The organic phase is then extracted with aqueous acid as follows.

a) When the starting material is either Nb_2O_5 or an Nb-rich mixture, the organic phase is shaken with the same volume of an aqueous solution that is 3 N in H_2SO_4 and 1 N in HF. This aqueous phase then contains 90% of the Nb, but less than 0.1% of Ta. A second extraction of the ketone phase with fresh acid solution gives a second, smaller Nb fraction of lower purity. A small amount of high-purity Ta remains in the organic phase.

b) When the starting material is $Ta_{2}O_{5}$ or a Ta-rich mixture, the organic phase stemming from the first extraction is shaken with the same volume of an aqueous acid solution which is 4.5 N in H₂SO₄ and 2.8 N in HF, thus removing all of the Nb together with a small amount of Ta. The remaining ketone solution contains most of the Ta (99.9% purity).

Pure Nb or Ta is obtained from the ketone solutions by extraction with pure H_3O . The pentoxide, dissolved in the aqueous (more or less acidic) final solutions, is then precipitated with ammonia.

In special cases or when the starting materials contain a moderate Nb: Ta ratio the procedure can be modified. These modifications are summarized in the following table.

Extraction of Nb and Ta with Methyl Isobutyl Ketone (MIBK)

| Extraction system | Optimum extraction for Ta alone (from the aqueous phase) | Optimum extraction for Nb or Nb + Ta (from the aqueous phase) | | |
|---|---|--|--|--|
| (HF + HNO ₃)/MIBK (HF + H ₂ SO ₄)/MIBK (HF + HCh)/MIBK | 0.5 N HF + 1 N HNO ₃ 1 N HF + 3 N H ₂ SO ₄ 3 N HF + 3 N HCl or 3 N HF | 7 N HF + 5 N HNO3 5.6 N HF + 9 N H3SO 6.5 N HF + 7.2 N HC1 | | |

1322

Alternate methods:

IV. FLUORIDE SEPARATION BY THE METHOD OF MARICNAC

Fractional crystallization of K_3TaF_7 is accomplished by adding KF to hydrofluoric solutions of Nb and Ta, while K_3NbOF_5 accumulates in the mother liquor. This procedure is more suitable for a large-scale process than the laboratory [O. Hönigschmid and K. Wintersberger, Z. anorg. allg. Chem. 219, 161 (1934); C. W. Balke, Trans. Electrochem. Soc. 85, 89 (1944); G. S. Savchenko and Ya. V. Tananayev, Zh. Prikl. Khimii 19, 1093 (1946); 20, 385 (1947)].

V. TANNEN PRECIPITATION

Small amounts (about 1 g.) of very pure Nb_9O_5 and Ta_3O_5 can be obtained from the corresponding crude oxides via a simple fractional precipitation of oxalate complex solutions with tannin. The procedure is based on the analytical method of Schoeller (1937).

VI. SEPARATION WITH ION EXCHANGERS

The separation of Nb and Ta on an ion exchange column is promising but not yet sufficiently developed. The Nb and Ta products can be obtained in 99% purity from solutions which are 9 M in HCl and 0.05 M in HF [K. A. Kraus and G. D. Moore, J. Amer. Chem. Soc. 71, 3855 (1949); E. H. Huffman, G. M. Iddings and R. C. Lilly, J. Amer. Chem. Soc. 73, 4474 (1951); J. L. Hague, E. D. Brown and H. A. Bright, J. Res. Nat. Bur. Standards 53/4, 261 (1954); P. Münchow, Chem. Ztg. 84, 490, 527 (1960)].

PROPERTIES;

 $Nb_{3}O_{5}$: White powder turning yellow on heating: insoluble in aqueous acids other than hydrofluoric. M.p. 1495°C. Crystallizes in various modifications; does not form well-defined hydrates.

 Ta_2O_5 : White powder; insoluble in aqueous acids other than hydrofluoric. M.p. 1872°C. Crystallizes in various modifications; forms no defined hydrates.

DEFERENCES:

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 - I. E. F. Weinland and L. Storz, Z. anorg. allg. Chem. <u>54</u>, 223 (1907); H. Schäfer and C. Pietruck. Z. anorg. allg. Chem. <u>264</u>, 106 (1951).

- II. H. Schäfer, L. Bayer and C. Pietruck. Z. anorg. allg. Chem. <u>266</u>, 140 (1951); J. Wernet, Z. anorg. allg. Chem. <u>267</u>, 213 (1952).
- HI. K. B. Higbie and J. R. Werning. U. S. Bur. Min. Rep. Invest. No. 5239 (1956); E. L. Koerner, M. Smuts and H. A. Wilhelm. Meeting of Extractive Metallurgy Section of the A.I.Ch.E., Chicago, 1957; G. H. Faye and W. R. Inman. Canad. Dept. Min. Techn. Surv. Res. Rep. No. MD 210 (1957); J. L. Tews and S. L. May. U. S. Bur. Min. Rep. No. USBM-U-252 (1957); C. W. Carlson and R. H. Nielsen, J. Metals <u>12</u>, 472 (1960).

Alkali Niobates and Tantalates

Either Nb₃O₅ or Ta₃O₅ is heated with an alkali hydroxide or alkali carbonate. Salts of differing composition are obtained, depending on the reactant ratios, the temperature, and workup of the reaction product. Systematic investigation has shown that the system alkali oxide-pentoxide contains a wide range of compounds.

The thoroughly dried starting Nb₃O₅ (or Ta₄O₅) and Li₂CO₃, Na₃CO₃ or K_3CO_3 are mixed in ratios calculated to give the desired final composition; the mixtures are heated in a crucible at a slowly increasing temperature (e.g., 100°C/hour) to insure a smooth reaction without loss of reactants. The best crucible material is Pt or (particularly for mixtures with high alkali concentrations) an 80% Au, 20% Pd alloy. The temperature is increased to just below the meiting point of the mixture and kept at this point several hours; the mixture is then cooled and pulverized. The heating and pulverization are repeated an additional two times. An oxygen atmosphere is maintained over the crucible during the heating to prevent the product from splitting off oxygen.

In the preparation of the meta salts

 $Nb_2O_5 + Li_2CO_3(Na_2CO_3, K_2CO_3) \rightarrow 2 LiNbO_2(2 NaNbO_4, 2 KNbO_3)$ 106.0 138.2 295.7 327.8 \$60.0 285.8 73.9 $T_{B_2O_3} + L_{i_2CO_3}(N_{B_2CO_3}, K_2CO_3) \rightarrow 2 LiT_BO_3(2 N_BT_BO_3, 2 KT_BO_3)$ 471.8 503.9 538.1 138.2 441.9 73.9 186.0

the amount of alkali carbonate may be somewhat greater than that indicated by the 1:1 molar ratio (however, a 2:1 ratio should not be exceeded) and the reaction mixture may be extracted with warm H_2O . The meta saits remain as residues which dissolve only with difficulty. Larger single crystals of the meta saits can be obtained from a KF or KCl melt.

For information concerning polyniobates and polytantalates, see Part III. Section 3. PROPERTIES:

Colorless, crystalline compounds. The following phases are known:

11,0-Nb,05:

3 Li₂O • Nb₂O₅ (m.p. 1408°C); Li₂O • Nb₂O₅ (m.p. 1253°C); Li₂O • 4 Nb₂O₅ (m.p. 1231°C, incongruent); Li₂O • 14 Nb₂O₅ (m.p. 1268°C, incongruent).

Na 20 - Nb 205:

3 Na₂O · Nb₂O₅ (m.p. 997°C); Na₂O · Nb₃O₅ (m.p. 1422°C, polymorphous); Na₂O · 4 Nb₂O₅ (m.p. 1277°C, incongruent); Na₂O · 14 Nb₂O₅ (m.p. 1309°C, incongruent).

K₂O - Nb₂O₅:

 $3 K_2 O \cdot Nb_2 O_5 (m.p. 950°C); K_3 O \cdot Nb_2 O_5 (m.p. 1039°C, incongruent); <math>2 K_2 O \cdot 3 Nb_2 O_5 (m.p. 1163°C); K_2 O \cdot 3 Nb_2 O_5 (m.p. 1234°C, incongruent); <math>3 K_3 O \cdot 22 Nb_2 O_5 (m.p. 1279°C, incongruent); 6 K_2 O \cdot 7 Nb_2 O_5 and 7 K_2 O \cdot 6 Nb_2 O_5 (metastable, obtainable only by quenching).$

K₂O- Ta₂O₅:

 $3 K_2 O \cdot Ta_3 O_5$ (m.p. 1330°C); $K_2 O \cdot Ta_3 O_5$ (m.p. 1370°C, incongruent); $K_2 O \cdot 2 Ta_3 O_5$ (m.p. 1520°C, incongruent); $K_2 O \cdot 5 Ta_3 O_5$ (m.p. 1645°C, incongruent).

REFERENCES:

L. L. Quill. Z. anorg. allg. Chem. 208, 257 (1932); P. Süe. Comptes Rendus Hebd. Séances Acad. Sci. 198, 1696(1934); P. Süe. Ann. Chimie [11] 7, 493 (1937); F. Windmaisser. Österr. Chemiker-Ztg. 45, 201 (1942); B. T. Matthias and J. P. Remelka. Phys. Rev. (2) 82, 727 (1951); E. A. Wood, Acta Crystallogr. 4, 353 (1951); A. Reisman, F. Holtzberg, M. Berkenblit, M. Berry and E. Banks. J. Amer. Chem. Soc. 77, 2115 (1955); 78, 719, 4514 (1956); 80, 37, 6503 (1958); 81, 1292 (1959).

Peroxyniobic and Peroxytantalic Acids

HNbO, 'n H₂O, HTaO, 'n H₂O

HNbO, a H,O

 $\begin{array}{c} 2 \text{ K_sNbO}_{4} \cdot {}^{1}\!\!/_{2} \text{ H}_{2} \text{O} + 3 \text{ H}_{3} \text{SO}_{4} + 3 \text{ H}_{2} \text{O} = 2 \text{ HNbO}_{4} + 3 \text{ K}_{2} \text{SO}_{4} + 6 \text{ H}_{2} \text{O}_{2} \\ \hline 694.4 & 294.2 & 54.0 & 915.8 & 522.8 & 204.1 \end{array}$

Suffuric acid (2 N, 10 ml.) is gradually added to a solution of 2 g. of potassium peroxyniobate in 50 ml. of H_2O . The precipitate

formed (caution: this precipitate redissolves readily if there is an excess of sulfuric acid) is filtered off and washed three to four times with H_2O , ethanol and ether. The yield is poor (about 1 g. of peroxynicbic acid, in the form of a light yellow powder).

HTaO, nHO

A solution of 2 g. of K_3TaO_8 in 150 ml. of H_2O is prepared and an approximately equivalent quantity of dilute H_2SO_4 added all at once. The nascent precipitate is first centrifuged; it can then be filtered and washed with some H_3O , then with ethanol and ether.

II.
$$T_{24}O_3 + 2H_2O_2 = 2HT_8O_4 - H_4O_4$$

441.9 68.0 491.9

Tantalic acid, freshly precipitated with ammonia from a solution containing 10 g. of K_2TaF_7 , is treated with 50 ml, of H_2O and 50 ml, of 30% H_2O_3 . The tantalic acid dissolves completely within a few hours, affording a transparent, opalescent liquid. The latter is treated with equal amounts of ethanol and saturated NaCl solution. The mixture, which at first stays clear, slowly deposite out a precipitate of peroxytantalic acid, which is filtered off the next day and dried with ethanol and ether,

PROPERTIES:

White substance. Gelantinous when wet, fine powder when dry. Ta: peroxy oxygen ratio = 1:1.

REFERENCES:

A. Sieverts and E. L. Müller. Z. anorg. allg. Chem. <u>173</u>, 297 (1928); P. Melikow and L. Pissarjewsky. Z. anorg. Chem. <u>20</u>, 344 (1899).

Potassium Peroxyniobate, Potassium Peroxytantalate

K₃NbO₆, K₃TaO₆

| Nb ₂ O ₅ 265.6 | + | 6 KOH 336.6 | + | 8 H ₁ O ₂ 272.1 | - | 2 K ₃ NbO ₈ 676.4 | + | 11 H ₂ O 198.2 |
|---|---|----------------|---|--|---|--|---|------------------------------|
| Ta ₂ O ₃ 441.9 | ł | 6 KOH 336.6 | ÷ | 8 H ₁ O ₂ 279.1 | Ŧ | 2 K4TaO8 \$52.5 | + | 11 H _s O 198.2 |

KaNbOs · 1/2 HaO

I. A mixture of Nb₂O₆ (1 part) and KOH (8 parts) is fused in a silver crucible. The fused mass is dissolved in a minimum of

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H₂O. a small amount of H_2O_2 is added and the mixture heated for a short while on the water bath. The solution is filtered to remove the black Ag particles, 9-10 moles of H_2O_2 /mole of Nb_2O_3 is added, and the mixture is precipitated with an equal volume of ethanol. The precipitate is air-dried and washed with ethanol and ether; it is then redissolved in a mixture of three to four moles of H_2O_2 and 0.5 moles of KOH/mole of the Nb_2O_5 reactant and precipitated with 1-1.5 times its volume of ethanol. The precipitate is again dried with ethanol and ether.

II. The fusion step can be avoided by using freshly precipitated niobic acid or potassium niobate instead of Nb₂O₅. These compounds are dissolved in potassium hydroxide and the workup procedure is the same as that described in method I.

K₁TeO₆

Tantalic acid $Ta_2O_5 \cdot aq$. is precipitated with ammonia from a tantalum solution (e.g., that of K_2TaF_7). The precipitate is suction-filtered and washed with a large quantity of H_2O . The gelatinous intermediate, which should not be allowed to age, is added to a solution of 20 g. of very pure KOH in 250 ml. of 3% H_2O_2 (made from "Perhydrol," Merck) until the solution is saturated. Cooling to 0°C causes separation of granular peroxytantalate crystals, which are suction-filtered and dried with ethanol and ether or in a vacuum desiccator over H_2SO_4 .

The pure white crystals have a composition corresponding to $K_3 TaO_8$; the yield is poor.

KeTaOe · 1/2 HeO

A mixture of Ta_2O_5 (5 g.) with three times the stoichiometric quantity of KOH is fused in a silver crucible. The product is allowed to cool and is then dissolved in 3% H₂O₂; any separated silver is filtered off. The solution is treated first with 20 times the stoichiometric quantity of H₂O₂ and then with an equal volume of ethanol. The precipitated, fine powder of the salt is suctionfiltered and dried with ethanol and ether. Yield: 6 g. of pure white K₃TaO₆ · $\frac{1}{2}$ H₂O.

REFERENCES:

A. Sieverts and E. L. Miller. Z. anorg. allg. Chem. <u>173</u>, 297 (1928); C. W. Balke. J. Amer. Chem. Soc. <u>27</u>, 1140 (1905);
 C. W. Balke and E. F. Smith, J. Amer. Chem. Soc. <u>30</u>, 1637 (1908); P. Melikow and L. Pissarjewsky, Z. anorg. Chem. <u>20</u>, 344 (1899).

Niobium and Tantalum Sulfides

I. FROM THE METALS

In general, the synthesis from the elements gives products of any desired composition. If the reactant ratios correspond exactly to the region in which a phase is homogeneous, the product is pure; otherwise, it is a mixture of phases.

A mixture of about 1-3 g. of solid Nb metal (or, better, Nb filings or powder) and that quantity of vacuum-distilled sulfur which will give the desired product composition is placed in a quartz tube, which is then evacuated. The mixture is heated slowly and then kept at 700-1000°C for two days. Under these conditions, dpending on the temperature used, either the highor the low-temperature modification of a phase is obtained. Special conditions are required for some compounds (e.g., hexagonal NbS₂:850°C < T < 1050°C, with the niobium placed in the hottest zone of the ampoule; rhombohedral Nb_{1+x} S_a: T > 800°C, niobium in the coldest zone of the ampoule).

In no case is the sulfur quantity absorbed greater than that corresponding to the formula NoS_{2} . No preparative methods are known as yet for NoS_{3} . Traces of this compound are formed during the preparation of other niobium sulfides. The heating of mixtures low in sulfur should be occasionally interrupted, the intermediate product repulverized and remixed, then replaced in the evacuated tube, and the heating continued.

The lower sulfides may also be obtained by homogenization of the corresponding mixtures of niobium sulfide + Nb. In addition, partial degradation of the higher sulfides by distilling off the sulfur in a high vacuum also yields lower sulfides. Another preparative method is based on the reaction of Nb with H_2S at temperatures between 550 and 900°C.

The tantalum sulfides are prepared by procedures based on the same principles. Since the phase relationships are less complicated, one has greater lattitude in selecting the preparative conditions. The tantalum sulfide with the highest known S concentration is TaS_3 , which can be obtained at 600°C.

II. FROM THE PENTOXIDES

Either Nb₂O₅ or Ta₂O₅ (2-10 g.) is placed in a loose layer in a porcelain reactor tube and exposed for three to six hours at 960-1300°C to a CS₃-saturated stream of H₃S; prior to entering the tube, the latter passes through a purification and drying train, as well as through a wash bottle containing CS₂ at 25-35°C. The reactor must be thoroughly purged of air prior to the run and air leaks must be avoided during the reaction. In particular, the **H_S** must be air-free. The crude sulfides are then extracted with **CS**₂ to remove traces of precipitated S. The Nb product has the composition $NbS_{1,24}$, the Ta product $TaS_{2,0}$. It appears that no other compositions can be obtained by this method.

PROPERTIES:

The hexagonal NbS₂ and the rhombohedral Nb_{1+x}S₂ are blueblack, shiny crystalline compounds: NbS₂ single crystals 0.5 mm, in size can be obtained. The remaining niobium sulfides are dark-gray to black or dark-brown powders devoid of luster.

The TaS₂ consists of microscopically small leaflets, not appreciably volatile in vacuum up to 1100°C, whereas TaS₃ consists of a mass of loose, feltlike crystalline fibers which are always obtained when other modifications are heated for 14 days at 600°C. At 650°C, TaS₃ decomposes rapidly into TaS₂ and sulfur, which dissolves in the TaS₂. The sulfides are unaffected by hydrochloric acid and sodium hydroxide, but vigorously oxidized by hot concentrated H_2SO_4 or HNO₃.

Seven phases are known in the Nb-S system: "H-NbS" (temporary general designation, probably comprising two or more phases), hexagonal $Nb_{2-y}S_z$ (0 < y < 0.3) and the closely related hexagonal $Nb_1 S_2$ (0.3 < x < 0.43), rhombohedral $Nb_{1+x}S_2$ (0.12 < x < 0.5), hexagonal NbS₂, rhombohedral NbS₃ and monoclinic NbS₃.

REFERENCES:

- Nb-S: W. Biltz and A. Köcher. Z. anorg. allg. Chem. 237, 369 (1938); O. Hönigschmid and K. Wintersberger. Ibid. 219, 161 (1934); H. Biltz and W. Gonder. Ber. dtsch. chem. Ges. 40, 4963 (1907); G. Hägg and N. Schönberg, Ark. Kemi. 7, 371 (1954); Hörst Müller. Thesis, Univ. of Freiburg i Br., 1938; F. Jellinek, G. Brauer and H. Müller. Nature 185, 376 (1960).
- Ta-S: W. Biltz and A. Köcher. Z. anorg. alig. Chem. 238, 81 (1938); H. Biltz and C. Kircher. Ber. dtsch. chem. Ges. 43, 1636 (1910); G. Hägg and N. Schönberg. Ark. Kemi 7, 371 (1954).

Niabium and Tantalum Nitrides

I. The pure Nb and Ta nitrides are prepared by synthesis from the elements. The reactant metals should be fine powders and should be degassed by heating in high vacuum. The N₂ must be completely free of O₂ and H₂O. With fine metal powders, the reaction temperature should be 1200°C; with fillings or solid metal, it must be 1300 to 1500°C. Temperatures higher than these naturally increase the nitridation rate; however, because of equipment limitations, they are employed only in the case in which the metal, in the form of wire, is clamped onto terminals and heated electrically in an N_2 atmosphere.

Hydrides of Nb and Ta can be used instead of the metal. The hydrides lose their hydrogen during the first stages of the reaction, affording an especially reactive, fine metal powder; this, in turn, permits lower reaction temperatures. In addition, very pure $\rm NH_3$ may be used instead of N₂. The reaction of the metal with ammonia occurs at a temperature which is usually 300-400°C lower than that required for N₂.

a) Nitridation of thin metal wire can be achieved at temperatures between 1350 and 2800 °C. This procedure, which uses nitrogen under pressure, always yields products with an N content corresponding to the upper limit, NbN. The rates of reaction are high but the amount of obtainable product is obviously small. Products with a low N content can be obtained by shortening the heating period and lowering the N₂ pressure; product homogeneity cannot be guaranteed, however.

b) To obtain nitrides from metal powder, the latter is placed in a sintered alumina boat inserted into a ceramic reactor tube. Because the nitrides are so extremely sensitive to oxygen, completely oxygen-free products can be obtained only if penetration of foreign gases is reduced by using the best, least porous ceramic reactor materials. Even these exhibit some porosity, however. The best method is to insert the reactor tube into another protective tube and fill the annular space between them with very pure N_3 . The products vary in N content depending on the temperature and duration of nitridation, and can range up to NbN or TaN. To achieve high homogeneity and nitrogen contents, the mixture of reactants must be cooled from time to time, removed from the apparatus, reground to a fine powder, and nitridized again.

The best method for obtaining products of a given desired N content is synthesis starting from a homogeneous mixture of highly nitridized materials and metal powder. Such mixtures are homogenized by prolonged calcination at at least 1400°C (high vacuum or Ar atmosphere) with occasional cooling and regrinding of the calcined intermediate product.

II. Less pure niobium nitrides can be obtained from the oxide, carbon and nitrogen:

$$NbO_{a} + 2C + \frac{1}{2}N_{a} = NbN + 2CO$$
.

An intimate mixture of NbO₂ and the stoichiometric quantity of ash-free carbon is calcined in a stream of very pure N_2 or NH_3 at 1250°C. The products probably still contain some O and C. This method is completely unsuitable for the preparation of The nitrides because in this case the product contains considerable quantities of O and C.

The nitrides can also be obtained from the oxides and NH₃, provided the reaction time is sufficiently long.

PROPERTIES:

Dark products with submetallic appearance. Products with a high N content are yellowish-gray or brown, those with a low N content are dark gray. M.p.: NbN about 2000°C, TaN about 2800°C. The N₂ decomposition pressures become appreciable at temperatures exceeding 1400°C. Not attacked by acids. Readily and quantitatively converted to the pentoxides by moderate calcination in the presence of air (this is an analytical method).

The independent phases which exist in the Nb-N system correspond to the compositions $NbN_{1.00-0.87}$, $NbN_{0.78-0.76}$ and $NbN_{0.50-0.40}$; density of these ranges from 8.3 to 8.4.

The independent phases in the Ta-N system correspond to the compositions $TaN_{1,00}$ (d 13.8) and $TaN_{0.50-0.40}$ (d 15.4).

REFERENCE:

- Ia. K. Becker and F. Ebert, Z. Physik <u>31</u>, 269 (1925); K. Moers. Z. anorg. allg. Chem. <u>198</u>, 243 (1931); H. Rögener. Z. Physik <u>132</u>, 446 (1952).
- Ib. C. Agte and K. Moers. Z. anorg. allg. Chem. <u>198</u>, 233 (1931);
 G. Brauer, Z. Elektrochem. <u>46</u>, 397 (1940); F. H. Horn and
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 G. Brauer and J. Jander. Z. anorg. allg. Chem. <u>270</u>, 160 (1952);
 G. Brauer and K. H. Zapp. Z. anorg. allg. Chem. <u>277</u>, 129 (1957);
 R. P. Elliot and S. Komjathy. Columbium Metallurgy Symposium, New York, 1960;
 G. Brauer and R. Esselborn. Z. anorg. allg. Chem. <u>309</u>, 151 (1961).
- IL E. Friederich and L. Sittig. Z. anorg. allg. Chem, 143, 308 (1925).

Niobium and Tantalum Phosphides

NbP₁, TaP₁, NbP, TaP

These phosphides are prepared by synthesis from the elemente, either in a "Faraday apparatus" (see Part I, p. 76) or by

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beating a mixture of metal powder and P in an $Al_{2}O_{3}$ crucible. In either case the reactor is a sealed, evacuated quartz tube.

 $\begin{array}{l} Nb + P (2 P) = NbP (NbP_2) \\ 92.9 & 31.0 (62.0) & 123.9 (154.9) \\ Ta + P (2 P) = TaP (TaP_3) \\ 160.9 & 31.0 (62.0) & 211.9 (242.9) \end{array}$

In the "Faraday method," that end of the tube which contains the P is heated to 450-530 °C, while that containing the metal is heated first to 756 °C and then to 950 to 1100 °C.

In the method which uses a mixture, a fast onset of the reaction sometimes leads to explosion of the sealed tube, particularly if the P content of the reactant mixture is high.

The lower phosphides can also be obtained by degradation of products higher in phosphorus. This is done in high vacuum at 650-800°C.

PROPERTIES:

Black to dark-gray substances; fairly resistant to common reagents, vigorous reaction only with conc. H_2SO_4 ; in the case of products high in phosphorus, also with conc. HNO₃. Completely decomposed by fusion with alkaline oxidizing agents. d: TaP₃ 8.4; TaP 10.85.

REFERENCE:

M. Zumbusch and W. Biltz. Z. anorg, allg. Chem. <u>246</u>, 35 (1941); A. Reinecke, F. Wiechmann, M. Zumbusch and W. Biltz. Z. anorg. allg. Chem. <u>249</u>, 1 (1942).

Niobium and Tantalum Carbides

I. a) Pure products must be synthesized from the elements.

Nb + C = NbC; Ta + C = TaC92.9 12.0 104.9 180.9 12.0 192.9

Intimate mixtures of Nb or Ta metal powders (or Nb or Ta hydrides with carbon (as ash-free as possible) are placed by graphite boats or graphite crucibles and heated in a vacuum or fi an H_2 atmosphere. Reaction temperatures vary between 1400 and 2100°C. When a tubular carbon furnace is used as the heat source and an H_2 stream as the protective gas, the carbon content of the mixtures should be 15-20% lower than stoichiometric; this da

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because the heating causes the H_2 to react with the carbon of the furnace and the boat, and the resultant hydrocarbons supply the additional carbon needed to achieve the desired composition.

An additional purification of the carbide powder can be obtained by sintering (see TiN, p. 1233 f.). For purposes of presintering, the carbide powder is pressed into pellets which are embedded in loose carbide powder to protect them from chemical agents. These pellets are then presintered at a temperature of 2500-3000°C for about 15 minutes. The subsequent high-temperature sintering in argon at above 3000°C produces "self-purification" because of volatilization of impurities.

b) For small quantities of carbides, Nb (or Ta) wire is heated at temperatures exceeding 2500°C in an H₂ atmosphere which contains small amounts of hydrocarbon vapors. The presence of N₂ makes so little difference that up to 80% of the H₂ may be replaced by N₂. Suitable hydrocarbons are toluene, methane and acetylene. The nascent carbides formed may lose carbon at the high temperatures if the CH₄ content of the gas is less than about ¹/₄%, or that of C₂H₂ is less than about ¹/₈%.

IL The carbides can also be obtained by reacting the oxide with carbon.

| NbO: | + 3C = | NbC | + 2 CO |
|--------------------------------|---------|-------|--------|
| 124.9 | 36.0 | 104.9 | 58.0 |
| Ta _r O _s | + 7 C = | 2 TaC | + 5 CO |
| 441.9 | 84.1 | 385.9 | 140.1 |

The respective powder mixtures, in Mo or carbon boats, are reacted at 1250-2300°C in an H₂ stream. At 2300°C, a one-hour beating is recommended. When carbon tubes or boats are used as in method Ia, the mixture may be less than stoichiometric with respect to carbon. The products may be further purified via the above-cited sintering.

Alternate methods: Crystal growing procedures.

a) A carbon fiber is resistance-heated to above 2000°C with current. The fiber is in a "reaction lamp," which also holds thoroughly degassed $TaCl_{\pm}$ (this process cannot be used with Nb). The quantity of $TaCl_{\pm}$ needed is difficult to measure out (also, with excess chloride, free metal or lower carbides are formed on the incandescent fiber). At any rate, this process may be followed by carbidization in the presence of H_{\pm} and a hydrocarbon vapor [W. G. Burgers and J. C. M. Basart, Z. anorg. allg. Chem. 216, 297 (1934)].

b) Carbide may also be deposited on a tungsten wire exposed at 1909-2300 °C and 0.1 mm. Hg to an H₂ carrier gas containing small amounts of TaCl₅ (NbCl₅) and toluene vapor. However, this

March 1

carbide product will contain a large amount of free metal and must be subjected to a postcarbidization treatment [K. Becker and H. Ewest, Z. techn. Physik <u>11</u>, 148 (1930); K. Moers, Z. anorg. allg. Chem. <u>198</u>, 243 (1931)].

c) According to a patent [D. Gardner, U.S. Patent 2,532,295 (1946/50)], the pentachlorides can be reacted with H₂ and carbon derivatives such as CCl₄ or CaC₂ even at 600 to 700°C.

LOWER CARBIDES

Most preparative methods describe the synthesis of carbides of the limiting composition NbC and TaC. However, method I (or, if properly executed, also the above-described crystal growing procedure) also gives products with a low C content, e.g., products corresponding to the lower carbides Nb₂C (and Ta₂C).

PROPERTIES:

Iron-gray to dark-gray powders; the sintered solid exhibits a bright metallic luster; tarnishing frequently changes the surface color to brown to yellow. Does not lose carbon at high temperatures in the presence of hydrogen, provided a small amount of hydrocarbons is present in the gas (see method lb). Stable to N₃ up to about 3300°C. Quite sensitive to O₃ and H₂O on heating, undergoing rapid oxidation above 800°C in air. Not very volatile in high vacuum up to 3000°C.

NbC: m.p. 3500°C; d 7.6. TaC: m.p. 3900°C; d 13.9.

REFERENCE:

- Ia. C. Agte and K. Moers. Z. anorg. allg. Chem. 198, 233 (1931);
 G. Brauer, H. Renner and J. Wernet. Z. anorg. allg. Chem. 277, 249 (1954);
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 E. K. Storms and N. H. Krikorlan, J. Phys. Chem. 63, 1747 (1959);
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- H. E. Friederich and L. Sittig. Z. anorg. alig. Chem. <u>144</u>, 169 (1925); C. Agte and K. Moers. Z. anorg. alig. Chem. <u>198</u>, 233 (1931); A. Y. Kovalskiy and Y. S. Umanskiy. Zh. Fizich. Khimii <u>20</u>, 769 (1946); Chem. Zentr. <u>47</u>, II, 1546.

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SECTION 24

Chromium, Molybdenum, Tungsten, Uranium

F. HEIN and S. HERZOG

Chromium

Сг

I.

| Çt ₂ O ₃ | - i - | 2 A1 | - | 2 Cr | Ŧ | Al ₂ O ₃ | |
|--------------------------------|--------------|------|---|-------|---|--------------------------------|--|
| 152.0 | | 53.9 | | 104.0 | | 101.9 | |

An intimate mixture of 70 g. of pure ignited Cr_2O_3 , 33 g. of Al granules (or Al powder), and 25 g. of fused and powdered $K_2Cr_2O_7$ is placed in a clay crucible whose bottom is covered with 10 g. of CaF_2 . The mixture is caused to react by means of ignition mixture and a strip of Mg.* After cooling, the contents of the crucible are broken up, and the spheres of metal are mechanically extracted. This gives about 99% pure chromium metal in 50~75% yield (the larger the quantity of reactants, the better the yield).

IL $2K_{z}[CrCl_{s}(H_{z}O)] + 3Mg = 2Cr + 3MgCl_{2} + 4KCl + 2H_{2}O$ 851.0 37.0 104.0

The $K_2[CrCl_5(H_2O)]$ is obtained by dissolving 100 g. of $K_2Cr_2O_7$ in the minimum quantity of water, treating the solution with 400 mL of HCl (d 1.124), and gradually adding 100 ml. of 80% alcohol. The reaction is accompanied by vigorous evolution of heat. Then, 170 g. of KCl is added and completely dissolved, the mixture filtered, and the filtrate evaporated to dryness. The mass is then completely dehydrated by further heating. The resulting violet solid is then

[&]quot;The ignition mixture, called "Zündgemisch" or "Zündkirsche" (igniting cherry), consists of an intimate mixture of 15 parts by weight of barium peroxide and 2 parts of powdered magnesium metal held together with collodion. The whole is wrapped in magnesium ribbon, which acts as fuse (H. Blücher, Auskunftsbuch für die chemische Industrie [Data Book for the Chemical Industry], 18th ed., de Gruyter, Berlin, 1954, p. 1314).

24. CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM

ground, and any green portions are removed as completely as possible. The potassium chromium (III) chloride thus obtained is mixed with 50 g. of Mg filings. The mixture is placed in a covered Hessian crucible, brought to red heat and held at this temperature for one half hour. However, not all of the KCl must be allowed to volatilize, otherwise a fraction of the Cr will be converted to the oxide and will contaminate the product. After this calcination, the crucible is cooled and broken. The shards and the particles of green chromium oxide, which appear on the surface of the grayblack melt, are removed. The mechanically cleaned mass is then placed in water, where it crumbles to a powder. The soluble salts are removed by decantation. The residue is boiled with dilute nitric acid to remove the excess Mg (and the MgO which has formed from it).

Any $Mg(NO_3)_3$ and excess acid present are separated by further decantation; filtration is not recommended because of the fine particle size of the metal. The Cr residue is dried on a steam bath. Yield about 27 g. of light-gray, microcrystalline powder whose Cr content is 99.6%.

III. ELECTROLYSIS

The electrolytic cell consists of a beaker with a copper cathode rod suspended in the center. A lead sheet or a coil of lead tubing placed along the wall of the cell serves as the anode; if the latter arrangement is used, cold water is circulated through the tubing. The electrolyte consists of a solution of 240 g. of CrO_3 , 3 g. of $Cr_3(SO_4)_3 \cdot 12 H_3O$, and 8.8 g. of $Cr(OH)_3 \cdot 3 H_3O$ in one liter of water. A current density of 0.10 amp./cm.² and a potential of 3.2 volts are used. It is essential that the electrolyte remain undisturbed (no stirring) during electrolysis. The thick layer of Cr which forms on the cathode in a few days is readily stripped off. If it should prove necessary to remove the H₃ which accumulates in the metal voids during deposition of the Cr, the product should be heated to 600°C in high vacuum.

IV. Ductile Cr is obtained from CrCl₃ and Ca in a steel bomb under argon. For details of the method, see section on Titanium p. 1161.

PROPERTIES:

Atomic weight 52.01, Solid Cr has a silvery luster; very hard and brittle, but very pure Cr is ductile. M.p. about 1920°C (in vacuum), b.p. about 2200°C; d^{28} 7.138. Body-centered ouble crystals; hexagonal form also exists.

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- III. Private communication from Prof. G. Grube, See H. Haraldsen and E. Kowalsky. Z. anorg. allg. Chem. <u>224</u>, 330 (1935).
- IV. W. Kroll. Z. anorg. allg. Chem. 226, 23 (1935).

Chromium (II) Chloride

CrCl₂

I.

 $C_{T}Cl_{3} + \frac{1}{2}H_{2} = C_{T}Cl_{2} + HCl_{158.4}$ 158.4 11.24 122.9

The special vessel $(2.5 \times 50 \text{ cm.}, \text{Fig. 313})$ used for the reduction is made of high-melting glass. For reasons of safety it is first baked in vacuum at 500°C while empty. It is provided with a twobole rubber stopper, through which the outlet tube *a* and the longer inlet tube *b* (8-mm. diameter) are inserted. The reactor is charged with CrCl₃ (prepurified by sublimation in a stream of Cl₂). The tube is heated to 500°C in a thermostatically controlled electric

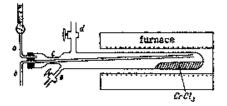


Fig. 313. Preparation of chromium (II) chloride. b inlet tube for hydrogen, H₂-HCl mixture, or nitrogen; d stopcock with10-mm. hore for withdrawal of reaction product.

furnace, while a mixture of H_2 and HCl (the latter serving to hinder any further reduction to Cr) is admitted through b (the dry, O_2 -free, 50 ml./min. gas streams are mixed in a tee prior to introduction into the apparatus). The cutlet tube a is connected to a drying tube filled with CaCl₂. To test for completeness of reduction, the furnace is removed briefly from time to time (pure CrCl₂ is white). When

the reaction is complete, the furnace is cooled, the H_2 -MCI mixture displaced with dry N_2 or CO_2 , and the inlet tube pulled back until its tip is at the rubber stopper. The reactor tube is then melt-sealed at constriction c. Any required quantity of CrCl₂ can be shaken out of the tube through the 10-mm.-bore stopcock d; in this operation, the CrCl₂ must always be under dry, O_2 -free inert gas, which is admitted through stopcock e. (For special apparatus for storage under inert gas, see also Part I, pp. 71 and 75.)

п.

$$Cr + 2 HCl = CrCl_{0} + H_{0}$$

52.0 44.51. 122.9

A small porcelain boat is charged with pea-sized pieces (or, better, powder) of metallic Cr and inserted in a quartz reactor tube. Dry, O_2 -free HCl is passed through the tube, which is heated to as high a temperature as possible (1150 to 1200°C). On cooling in the HCl stream, an asbestoslike mass of white (or, if impure, gray) crystalline needles of $CrCl_2$ is obtained. Because of its toughness, the mass is very difficult to remove from the boat. The preparation must be sealed as rapidly as possible into a sample tube filled with N_2 or CO_2 ; if this is not done, the anhydrous $CrCl_2$ is rapidly hydrated by atmospheric moisture, after which oxidation also occurs at once. Because of its high meiting point, some metal may be trapped within the chloride and thus remain unreacted.

 $\begin{array}{c} \text{ether} \\ \text{III.} \\ \text{Cr}_{s}(\text{CH}_{3}\text{COO})_{s} + 4 \text{HCl} = 2 \text{CrCl}_{s} + 4 \text{CH}_{3}\text{COOH} \\ 340.2 \\ 145.8 \\ 245.9 \end{array}$

Ten grams of fine chromium (II) acetate hydrate $Cr_{0}(CH_{3}COO)_{4}$ 2 H₃O crystals is dehydrated in a three-neck flash at 110 to 120°C (aspirator vacuum); the color changes from brick-red to brown. Then, 60 ml. of air-free ether is added and dry HCl is passed through the vessel with the suspension (the vessel is in an ice bath and is protected against atmospheric moisture by a P₂O₈ tube). After several minutes, a violet color is observed in the solution, and the chromium acetate powder is transformed (with an increase in bulk) into chromium (II) chloride which still contains some acetic acid. The flask is swirled during this operation to prevent clogging of the inlet tube. The white crystals are filtered in the absence of air, washed with absolute, air-free ether, and dried at 110 to 120°C. The acetic acid is thus eliminated, and pure whits, analytically pure $CrCl_{2}$ is obtained as a residue. Yield 4-5 g.

PROPERTIES:

White crystals or fused, fibrous mass. M.p. 824°C; d¹⁴ 2.751; Very hygroscopic. Can be sublimed in vacuum. Dissolves readily in water, giving a sky-blue solution.

1337

1330

REFERENCES:

- J. Reschke. Thesis, Univ. of Leipzig, 1925, p. 43; F. Hein, Z. anorg. alig. Chem. 201, 314 (1931); F. Ephraim. Helv. Chim. Acta 17, 291 (1934); A. B. Burg in: L. F. Audrieth. Inorg. Syntheses, Vol. III, New York-Toronto-London, 1950, p. 150.
- H. J. Koppel, Z. anorg. Chem. 45, 361 (1905); W. Biltz and E. Birk. Z. anorg. allg. Chem. 134, 134 (1924); W. Fischer. Z. anorg. allg. Chem. 222, 309 (1935); H. Hecht. Präparative Anorganische Chemie [Preparative Inorganic Chemistry], Berlin-Göttingen-Heidelberg, 1951, p. 80.
- III. Private communication from F. Hein, E. Kurras and W. Kleinwächter (unpublished).

Chromium (III) Chloride

CrCi₁

L

 $2 Cr + 3 Cl_z = 2 CrCl_s$ 104.0 66.0 l 315.8

Coarse Cr metal powder (10-20 g.) is placed in a 50-cm.-long and 3-cm.-I.D. horizontal porcelain reactor tube, which is heated in a blast lamp flame. It is essential that all residual air be displaced by a fast stream of completely dry Cl₃ (for at least half an hour prior to introduction of the Cr). The temperature is then raised as high as possible; the tube is allowed to cool, and the Cl₃ is displaced with dry CO₃. Violet leaflets of CrCl₃ form, with a large increase in volume (to avoid plugging the tube as a result of this volume increase, the Cr reactant should be distributed over a long stretch of the tube).

The CrCl₂ is purified by sublimation in the stream of Cl_2 , then repeatedly boiled with conc. HCl, washed with distilled water until disappearance of chloride reaction, and dried at 200 to 250 °C.

The high sublimation temperature of over 1200 °C is a disadvantage of this method. Under certain conditions the procelain tube can be markedly corroded in this operation and, in addition, it may be plugged as a result of the large volume increase occurring during the formation of the chromium (HI) chloride. The following method, in which green chromium (HI) chloride hydrate is debydrated in a stream of CCI₄ at 500 °C, avoids these difficulties.

II. OVERALL EQUATION:

 $[CrCl_t(OH_t)_t]Cl \cdot 2H_tO = CrCl_t + 6H_tO$

-3

SIDE AND INTERMEDIATE REACTIONS:

 $2[CrCl_{4}(OH_{F})_{4}]Cl \cdot 2H_{2}O = Cr_{3}O_{3} + 6HCl + 9H_{3}O$ $Cr_{3}O_{3} + 3CCl_{4} = 2CrCl_{3} + 3COCl_{8}$ $2Cr_{2}O_{3} + CCl_{4} = 4CrCl_{3} + CO_{2}$

Thus, one by-product is phosgene, which must be carefully vented (use a hood!). Simple absorption in water is not adequate, since the hydrolysis is not instantaneous.

The apparatus is shown in Fig. 314. Forty grams of green chromic chloride is placed in quartz flask c, which is placed in an electric furnace capable of delivering 650°C. The apparatus for generating and superheating CCl₄ vapor is then attached. This apparatus consists of the 250-ml. distilling flask c with its superposed dropping funnel and a U tube immersed in a silicone oil bath at 150°C.

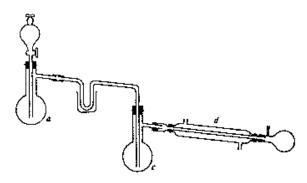


Fig. 314. Dehydration of chromium (III) chloride hydrate with carbon tetrachloride.

After brief heating of the furnace (flask temperature of 100-150°C), one drop of CCl₄ per second is admitted from the dropping funnel into flask a, which is heated with a Bunsen burner in such a manner that each drop vaporizes at once. After some time (furnace temperature of about 300°C), a mixture of water, CCl₄, etc.₃, distills over. It condenses in d; the noncondensing gases (including phosgene) are vented through the hood. After some two hours of reaction, when the furnace temperature has reached 650°C, the gas stream is interrupted and the apparatus allowed to cool. The anhydrous CrCl₃ remains in the flask in about 90% yield (some of it sublimes). The lustrous violet crystalline leaflets are extracted with boiling dilute HCl and dried. About 20 g. of chromium (III) chloride is obtained. PROPERTIES:

Formula weight 158.88. Red-violet crystalline scales with metallic luster. M.p. ~ 1150 °C. May be sublimed in Cl_2 stream; rate of solution in water, acids and organic solvents immeasurably slow. Addition of a very small amount of $CrCl_2$ aids in rapid solution of $CrCl_3$ in water or alcohol.

REFERENCES:

- Private communication from H. Hecht, Greifswald; F. Hein, Z. anorg. allg. Chem. 201, 314 (1931).
- IL G. B. Heisig, B. Fawkes and R. Hedin in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 193; A. Vavoulis et al. Ibid., Vol. VI, New York-London, 1960, p. 129.

Chromium (II) Bromide

CrBrz

L

 $C_{f}B_{T_{8}} + 0.5 H_{2} = C_{f}B_{T_{8}} + HB_{f}$ 291.8 1).21. 211.8

A weighed quantity of $CrBr_3$ is reduced to constant weight in a U tube at 350-400°C for 6-10 hours. The most painstaking purification of the H_2 is essential for success. For uniform heating, the U tube is surrounded with an asbestos box.

11. $Cr_{2}(CH_{3}COO)_{4} + 4HBr = 2CrBr_{2} + 4CH_{3}COOH_{340,2} + 323.7 + 423.7$

The procedure is the same as for chromium (II) chloride (method III), but hydrogen bromide is used instead of hydrogen chloride.

PBOPERTIES:

White crystalline powder; d_2^{26} 4.356. Soluble in air-free water, yielding a blue color. Rapidly oxidized in air.

SEPERENCES:

- L. W. Biltz and E. Birk. Z. anorg. allg. Chem. <u>134</u>, 134 (1924); W. Fischer and R. Gewehr. Ibid. <u>222</u>, 309 (1935).
- II. Private communication from F. Hein, E. Kurras and W. Kleinwächter (unpublished).

Chromium (III) Bromide

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CrBr₂

| 2 Cr | + | 3 Br ₂ | 2 CrBr, |
|-------|---|-------------------|---------|
| 104.0 | | 479.5 | 583.5 |

Electrolytic Cr powder is spread in a thin layer in a quartz reactor tube and bromine vapor, predried over $P_{\rm g}O_5$, is passed over the Cr in a stream of O_2 -free, dry N_2 or Ar. The quartz tube is heated to about 1000°C, whereupon the two elements combine with incandescence at the beginning of the reaction. The unconverted Br_2 is condensed in a receiver cooled in ice-sait mixture. After 45-60 minutes, the material is allowed to cool while maintaining the gas stream. The lustrous black, leafy crystals of CrBr₃ are purified by several extractions with absolute ether and decantations with ice water (to remove traces of adhering CrBr₃). This is followed by washing with absolute alcohol and ether; the product is dried in a vacuum desiccator over P_2O_5 .

PROPERTIES:

Formula weight 291.76. Black lustrous crystals, green in transmitted and reddish in reflected light. Soluble in water only upon addition of Cr (II) salts.

REFERENCES:

J. Reschke. Thesis, Univ. of Leipzig, 1925; F. Hein and I. Wintner-Hölder. Z. anorg. allg. Chem. 201, 319 (1931).

Chromium (II) lodide

Cr1,

 $Cr + 1_r = CrI_s$ 52.0 253.8 303.9

The starting materials are electrolytic Cr reduced to the size of millet seed and I_2 resublimed over KI (see p. 277). The appratus is shown in Fig. 315. The quartz reactor tube 7 has a overall length of about 56 cm, and an I.D. of 2 cm. (2.5 cm. at the bulged-cut section). The tube ends (on the right side of the drawing) in a quartz capillary spiral which is somewhat constricted as a on the opposite side, it can be closed off by a large-diameter ground joint connected to stopcock h_1 . The 'cooling trap with

connected via stopcock h_2 to a tee adapter; thus, it can be in line either with the high-vacuum system (via stopcock h_3) or with the two-way stopcock z, which in turn leads either to the N₂ source or to a vacuum oil pump.

The movable tubular resistance furnace o serves to heat the quartz reactor at any desired spot.

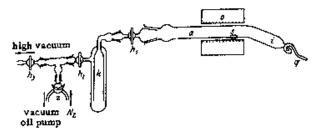


Fig. 315. Preparation of chromium (II) iodide. a quartz reactor tube; s boat with Cr; o electric furnace; k cold trap.

First, a trace of very fine Cr powder is placed in the tip of the capillary spiral, and then I_2 (10% excess over the stoichiometric quantity) is placed in the slightly inclined tube section *i*. A small porcelain boat with the Cr is placed in the bulge *s*. Trap *k* is now cooled to -80° C and the apparatus is evacuated (with stopcock *z* closed) to ≤ 0.001 mm.

The vacuum is then broken with N2 and the evacuation repeated (this procedure is repeated 3 or 4 times). Stopcock h_1 is closed and the Cr powder at the tip of the spiral is heated with a torch to a bright red glow to bind the last traces of Oa. Then the tube furnace is set in place over spot s and the Cr heated at 700 to 850°C; to minimize undesirable heat losses, asbestos paper (not shown in the figure) is placed in both furnace openings. As the I2 now diffuses slowly toward the Cr, the nascent Crl₂ solidifies as a crystalline mass at both sides of the tube protruding from the furnace. This slow procedure yields very beautiful leaf- or needle-shaped redbrown to iodine-colored crystals. At the beginning of the iodination, a deep-black coating always forms on the colder portions of the tube; this material is more volatile than CrI2 and converts to CrI2 at higher temperatures, evolving iodine. Even though the CrI₂ itself is not particularly volatile, the crystal deposit extends on both sides for up to 2 cm, beyond the hot zone. By gradually shifting the furnace, the crystalline deposit is shifted away from the spot where the Cr is situated; in this way, one prevents it from becoming too dense and provides a surface for fresh depceition. By following this procedure, almost all the Ia is introduced little by little, with the long heating producing a type of resublimation

and yielding beautiful single orystals. Such a run takes 8-14 days; some unreacted metal is still invariably found after this time at the bottom of the boat, because the sublimation of CrI_3 from the (protective) melt is very slow. When the iodination has proceeded as far as possible, the excess I_3 must be displaced before the CrI_3 itself can be removed. Thus, the reactor is connected to the high vacuum (via h_3), with the cold trap at -80°C. The I_3 is driven off by careful fanning with a flame (250-300°C) and continuous evacuation. Evacuation is continued after complete removal of the I_3 until the quartz tube is cool; the apparatus is then closed off at h_1 .

Transfer of the CrI_2 from the reactor requires great care, since the compound is extremely sensitive to air and moisture. Further, the solid material possesses a relatively large surface. The following procedure is the safest: The vacuum is broken with compressed N₂ via h_1 , and pressure above atmospheric is created in the apparatus. The quartz capillary is then broken off at a and this opening is attached to another N₂ connection. The

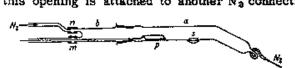


Fig. 316. Transfer of chromium (II) iodide following its preparation. *a* reaction tube of Fig. 315; *p* porcelain boat with front wall broken off (scoop).

joint with h_1 is then removed and the adapter tube b is inserted in its place, as shown in Fig. 316 (an Na stream also passes through b). The adapter carries at one end the same standard taper joint as h_1 , and at the other end two short connectors m and n. An N₂ stream enters at n; a long glass rod, the forward end of which is bent into a small hook, is introduced through m. This hook supports a fairly large porcelain boat p, whose front wall is broken off at a sharp angle. The boat is of such a size that it is still able to move in the quartz reactor. Now, with the fast N₂ stream always maintained, this "dredge" is pushed forward through the loose crystal aggregate, whereupon most of the latter drops into boat s. This operation is aided by gentle tilting and tapping of the reactor. The filled boat s is now pulled back into the adapter or the adapter is quickly detached from the reactor and closed off with a ground cap. Finally the boat with the CrI2 is transferred for storage into a tube provided with a ground joint (see Parti, p. 75); as a precaution, this tube is evacuated several times and then filled with N2 (slight gage pressure). All of these operations must be carried out in sequence and without undue delay. 12.82

PROPERTIES:

Brown-red leaflets; thin leaflets are somewhat transparent, thick crusts often have an iodinelike color. Very sensitive to air and moisture, easily soluble, with bright blue color, in airfree water. M.p. 790-795 °C; d_5° 5.02₃.

REFERENCE:

F. Hein and G. Bähr. Z. anorg. allg. Chem. 251, 241 (1943).

Chromium (III) lodide

CrI

 $2 \operatorname{Cr} + 3 \operatorname{I}_{2} = 2 \operatorname{Cr} \operatorname{I}_{3}$ 104.0 761.5 865.5

The apparatus (Fig. 317) is made of high-melting glass. The diameter of the tube at e, f and h is 25-30 mm. Three grams of fine chromium metal powder (electrolytic chromium is best) is introduced into e, and an excess (30 g.) of iodine into h. Then k is sealed off and the apparatus is evacuated to appr. 10^{-8} mm. (with occasional gentle heating). The iodine is now sublimed into f by cooling the latter section (Dry Ice) and heating h (during this operation stopcock b is turned off and on). Following this, g is sealed off in high vacuum, and then d is sealed off as well.

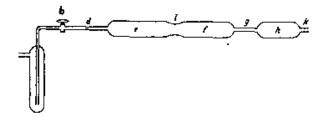


Fig. 317. Apparatus for synthesis of chromium (III) iodide.

Now sections e and f are enclosed in separate tubular furnaces; e is beated for 24 hours at 475°C, and f for the same period at 225°C. (The vapor pressure of iodine at this temperature is approximately 3 atm.) The apparatus is then allowed to cool, and the unreacted iodine is sublimed out from e (which is held at 100°G) into f (held at room temperature). The tube is then broken, in drift

air, at constriction l (careful!). The material is transferred to suitable storage vessel, which is then evacuated for some time for remove the last traces of todine. The yield is almost quantitative.

If necessary, further purification may be achieved by beating for several hours at 500°C in an evacuated quartz tube. The operation yields chromium (II) iodide; the iodide can be sublimed in vacuum at 700°C and finally reiodinated as described above.

PROPERTIES:

Black crystals; dissolve rapidly in water upon addition of some Cr (II) lodide. Stable at room temperature; thermally dissociated at higher temperatures according to: $2 \text{ CrI}_3 = 2 \text{ CrI}_3 + I_2$. The iodine pressure reaches 1 atm. at about 670°C.

REFERENCES:

L. L. Handy and N. W. Gregory. J. Amer. Chem. Soc. <u>72</u>, 5049 (1950); N. W. Gregory and L. L. Handy in: T. Moeller, Inorg. Syntheses, Vol. V, New York-Toronto-London, 1957, p. 128.

Chromium (III) Hydroxide

Cr(OH), n H₂O

1. A-HYDROXIDE Cr(OH)3 * 3 H₂O

A solution of 12 g, of gray-blue $[Cr(H_2O)_6]Cl_5$ (for preparation, see p. 1348 f.) in 500 ml. of water is treated with 100 ml. of 2 M ammonia. After settling of the precipitate (centrifuge if necessary), the mother liquor is decanted; the suspension is filtered through a leaf filter, thoroughly washed until free of NH₄Cl, and dried in air.

PROPERTIES:

Bright blue-green powder; gives blue salts of the $[Cr(H_3O)_0]X_3$ type with dilute acids.

B-HYDROXIDE Cr(OH)3 · 3 H2O

PROPERTIES:

Dark blue-green powder; gives green saits of the $[Cr(H_2O), X_1]$ 2 H₂O type with dilute acids. In contrast to the A-type, the hydroxide is insoluble in acetic acid.

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IL $3C_{7}O_{3} + 3C_{9}H_{3}OH = 2C_{7}(OH)_{3} + 3CH_{3}CHO + 3H_{9}O_{(-n}H_{7}O)$

This is a convenient method for preparation of larger quantities of $Cr(OH)_{3}$. A solution of 160 g. of CrO_3 in 2 liters of water is prepared and alcohol (8 portions of 10 ml, at 5-minute intervals) is added with vigorous stirring (caution: a hood is needed!). After 4 hours of standing, an additional 80 ml, of alcohol is added in the same manner. The mixture is then refluxed for 16 hours (stirring is required to avoid bumping). The finely divided, dark brown precipitate is filtered through a 24-cm.-diameter Büchner funnel and dried at 110°C without washing. Yield: 145 to 150 g. Additional quantities (30-35 g.) can be recovered from the filtrate by concentration of the latter. Alternately, the Cr-containing liquid may be used as solvent (instead of water) in the next run.

PROPERTIES:

This method affords a black product with a pitchlike luster, probably because of a small admixture of higher oxides. This material has a higher catalytic activity than that obtained by precipitation.

REFERENCES:

 I. A. Hentzsch and E. Torke. Z. anorg. allg. Chem. <u>209</u>, 73 (1932).
 II. R. F. Ruthruff in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 190.

Chromium Sulfides

CrS, Cr₂S₁

Ľ

Cr + S = CrS52.0 32.1 84.1 2 Cr + 3 S = Cr₂S₃ 184.0 95.2 209.2

The sulfides are prepared by heating exact stoichiometric mixtures of electrolytic Cr (for preparation, see p. 1335) and pure S for 24 hours in small, evacuated, sealed quartz tubes placed in an electric furnace at 1000°C. All of the S does not react even if heated for 3-4 days and slowly cooled. The product is freed of unreacted sulfur by famming with a Bunsen flame while simultaneously cooling the empty seal-off point of the tube. The

quantity of S which condenses in that section is determined by reweighing, and the composition of the sulfide is calculated by using this value.

Cracking of the quartz tube during cooling of preparations which are high in S can be avoided by scaling the reaction recent proper in a second, similarly evacuated quartz tube.

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II. $2 \operatorname{CrCl}_{s} + 3 \operatorname{H}_{s} S = \operatorname{Cr}_{s} S_{s} + 6 \operatorname{HCl}_{s}$ 316.8 69.41. 200.2

Exactly stolchiometric Cr_3S_3 may be obtained by heating $CrCl_3$ in a stream of H_3S at 600-650°C.

PROPERTIES:

The chromium sulfide preparations obtained via method I have a metallic appearance and become fused at the temperature of preparation. The CrS possesses a hexagonal superstructure of the B 8 type, while at 59.7 atom % of S, a B 8 structure with the axial ratio $c/a = 1.62_5$ has been shown to exist. The Cr₂S₉ obtained by method II consists of hexagonal black leaflets, resistant to nonoxidizing acids, easily soluble in HNO₃.

REFERENCES:

- I. H. Haraldsen and E. Kowalsky. Z. enorg. allg. Chem. 224, 331 (1935); H. Haraldsen and A. Neuber. Ibid. 234, 388 (1937).
- II. W. Rüdorff and E. Stegemann, Z. anorg, allg. Chem. <u>251</u>, 890 (1943).

Chromium Nitride

CrN

I.

 $Cr + \frac{1}{2}N_{z} = CrN$ 52.0 11.41, 66.0

Electrolytic chromium powder is heated for 2 hours are 00° C in a quartz or porcelain tube while a dry, O₂-free stream of N_a is passed through. After cooling, the product is ground in an agate mortar and calcined again for 2 hours in a stream of N_a. The final product is treated with HCl until nothing further dissolves (the HCl liquid remains colorless). The black residue is thoroughly washed and dried.

1348

Ш.

 $C_{1}C_{2} + 4 NH_{3} = C_{7}N + 3 NH_{4}C_{1}^{2}$ 138.4 88.31. 66.0

A tube of high-melting glass $(25-30 \text{ cm}, \log)$ is used and 5-10 g. of aphydrous CrCi₃ is calcined, first gently and then vigorously, in a stream of NH₃. The heat source is a series of burners. The NH₃ is obtained either from a bomb or by heating about 300 ml. of conc. ammonia; it is dried by passage through a lime tower and a large U tube filled with CaO. The reactor tube carries no outlet tube, since the latter would be plugged by sublimed NH₄Cl (use a hood!). Strong heating is continued until no further NH₄Cl vapor is evolved; then (after cooling) the product is ground and recalcined in a stream of NH₃. The yield is almost quantitative.

If it is desired to remove traces of $CrCl_3$, the product is extracted in the cold with some dilute HCl (add some Sn), then washed with water, filtered and dried at 100-120°C.

PROPERTIES:

Black, magnetic powder; insoluble in acids and alkalies; d 5.9. Crystal structure: NaCl type.

REFERENCES:

- I. F. Briegleb and A. Geuther. Liebigs Ann. <u>123</u>, 239 (1862); R. Blix. 2. phys. Chem. B 3, 236 (1929).
- II. H. Biltz and W. Biltz. Übungsbeispiele aus der unorg. Experimentalchemie [Exercises in Experimental Inorganic Chemistry], 3rd and 4th eds., 1920, p. 20.

Hexaaquochromium (III) Chloride

[Cr(OH₂)₀]Cl₁

L $[Cr(OH_2)_1](NO_3)_5 + 3 HC1 = [Cr(OH_2)_0]Cl_3 + 3 HNO_3$ $(\cdot 3 B_1O)_{400,2}$ 268.5

A solution of 100 g. of chromium (III) nitrate $Cr(NO_3)_3 \cdot 9 H_2O$ in 100 ml. of H_2O and 100 ml. of 38% HCl is prepared. Hydrogen chloride gas, predried in H_3SO_4 , is introduced with ice cooling, until the precipitation of $[Cr(H_2O)_6] Cl_3$ is complete.

The crystal slurry is rapidly filtered on a large glass suction funnel and washed with some furning HCl. It is dissolved in 100 ml. of water and 100 ml. of furning HCl, and reprecipitated with HCl gas while cooling in ice. After precipitation is complete, the greenish supernatant solution is decanted and the gray-blue chloride is freed of most of the adhering HCl and the green chloride by stirring three times with acetone. The remaining impurities are completely extracted by treating the product with small quantities of acetone on a fritted-glass funnel (the filtrate must become colorless in the end). The acetone is removed by rinsing with absolute ether. The salt is freed of ether and traces of moisture by drying in a desiccator over H_2SO_4 . The yield is about 72%.

$\Pi_{*} \qquad [CrCl_{2}(H_{2}O)_{4}]Cl \cdot 2 H_{2}O = [Cr(H_{2}O)_{4}]Cl_{3}$ 266.5 266.5

A solution of 50 g, of green chromium chloride hydrate in 50 g. of water is refluxed for one half hour, during which time almost no color change is observed. The flask is then cooled by immersion in an ice-salt mixture and HCl gas is introduced with periodic shaking of the flask. The temperature inside the flask must always be held below 0°C; this is achieved by frequent renewal of the freezing mixture. After saturation with HCl, the fine powder which separates is allowed to settle to the bottom and the supernatant blue-green liquid is decanted. The powder itself is rinsed out of the flask onto a fritted glass funnel with cold saturated HCl, dried as much as possible by suction, then stirred with acctone and washed until the acetone is no longer green. As soon as the acetone traces have evaporated, the crude product is dissolved in 20 ml. of water; it is filtered if necessary, and HCl gas is introduced into the blue solution (while cooling the flask with cold water) until saturation. At this point the gas flow is interrupted and the flask is placed in finely crushed ice. The solution becomes almost coloriess after some time while the chloride separates in granular, bluegray crystals. After filtering through a fritted-glass funnel, the product is washed with acctone and dried over HaSO4. Yield: 12 g.

III. $KCr(SO_4)_t \cdot 12 H_sO + 3 HCl \rightarrow [Cr(H_tO)_s]Cl_s$

Chrome alum (250 g.) is dissolved in a chilled mixture of 1 liter of conc. hydrochloric acid and 250 ml. of water. The solution is filtered and saturated with hydrogen chloride gas at 10 to 15 °C. It becomes almost colorless during this step, and the crude product separates in crystalline form. The crystals are filtered and purified by dissolving in 175 ml. of water, reprecipitating at 10°C as described above, filtering again, washing with dry acetone, and drying over sulfuric acid. Yield: about 90 g.

PROPERTIES:

Blue-gray crystals, very deliquescent in air, soluble in water with a blue-violet color, readily soluble in alcohol, insoluble in acctone.

REFERENCES:

- L A. Hantzsch and E. Torke. Z. anorg. alig. Chem. 209, 72 (1932).
- II. A. Werner and A. Gubser. Ber. disch. chem. Ges. 34, 1591 (1901).
- III. G. O. Higley. J. Amer. Chem. Soc. 26, 620 (1904).

Chloropentasquachromium (III) Chlaride

$[C_{r}Cl(OH_{t})_{s}]Cl_{r} \cdot H_{t}O$

| A) | [CrCl ₂ (OH ₂) ₄]Cl | Ŧ | H ₂ SO ₄ | = | $[CrCl(OH_2)_3]SO_4$ | + | 2 HCl |
|----|--|---|--------------------------------|---|-----------------------|---|-------|
| • | (+2 H ₂ O) | | | | (8 H ₄ O) | | |
| | 266.5 | | 95.1 | | 327.7 | | |

B) $[CrCl(OH_2)_5]SO_4 + 2 HCl = [CrCl(OH_2)_5]Cl_2 + H_2SO_4$ $(+3 H_2O)$ $(+H_2O)$ $(+H_2O)$ $(+H_2O)$ 266.5

A) PREPARATION OF [CrCl(OH₂)₅]SO₄ + 3 H₂O

A solution of 26.8 g. of green chromium chloride hydrate $[CrCl_2(H_3O)_4]Cl \cdot 2 H_2O$ in an equal amount of water is allowed to stand for 24 hours at room temperature, and a mixture of 10 g. of conc. H_2SO_4 and 4 g. of water is then added. The sulfate soon separates in bright green tablets.

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B) PREPARATION OF [CrCl(OH<sub>2</sub>)<sub>5</sub>]Cl<sub>2</sub> · H<sub>2</sub>O
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A conc. aqueous solution of the sulfate, cooled to 0° C, is allowed to flow into ether at 0° while a stream of dry HCl is introduced. The yield is greater than 87%.

PROPERTIES:

Bright green, microcrystalline, very hygroscopic powder; readily soluble in water, alcohol and acetone. Differentiated from its isomers by its solubility in a mixture of equal volumes of ether and fuming hydrochloric acid. Insoluble in HCl-saturated ether.

REFERENCES:

- B. F. Weinland and Th. Schumann. Ber. dtsch. chem. Ges. <u>40</u>, 3094 (1907).
- II. M. Gutiérrez de Celis. An. Soc. Españ. Fisica Quim. <u>34</u>, 553 (1936), abstract in Chem. Zentr. <u>1936</u>, 11, 1874.

Hexaamminechromium (III) Chloride and Nitrate

[Cr(NH₄)₄]Cl₄, [Cr(NH₄)₄](NO₄)₂

1. PREPARATION BY AUTOOXIDATION OF AN $NH_4CL-CONTAINING$ AMMONIACAL SOLUTION OF A $C_7(H)$ SALT

A solution of chromium (II) sait is prepared as indicated in the preparation of rhodochromium chloride (see p. 1359). This solution is forced under pressure (in the absence of air) into a flask containing a mixture of 525 g, of NH₄Cl and 540 g, of ammonia (d 0.91). The vessel should be almost full at this point. The flask is stoppered at once with a cork which carries a gas outlet tube; the tube terminates under water. The flask is placed in cold water until H_z evolution ceases (about 18-24 hours). The {Cr(NH₃)_d|Cl₃ that deposits on the undissolved NH₄Cl and that dissolved in the liquid are worked up separately.

The red solution is decanted and treated with an equal volume of 95% alcohol. The chloride, which settles after several hours, is washed by decantation with alcohol, filtered, rewashed with alcohol, and dried in air. It is then dissolved in lukewarm water and the solution passed through a filter into well-cooled nitric acid (d 1.39), whereupon the [Cr(NH₃)₈] (NO₃)₈ separates in long, yellow needles. The precipitate is washed several times by decantation with nitric acid, then with a mixture of l volume of nitric acid and 2 volumes of water, filtered, washed with alcohol until free of the acid, and dried in the air.

The product-containing NH_4C1 is treated several times with 150-ml. portions of water at room temperature, but only as long as the extracts are still yellow. They are treated with an equal volume of nitric acid (d 1.39; good cooling is essential). Yellow needles appear, either at once or after several hours; they are worked up as above. Total yield: 35-40 g.

The salt is purified by dissolving in a minimum quantity of cold water. The solution is passed through a filter into dilute nitric acid (1 vol. of nitric acid, d 1.4, and 2 vol. of water); the crystals are washed with alcohol and dried in air.

II.

 $CrCl_{3} + 6 NH_{5} = [Cr(NH_{3})_{6}]Cl_{3}$ $158.4 \quad 102.2 \quad 260.6$ $[Cr(NH_{5})_{6}]Cl_{3} + 3 HNO_{5} = [Cr(NH_{5})_{5}](NO_{5})_{5} + 3 HCl$ $260.6 \quad 189.0 \quad 840.2$

The presence of NaNH₃ catalyst prevents the coproduction of $[CrCl(NH_{a})_{5}]Cl_{3}$.

A hood with a good draft is needed; a one-liter Dewar flask is placed under this hood, charged with about 800 ml. of liquid NH_{31} and 0.5 g. of pure Na metal and 0.2 g. of $Fe(NH_4)_3(SO_4)_2 \cdot 6 H_3O$ are added. (Instead of the Dewar flask, a one-liter beaker inserted in a second, 1.5-liter beaker may also be used.) After disappearance of the blue color of the NH_3 solution, 50 g. (nearly 0.3 mole) of CrCl₃ is added with constant stirring (2-g. portions over a period of 1-2 hours). The brown precipitate is allowed to settle and the clear supernatant liquid is decanted or siphoned off.

The residue is transferred to a large dish and allowed to stand (with occasional stirring) until the odor of NH_3 disappears and a lustrous yellow, free-flowing powder remains. The yield of crude $\{Cr(NH_3)_6\} Cl_3$ is almost quantitative (about 80 g.).

The crude product is purified by dissolving rapidly in a mixture of 10 ml. of conc. HCi and 150 ml. of water at 40 °C. After filtration, the solution is treated at once with 50 ml. of conc. nitric acid to precipitate pure $[Cr(NH_3)_{el}](NO_3)_3$. The liquid is allowed to cool to room temperature, the yellow crystalline salt is filtered on a Büchner funnel and washed with distilled water containing some HNO₃, then with alcohol, and finally with ether. The product is dried in a vacuum desiccator in the absence of light and stored in a brown bottle. Yield: 80 g. (75%).

SYNONYM:

Luteochromic chloride or nitrate.

PROPERTIES:

The chloride (as well as the nitrate) forms orange-yellow crystals, only moderately soluble in water at room temperature (the nitrate in the ratio 1:40). Solubility is still further decreased by addition of nitric acid. All $[Cr(NH_3)_3]^{S+}$ salts are sensitive to light even when dry. Decomposes slowly in solution, more rapidly on boiling, depositing chromium hydroxide. Heating with conc. HCl produces $[CrCl(NH_3)_5] Cl_2$.

REFERENCES:

- L. S. M. Jörgensen. J. prakt. Chem. 30, 2 (1884).
- II. A. L. Oppegard and J. C. Bailar, Jr. in: L. F. Audrieth, Inorg. Syntheses, Vol. III, New York-Toronto-London, 1950, p. 153.

Chloropantaamminachromium (III) Chloride

{CrCl(NH₄)₅}Cl₄

1. BY AEACTION OF LIQUID NH3 WITH CrCl3

Dry CrCl₃ (8 g.) is added to liquid NH₃. The reaction starts at the boiling point of the NH₃, and the CrCl₃ is transformed into a red

product. After evaporation of excess NH2, the residue is triburated with 30 ml. of ice-cold water, filtered, then washed with some cold water until the filtrate is reddish. Concentrated nitric acid is added to the filtrate and [Cr(NH2)e] (NO2) is obtained (see p. 1351). Yield: about 7 g.

The red residue, consisting of [CrCl(NH3)5] Cla, is boiled with conc. HCl, cooled, mixed with water, filtered and washed with some cold water. It is then dissolved as rapidly as possible at 50°C in 400-500 ml. of water which is acidified with a few drops of HoSO4. The solution is immediately filtered through a large fluted filter paper and treated with an equal volume of conc. HCL. The salt precipitates in beautiful red crystals; after one hour, these are filtered, washed with 1:1 HCl, then with alcohol, and dried in a desiccator. Yield: about 5 g.

H. FROM THE RHODOCHLORIDE BY BOILING WITH HYDROCHLORIC ACID

The procedure for the preparation of rhodochromium chloride (see p. 1359) is followed, except that after the introduction of O_2 the entire mixture is boiled for a few minutes with 2.5 times its volume of conc. HCl, whereupon the [CrCl(NH₃)₅] Cl₂ precipitates.

After cooling, the supernatant liquid is decanted. In 24 hours, additional purpureochromic chloride separates from the supernatant; it is, however, contaminated with NH4Cl. The NH4Cl is removed with dilute HCl; the residue is washed with alcohol and dried in a desiccator.

Yield: about 45 g. (from 60 g. of K₂Cr₂O₇).

Purification is the same as in method I (solution in water containing some H₂SO₄ and addition of HCi).

SYNONYM:

Purpureochromic chloride.

PROPERTIES:

Formula weight 243.54, Carmine-red crystals; d418.8 1.687, Solubility (16°C) 0,65 g./100 g. H 2O. In aqueous solution, even on moderate heating, adds a water molecule to give [Cr(H 20)(NHs) siClas Space group V¹⁵_b.

AEFERENCES:

- I. O. T. Christensen, Z. anorg. Chem. 4, 229 (1893); H. Biltz and W. Biltz. Übungsbeispiele a. d. unorg. Exp. chemie [Exercises in Inorg. Experimental Chemistry], 3rd and 4th eds., 1920; p. 176.
- II. O. T. Christensen, J. prakt. Chem. 23, 57 (1881).

Triethylenediaminechromium (III) Sulfate, Chloride and Thiocyanate [Crens]:(SO:);, [Crens]Cls:3.5HsO, [Crens](SCN); HsO

A) ANRYDROUS CHROMIUM (HI) SULFATE

 $Cr_2(SO_4)_3 \cdot 18 H_2O = Cr_2(SO_4)_3 + 18 H_2O$ 716.5 392.2

Heating of $Cr_2(SO_4)_3 \cdot 18 \text{ H}_2O$ for 2-3 days at 100-110°C gives a lumpy product; this is ground and dried further. Complete dehydration is indicated by the fact that the powder is no longer soluble in water.

B) ANHYDROUS ETHYLENEDIAMINE

Since anhydrous ethylenediamine attacks cork and rubber stoppers, ground glass equipment must be used. Five hundred grams of NaOH and 875 ml. of commercial ethylenediamine hydrate are heated overnight on a steam bath. Two layers form; the upper layer is decanted, treated with additional 150 g. of NaOH for several hours; the supernatant is decanted again and distilled. B.p. 116-117°C at 760 mm. Yield; almost quantitative. (Propylenediamine can be dehydrated in the same manner.)

The ethylenediamine thus obtained still contains some water. Absolutely dry ethylenediamine reacts only very slowly with the $Cr_{3}(SO_{4})_{3}$.

C) TRIETHYLENEDIAMINECHROMIUM (III) SULFATE

 $Cr_2(SO_4)_s + 6 H_2 N \cdot C_2 H_4 \cdot N H_2 = [Cr en_3]_2(SO_4)_3$ 392.2 380.6 752.8

A 300-mi. Erlenmeyer flask, to which an air-cooled condenser is attached by a ground joint, is used to reflux 49 g. of $Cr_3(SO_4)a$ and 50 ml. of anhydrous ethylenediamine on a steam bath. Within one hour (and often much less), the sulfate begins to lose its bright green color and its powdery nature. If this should not occur after two hours, the reaction is induced by addition of a drop of water. From this time on, the flask must be shaken to and fro, to bring unreacted $Cr_2(SO_4)_3$ into contact with the amine; the shaking is discontinued when a brown, solid mass forms; this is allowed to remain on the steam bath overnight. The solid, which is orangeyellow after cooling, is then broken up with a spatula, ground, washed with alcohol, and dried in air. Yield: 89 g. [95%, based on $Cr_3(SO_4)_3$].

D) TRIETHYLENEDIAMINECHROMIUM (III) CHLORIDE HYDRATE

 $[Cr en_{s}]_{t}(SO_{t})_{s} + 6 RCl = 2[Cr en_{s}]Cl_{s} + 3 H_{s}SO_{t}$ $752.8 \qquad (\cdot 3.5 H_{s}O)$ 874.4

A solution of 32 g. of $[Cr en_3]_3$ (SO₄)₃ in dilute HCl (5 ml. of conc. HCl and 30 ml. of water) is prepared at 60-65°C and rapidly filtered through a Büchner fumel. The filtrate is stirred and cooled in ice while 27 ml. of conc. HCl is added; the chloride [Cr en₃] Cl₃ · 3.5 H₂O separates at once. Filtration yields 20 g. or 60% based on the sulfate used.

This chloride is still contaminated with sulfate. It may be purified by recrystallization from water. Thus 20 g. of the crude product is dissolved in 20 ml. of water at 65°C. On cooling, 12 g. of pure chloride is obtained.

E) TRIETHYLENEDIAMINECHROMIUM (III) THIOCYANATE

| [Cr ens]Cls | ÷ | 3 NH SCN | ** | $[Cren_4](SCN)_4 + 3 NH_4Cl$ |
|-------------------------|---|----------|-----------|------------------------------|
| (+3.5 H ₁ O) | | | | (•H ₄ O) |
| 437.2 | | 228.4 | | 424.6 |

A solution of 30 g. of $[Cr en_3] Cl_3 \cdot 3.5 H_2O$ in 100 ml. of warm water is mixed, while ice-cooled and rapidly stirred, with a conc. aqueous solution of 36 g. of NH₄SCN. The sparingly soluble $[Cr en_3]$ (SCN)₃ • H₂O separates at once. Filtration yields 30 g. of the crude product, or 94% based on the chloride charged.

For purification, the product is recrystallized from 100 ml. of water at 65°C, cooled, filtered, washed with alcohol and ether, and dried in air. Yield 23 g., or 77% based on the crude.

The bromide and the iodide can be obtained in exactly analogous fashion, that is, by addition of the corresponding ammonium salt.

Alternate methods: From violet chromium (III) chloride or dehydrated chrome alum, with ethylenediamine hydrate or ethylenediamine, respectively.

PROPERTIES:

The $[Cr en_s]^{3^+}$ salts are distinctly crystalline, orange-yellow substances, which are slightly sensitive to light even when dry. Their aqueous solutions have poor stability, particularly when heated or placed in sunlight: then the initial red color is followed shortly by complete decomposition. While the sulfate is extremely soluble in water and the chloride is also very soluble, the thiscyanate, the bromide and the iodide are relatively sparingly soluble. The chloride and the thiocyanate are readily converted by beating to the corresponding $[CrX_3 en_3]^+$ salts (see the two preparations which follow).

REFERENCES:

C. L. Rollinson and J. C. Bailar, Jr. in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 196, P. Pfeiffer, Ber. dtsch. chem. Ges. <u>37</u>, 4277 (1904); Reschke, Thesis, Univ. of Leipzig, 1925; M. Linhard and M. Weigel. Z. anorg. allg. Chem. <u>271</u>, 115 (1952).

cis-Dichlorodiethylenediaminechromium (III) Chloride

[CrCl, en,]Cl · H,O

The [Cr en₃] Cl₃ · 3.5 H₂O, which serves as the starting material, is recrystallized from a 1% aqueous NH₄Cl solution; this imparts a small NH₄Cl content to the chloride complex, and the NH₄Cl catalyzes the thermal decomposition. If the [Cr en₃]Cl₃. 3.5 H₂O is prepared specifically as a starting material for this reaction, the NH₄Cl may be added already during the recrystallization of the impure [Cr en₃]Cl₃ · 3.5 H₂O.

The recrystallized salt is dried and is then spread in a thin layer on a large watch glass, which is heated to 210°C. Careful control of the temperature is essential, since the rate of decomposition is too high above 215°C, while below 200°C the reaction is very slow. The evolution of ethylenediamine starts after a few minutes; the salt gradually becomes darker and after 1-2 hours turns red-violet. The course of the reaction is checked by the weight loss, which should approach the theoretical value of 30.6%.

A crude product, in satisfactory purity for many purposes, is obtained by washing with ice-cold conc. HCl. For further purification, it may be recrystallized as follows: The salt is dissolved rapidly in water at 70°C, using 4 mL of water per gram of sait, and the filtered solution is cooled in a cooling mixture. Then 1 mL of ice-cold conc. HCl is added for each gram of the salt, whereupon small red-violet needles separate. These are filtered and washed with alcohol and ether. Yield: 0.45 g. (60%)per gram of starting compound.

Alternate method: From $K_3[Cr(C_2O_4)_3]$ via two intermediate steps [A. Werner, Ber. dtsch. chem. Ges. 44, 3135 (1911)].

PROPERTIES:

Small red-violet needles, readily soluble in water with a violet color. The solution becomes orange after a few hours, more rapidly when warmed.

REFERENCES:

C. L. Rollinson and J. C. Bailar, Jr. in; W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 201; P. Pfeiffer. Ber. dtsch chem. Ges. <u>37</u>, 4277 (1904); M. Linhard and M. Weigel. Z. anorg. alig. Chem. <u>271</u>, 119 (1952).

trans-Dithiocyanatodi(ethylenediamine)chromium (III)

Thiocyanate

[Cr(SCN); en,]SCN

trans-Dichlorodi(ethylenediamine)chromium (III) Chloride [CrCl_xen_t]Cl

a)

 $[Cr en_3](SCN)_3 = [Cr(SCN)_2 en_3]SCN + H_2N \cdot C_2H_4 \cdot NH_3$ $(\cdot H_2O)$ 424.6 348.6

The crude $[Cr en_3] (SCN)_3 \cdot H_2O$ used as starting material is prepared according to the directions given on p. 1355 and recrystallized from a 1% NH₄SCN solution as in the preparation of cis-[CrCl₂ en₃] Cl · H₃O. As in the latter case, the product is prepared by thermal decomposition, but at a temperature of 130°C (maximum 134°C). The theoretical weight loss is 16.40%. The product, which is a uniform yellow-red, is recrystallized several times from hot water, the solution concentration being such that the thiocyanate starts to crystallize slowly only after the solution is completely cold. This procedure yields 2 g. of pure [Cr(SCN)₂ en₂]SCN per 3 g. of crude; the material still contains 1-2 moles of water of hydration; this is removed in a desiccator.

b)

$$[Cr(SCN)_{2} en_{2}]SCN \xrightarrow{Cl_{2}} [CrCl_{2} en_{3}]Cl_{346.6}$$

A fast stream of Cl_{2} is passed through an aqueous slurry of the thiooyanate obtained in (a); good cooling is necessary. The green crystalline powder which separates from the violet solution is essentially trans-dichlorosulfate and -chloride. About 0.6 g. of this

orude dichloro salt is obtained from 2 g. of thiocyanate. A concentrated solution of the crude salt in conc. HCl is placed in an H₂SO₄ desiccator, which also contains a small dish with conc. HCl. The blue-green acid chloride [CrCl₃ en₂] Cl · HCl · 2 H₂O (0.3 g.) separates in one day. On heating to 100°C, this is transformed into [CrCl₂ en₂] Cl.

PROPERTIES:

Trans-[CrCl₂en₂]Cl consists of green crystals. A very thin layer of a conc. aqueous solution appears green, while thicker layers have a brown-red color.

REFERENCES:

- I. C. L. Rollinson and J. C. Bailar, Jr. in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 202; P. Pfeiffer, Z. anorg. Chem. <u>29</u>, 113 (1902).
- II. P. Pfeiffer, Ber. dtsch. chem. Ges. 37, 4282 (1904).

Dichloroaquotriamminechromium (III) Chloride

[CrCl₂(OH₂)(NH₃)₃]Ci

There are three position isomers: a, b, and c. The preparation starts from $(NH_3)_3CrO_4$ and hydrochloric acid.

a) One gram of $(NH_3)_3CrO_4$ (for preparation, see p. 1392) is carefully dissolved in 6 ml. of dilute HCl (the flask must be cooled with ice). It is added to the acid slowly in small portions, as soon as the vigorous reaction from the preceding portion has subsided. On addition of 10 ml. of conc. HCl and long standing in the cold, the red solution deposite red-violet snowflakelike crystals. These are recrystallized from the conc. aqueous solution by addition of conc. HCl. After washing with alcohol and ether, the crystals are dried over H₂SO₄. Yield: about 1.1 g.

b) About 2 g, of the chloride prepared in (a) is heated in HCl solution at about 60° C until the blue color of the solution is completely changed to green. By suction-filtration in a desiccator, dark green, needle-shaped crystals can be isolated from this solution; these are dried over H₂SO₄. This salt cannot be recrystallized; it is always contaminated with impurities.

c) If 8 ml, of conc. HCl is used to dissolve one gram of $(NH_3)_3CrO_4$ under the same conditions as in (a), one obtains a bright green solution, from which gray, needle-shaped crystals soon separate. These are washed with alcohol and ether and dried over H_2SO_4 . Yield: about 1 g.

1

PROPERTIES:

Formula weight 227.50. a) Red-violet dichroic crystals, soluble in water, giving a blue color. b) Dark green, needle-shaped crystals, soluble in water, giving a green color. c) Gray, needleshaped crystals, insoluble in cold water, soluble in warm H_2O , giving a red color.

REFERENCE;

E. H. Riesenfeld and F. Seemann. Ber. dtsch. chem. Ges. <u>42</u>, 422 (1909).

Hexaureachromium (III) Chloride

[Cr(OCN₂H₄)₄]Cl₁ · 3 H₂O

 $= [C_{f}(OCN_{2}H_{4})_{5}]Cl_{5} \cdot 3H_{1}O + 3H_{2}O$ 572.8

Green, crystalline chromium chloride hydrate $[CrCl_2(H_2O)_4]Cl \cdot 2 H_2O$ and somewhat more than the stoichiometric quantity of urea are dissolved in some water and treated with a few drops of HCl. The solution is concentrated in a drying oven at 75°C (or on the steam bath) until a crystalline crust forms. The crystal slurry thus obtained is dissolved in the minimum quantity of water at 50-60°C and rapidly filtered. The salt complex separates as green needles.

PROPERTIES:

Green needles, readily soluble in water, insoluble in absolute alcohol.

REFERENCE:

;

E. Wilke-Dörfurt and K. Niederer, Z. anorg. allg. Chem. 184, 150 (1929).

Rhodochromium Chloride

[(NH_s)_sCr(OH)Cr(NH_t)_b]Cl_s

The preparation involves oxidation of an ammoniacal, NH₄Cl= containing solution of Cr (II) salt.

1.27

Sixty grams of K2Cr2O7 powder is placed in a 2,5-liter beaker and covered with 200 ml. of cone, HCl and 75 ml. of alcohol (stirring). The resulting green solution of chromium (III) salt is reduced with zinc while still warm (but below 50°C) in the absence of air. The blue solution is poured into a mixture of 500 g. of NH 4Cl and 750 ml. of conc. ammonia, the necessary good cooling being achieved by adding pieces of ice (or by immersion in ice). After decanting from undissolved NH Cl, O2 is passed through the liquid, which is shaken vigorously to achieve rapid oxidation. The liquid becomes red and rhodochloride deposits out abundantly. The salt is filtered. washed first with a mixture of 2 vol. of water and 1 vol. of cone. HCl, and then once with cold water. It is dissolved in cold water and the solution allowed to flow into a chilled mixture of 2 vol. of conc. HCl and 1 vol. of water, whereupon the rhodochloride reprecipitates almost completely. It is washes with 1:1 HCl. then with alcohol until free of acid, and dried in air in the dark. Yield: about 25 g.

PROPERTIES:

Formula weight 468,64. Pale crimson-red crystalline powder; contains 1 mole of $H_{2}O$ when air-dried; this is slowly lost over conc. $H_{2}SO_{4}$.

REFERENCES:

S. M. Jörgensen, J. prakt. Chem. <u>25</u>, 328 (1882); for composition, see K. A. Jensen. Z. anorg, allg. Chem. <u>232</u>, 257 (1937), as well as W. K. Wilmarth, H. Graff and S. T. Gustin, J. Amer. Chem. Soc. <u>78</u>, 2683 (1956).

Erythrochromium Chloride

[(NH₄)₅Cr(OH)Cr(NH₂)₄(OH₂)]Cl₅

Seven grams of rhodochromium chloride (preparation as above) is dissolved in 56 ml. of 2 N ammonia. This blue solution becomes pure crimson red in about 15 minutes; it is then cooled in ice and treated with 100 ml. of ice-cold, conc. HCl. The erythrochloride which precipitates is filtered, washed with some dilute HCl, then with alcohol and ether, and dried over H_2SO_4 . Yield: 95%.

PROPERTIES:

Light-sensitive, crimson-red crystalline powder; more readily soluble in water than the rhodochloride.

100

24. CHROMIUM, MOLYBOENUM, TUNGSTEN, URANIUM

REFERENCES:

K. A. Jensen. Z. anorg. alig. Chem. 232, 264 (1937). W. K. Wilmarth, H. Graff and S. T. Gustin, J. Amer. Chem. Soc. 79, 2683 (1956).

Tris(2,2'-dipyridyl)chromium (II) Perchlorate

[Cr(dipy);](ClO₄);

 $Cr + 2 HC! = CrCl_{2} + H_{2}$ $52 \qquad (\cdot aq.)$ $CrCl_{2} + 3 dipy = [Cr(dipy)_{3}]Cl_{2}$ $(\cdot aq.) \qquad 468 \qquad (\cdot aq.)$ $[Cr(dipy)_{3}]Cl_{2} + 2 NaClO_{4} = [Cr(dipy)_{3}](ClO_{4})_{2} + 2 NaClo_{4}$ $(\cdot aq.) \qquad 719$

All operations are carried out under pure N_a and with descrated liquids.

A solution of 0.26 g. of electrolytic Cr (preparation on p. 1335) in 2.5 ml. of 1:1 HCl is prepared. After the H₂ evolution ceases; the solution is diluted with 20 ml. of water, and 2.35 g. of 2.2'dipyridyl, dissolved in some methanol, is added. The solution, now a deep wine-red, is filtered through a fine fritted-glass filter. The filtrate is treated with a solution of 1 g. of NaClO₄ and 0.5 ml. of 70% HClO₄ in 50 ml. of water. A slurry of black-violet crystals is formed at once. This is filtered on fine fritted glass, washed with water, alcohol and ether, and dried in vacuum over P_2O_{5} . Yield: 3 g. (83% of theory).

PREPARATION OF 2,2 DIPYRIDYL

a) From FeCi₃ and pyridine in an autoclave [F. Hein and H. Schwedler, Ber. dtsch. chem. Ges. <u>68</u>, 681 (1935)]; b) refluxing of Raney nickel and pyridine [G. M. Badger and W. H. F. Sasse, J. Chem. Soc. (London) <u>1956</u>, 616].

The corresponding complexes with 1,10-phenanthroline [Cr phen₃]_n X_n (where X = I or ClO₄ and n = 1, 2, 3) can be prespared in a similar manner [S. Herzog, Chem. Techn. 8, 544 (1956)].

PROPERTIES:

Small black crystals; completely stable in air when dry, but oxidized when damp (acquires a yellow color). Sparingly soluble in water or methanol, giving an intense wine-red color.

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Insoluble in other and benzene. In weak perchloric acid solution oxidized by air, forming yellow tris(2,2'-dipyridyl)chromium (II) perchlorate, which can be crystallized by concentrating the solution in the cold over H₂SO₄.

REFERENCES:

S. Herzog. Thesis, Univ. of Jena, 1952; F. Hein and S. Herzog. Z. anorg. alig. Chem. <u>267</u>, 337 (1952); G. A. Barbieri and A. Teitamanzi. Atti R. Accad. Lincei (Rome), Rend. [6] <u>15</u>, 877 (1932).

> Tris(2,2'-dipyridyl)chromium (1) Perchlorate [Cr(dipy)s]ClOs

 $2 [Cr(dipy)_{a}](ClO_{4})_{2} + Mg = 2 [Cr(dipy)_{a}]ClO_{4} + Mg(ClO_{4})_{2}$ 2.510 2.510

All operations are carried out under pure N_2 and with air-free liquids.

Tris (2, 2'-dipyridyi) chromium (II) perchlorate (1.0 g.; preparation as above) is covered with 250 ml. water, giving an opaque wine-red solution. This is treated with 60 mg. of Mg powder (about 3 times the stoichiometric quantity) and machine-shaken in a well-closed container. The solution becomes colorless after a maximum of 3 hours, and a fine, indigo-colored powder separates out. The powder, because of its fine particle size, imparts an apparent black-violet color to the solution on superflicial examination. Now 3 g. of NH₄ClO₄ is added and the mixture is shaken for an additional hour to dissolve the remaining Mg. After standing overnight, the dark-blue product is filtered through a fine fritted-glass filter, washed three times with 5-ml. portions of water, and dried in vacuum over P₂O₅. After a few hours, the preparation is dust-dry. Yield: about 0.65 g. (about 80% of theory)-

PROPERTIES;

Indigo-blue powder; soluble in methanol, ethanol, acetone and pyriding, giving a deep, inky blue color; insoluble in water, benzene and ether. The solution is oxidized almost instantly in air, becoming lighter in color. The dry product reacts spontaneously with atmospheric O_2 with considerable evolution of heat and loss of the 2,2'-dipyridyl.

REFERENCES:

S. Herzog. Thesis, Univ. of Jens, 1952. F. Hein and S. Herzog. Z., anorg. alig. Chem. <u>267</u>, 337 (1952).

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Tris(2,2'-dipyridyl)chromium (0)

[Cr(dipy),]

 $Cr_{2}(CH_{3}COO)_{4} + 3 dipy = [Cr(dipy)_{3}] + Cr(III)$ and Cr(H) complexes. (-2H₇O) 376.2 468.6 \$20.6

Two grams of chromium (II) acetate hydrate is mixed (in the absence of air) with 2.49 g. of 2,2'-dipyridyl (equivalent to 1.5 moles of dipyridyl per g.-atom of Cr). Now, 40 ml. of descrated water is added and the resulting suspension is machine-shaken for three hours. The black precipitate is filtered off from the deep-red mothor liquor (through a very fine fritted-glass filter), washed with water and alcohol, and dried over air-free P_2O_6 . Yield; about 1 g.

Alternate methods: Reduction of tris(2,2'-dipyridyl)chromium (II) salt in tetrahydrofuran with sodium.

PROPERTIES:

Small black crystals; soluble in benzene, tetrahydrofuran, pyridine or dimethylformamide with a red color. Ignites in air with oxidation to Cr_2O_3 .

REFERENCE:

S. Herzog, K. Chr. Renner and W. Schön. Z. Naturforsch. <u>12b</u>, 609 (1957).

Hexaphenylisonitrilochromium (0)

[Cr(C,H,NC)4]

 $3 C_{r_0}(CH_sCOO)_4 \cdot 2 H_sO + C_0H_sNC (excess) \rightarrow$

1128.7

2 [Cr(C₆H₅NC)₈] + 4 Cr(III) complex 1241.4

The reaction is carried out under N_3 ; a large excess of phenyl isonitrile is desirable. Six grams of chromium (II) scette $Cr_3(CH_3COO)_4 \cdot 2 H_3O$ is suspended in 40 ml. of methanol, and a solution of 20 g. of isonitrile in 10 ml. of methanol is added. After about one hour, well-formed garnet-red crystels separate from the deep black-red solution. The precipitate is filtered, washed with some methanol, and dried. The yield is 5-6 g., which is almost quantitative, based on the disproportionation shown above.

PROPERTIES:

Garnet-red crystals with metallic, yellowish-green reflectance, stable in air, diamagnetic. M.p. 178.5°C (undergoes deformation at 151°C). Soluble in chloroform and benzene in the cold, readily soluble in the hot solvents. Can be recrystallized by reprecipitation with alcohol from a chloroform solution. Can be obtained from methylene chloride; in this case, large crystals, similar in appearance to pyrites, are obtained.

REFERENCE:

L. Malatesta, A. Sacco and S. Ghielmi. Gazz. Chim. Ital. 82, 516 (1952).

If a Cr (II) halide is used instead of the Cr (II) acetate, the reaction is completely different: a crystalline precipitate of $[Cr(RNC)_4Cl_3]$ (orange-red) or $[Cr(RNC)_4Br_3]$ (olive brown), depending on the starting halide used, forms instantly. These compounds show a paramagnetism of 2.84 Bohr magnetons, corresponding to Cr^{2+} . They are again completely stable in air and can even be heated in water without decomposition; insoluble in ether, alcohol, benzene and carbon tetrachloride, but soluble in chloroform and methylene dichloride.

REFERENCE:

F. Hein and W. Kleinwächter. Private communication, unpublished.

Chromium Orthophosphate

CrPO₄

 $\begin{array}{rrrr} 4\,{\rm CrO}_{3}\,+\,4\,{\rm H}_{3}{\rm PO}_{4}\,+\,3\,{\rm N}_{8}{\rm H}_{4}\cdot\,{\rm H}_{2}{\rm O}\,=\,4\,{\rm CrPO}_{4}\,+\,15\,{\rm H}_{2}{\rm O}\,+\,3\,{\rm N}_{2}\\ 400.0 & 392.0 & 150.2 & 588.0 & 270.2 & 67.2\,i. \end{array}$

A mixture of 11.6 g. of 85% $H_3 PO_4$ (d 1.69), 12.5 g. of CrO_3 (125% of the stoichiometric quantity) and 200 ml. of H_3O is prepared, and 5.4 g. of 80% hydrazine hydrate (115% of the stoichiometric amount) in 100 ml. of H_2O is added in drops and with stirring. After stirring for 15 minutes at 50°C, the precipitate is washed, suctiondried, and then dried for 2 hours at 100°C. Yield: 19 g. of amorphous

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3.5-hydrate. Heating for 2 hours in vacuum at 800°C yields 13 g. of CrPO4, which gives a crystalline x-ray diffraction pattern.

PROPERTIES:

Hydrate: Turquoise green powder. d 2.15. Following the above directions gives a particle size of 0.1 μ , while a tenfold dilution of the reactants gives 1- μ particles.

Anhydrous: Gray-brown; insoluble in H_2O and CH_3COOH . d 3.05.

REFERENCES;

F. Wagenknecht. German Patents 1,046,597 (1957) and 1,056,104 (1957).

Chromium (II) Sulfate

CrSO₄ · 5 H₂O

 $C_{r} + H_{2}SO_{4} + 5H_{2}O = CrSO_{4} \cdot 5H_{2}O + H_{2}$ 52.0 98.1 90.1 238.2 2.0

Twenty grams of coarse, very pure electrolytic chromium (>99.99% Cr) is placed in 150 ml. of H_3O , and 46 g. of conc. H_2SO_4 is then added with agitation. The Cr is completely dissolved and massive crystals of CrSO₄ · 5 H_3O precipitated from the deep blue, highly supersaturated solution. Concentration of the liquid in vacuum gives an almost theoretical yield of the product. The salt is filtered, washed with some ice-cold water, and dried in vacuum or in a stream of N_3 ; any water present can be removed by thorough washing with acetone.

PROPERTIES:

Blue, massive crystals. Completely stable in air when day. Solutions are instantly oxidized on contact with atmospheric O_3 . Solubility (0°C): 21 g./100 g. H₃O. Isotypic with CuSO₄ • 5 H₃O:

REFERENCE:

H. Lux and G. Blimann. Chem. Ber. 91, 2143 (1958).

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Chromium (II) Salt Solutions

1. PREPARATION BY ELECTROLYTIC REDUCTION

 $\begin{array}{rll} K_{2}Cr_{4}O_{7} &+& 3\,SO_{7} &+& H_{2}SO_{4} &+& Cr_{5}(SO_{4})_{5} \ (\cdot \ aq)\\ & 294,2 & 65.7 \ l. & 96.1 & 392.2\\ & Cr_{5}(SO_{4})_{5} \left(\cdot \ aq\right) &+& 2 \ e &\rightarrow& 2\,CrSO_{4} \ (\cdot \ aq) &+& SO_{4}^{2-}\\ & & 392,2 & 296.1 \end{array}$

The electrolysis apparatus (see Fig. 318) comprises a 1.5-liter jar p and a cylindrical porous clay cell q of about 500-ml. capacity (height 17 cm., diameter 6.5 cm.); the cell is closed off with a

rubber stopper which carries a glass stirrer u with a mercury seal, a sampling tube s, a gas outlet tube t, and a lead cathode v having 230 cm.³ of surface. The cell is surrounded by the Pb anode w.

The Pb cathode should be prepared according to directions given by Tafel (see the references below). It is suspended in 20% sulfuric acid and surrounded coaxially by a second cylindrical Pb electrode. The current (0.13 amp./in.²) is turned on, and the working electrode is operated first as an anode, then as a cathode (5 min.), and finally again as an anode (15 min.). After this, it is brown. It is washed with boiling water and dried.

The chromium (III) sulfate solution required for the electrolytic reduction is prepared as follows: SO_2 is bubbled through a solution of 80 g. of $K_2Cr_3O_7$, 30 g. of conc. H_2SO_4 and 450 g. of water until reduction is complete. Good cooling is necessary to prevent the transformation of violet to green

Fig. 318. Preparation of chromium (II) sulfate by electrolytic reduction. p jar; q porous clay cell; s sampling tube; t gas outlet tube; u stirrer with Hg seal; v lead cathode; w lead anode.

chromium (III) sulfate [the latter is not as readily reduced to chromium (III) sulfate]. The excess SO_2 is driven off with a fast stream of air. The last traces of SO_3 must be removed by brief boiling. The solution, whose volume is now about 50 ml., is transferred to the clay cell. The anodic electrolyte is 2 N H₂SO₄. Electrolysis proceeds at a current density of 0.13 amp./in.⁹, that is, at a current of 4.6 amp. The reduction takes 12 hours, but up to 24 hours may be required if a great deal of green chromium (III) sulfate is present. The course of the reduction can be followed by

24. CHROMIUM, MOLYBOENUM, TUNGSTEN, URANIUM

removing samples and titrating with excess 0.1 N KMnO4, adding KI, and back-titrating with 0.1 N Na₃S₂O₃.

II. PREPARATION BY REDUCTION WITH ZINC

It is best to use a zinc reductor. This consists of a vertical glass tube, 45 cm. long and 2 cm. I.D., with a glass stopcock at the lower end. It is two-thirds filled with zinc granules. Before use the contents of the column are amalgamated for 10 minutes with a 0.1 M HgCl₂ solution in 1 M HCl, then washed with a large quantity of water and finally with some 1 N H₂SO₄; during this operation the liquid level should always be above the zinc. The reduction proper is carried out by adding a solution of 90 g. of green chromium (III) chloride hydrate in 120 ml. of water and 30 ml. of 2 N H₂SO₄ to the reductor tube; the rate of discharge from the reductor is so adjusted that only a pure, light blue chromium (II) salt solution drops into the directly attached storage or reaction vessel.

This solution obviously contains zinc salts. Solutions completely free of foreign salts are obtained either by dissolving chromium (III) acetate or, better, by dissolving electrolytic chromium in dilute HCl, as described, for example, in the procedure for tris(2,2'-dipyridyl)chromium (II) perchlorate.

APPLICATIONS

Useful for removing O_2 from gases, for reductometric titration, and as a reductant in organic chemistry.

PROPERTIES:

Blue solution, very sensitive to air; storage stability is highly dependent on the purity of the starting materials.

REFERENCES:

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- I. Ch. W. Hofmann. Thesis, Univ. of Bern, 1947; R. Flatt and F. Sommer. Helv. Chim. Acta <u>25</u>, 684 (1942); A. Asmanow. Z. anorg. allg. Chem. <u>160</u>, 210 (1927); W. Traube and A. Goodson. Ber. dtsch. chem. <u>Ges. <u>49</u>, 1679 (1916); J. Tafel. Z. phys. Chem. <u>34</u>, 187 (1900).</u>
- II. E. Zinti and G. Rienäcker. Z. anorg. allg. Chem. 161, 378 (1927); M. R. Hatfield in: L. F. Audrieth, Inorg. Syntheses; Vol III, New York-Toronto-London, 1950, p. 149.

Chromium (II) Acetate Crs(CH,COO), -2 H2O

I. $\operatorname{CrCl}_{s} + \frac{1}{2} \operatorname{Zn} = \operatorname{CrCl}_{s} + \frac{1}{2} \operatorname{ZnCl}_{s}$ $(-6H_{r}O)$ (-aq)266.5 32.7

Pure chromium (II) acetate may be prepared only if oxygen is completely excluded. This condition is approached in the apparatus of Fig. 319.

Fig. 319. Preparation of chromium
(II) acetate. a zinc reductor; b glass wool plug; c pinchcock or glass stop-cock with 10-mm. bore; d reaction vessel; e fritted-glass funnel; f glass stirrer; g rubber cap to seal stirrer against outside air; h dropping funnel; i suction flask; k dropping funnel for washing liquids; i bubble trap for outgoing inert gas; m rubber sleeve for sealing large stopper.

The chromium (II) salt solution is obtained in a Zn reductor (see previous preparation). This consists of a glass tube a (45 cm. long and 2 cm. I.D.) in which a glass wool plug is inserted at b. The Zn granules filling the tube are amalgamated before use (10 minutes with a 0.1 M HgCl₂ solution in 1 M HCl), then washed with large quantities of water and finally with some 1 N H₂SO₄; during this procedure the liquid level should always be above the zinc. A pinchcock or a glass stopcock with a 10-mm, bore is located at c. Reaction vessel d is attached with a rubber tube to the moderately coarse fritted-glass funnel e (diameter about 10 cm.). Glass stirrer f should provide thorough stirring of the precipitate during the washing and drying steps; it is held in place and turned by means of the rubber cap g which serves as a seal. Nitrogen or carbon dioxide (O₂-free) is passed through the reaction vessel during the precipitation, and over the precipitate during the filtration. The gage pressure in the apparatus (governed by the liquid height in the trap l) should be as small as possible.

A solution of 90 g, of green chromium (III) chloride hydrate in 120 ml. of water and 30 ml. of 2 N H_2SO_4 is poured into the reductor tube and its outflow rate so adjusted that only a pure light blue chromium (II) salt solution drops into the reaction vessel d. A filtered solution of 252 g, of Na acetate in 325 ml. of water is charged beforehand into the reaction vessel (via h). During the precipitation the vessel contents are stirred briefly by hand, using the stirrer provided.

After completion of the precipitation, N_3 or CO_3 is admitted into filter e and stopcock c is opened. In this operation the filtering flask : can be carefully put under a slight vacuum, provided a sufficient flow of N_3 (or CO_3) is maintained and the chromium (II) acetate is always surrounded only by the protective gas. The precipitate is washed on the filter with air-free distilled water, then several times with alcohol, and finally with peroxide-free ether, after which N_2 or CO_3 (H₃O-free) is passed through for 24 hours. The chromium (II) acetate must be completely dry before it can be exposed to air, since it oxidizes at an appreciably faster rate when moist. Yield: 55 g.

The preparation can also be carried out with smaller quantities, e.g., one third of those given above. In this case, the dimensions are reduced to 7 cm. I.D. for the precipitating vessel d and the funnel e. The reductor need be only 35 cm. high (filled to 25 cm.). The drawing of Fig. 318 is based on dimensions appropriate to this case.

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 $Cr + 2 HCl \rightarrow CrCl_{a} \cdot aq.$

 $CrCl_2 \cdot aq_* + 2 CH_3COONa \rightarrow {}^{1/2}Cr_2(CH_3COO)_4 + 2 NaCl_{(-2,H_3O)} 188.i$

Two grams of electrolytic chromium is covered with a minime of 6.2 ml. of conc. HCl and an equal volume of water (air should be

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excluded). After the start of the H_3 evolution, about 10 additional mi. of water is added and the vessel is heated on a steam bath. When the evolution of H_2 ceases, the sky-blue solution of chromium (II) chloride is slowly filtered through a fine fritted-glass funnel into a solution of 28 g. of sodium acetate in 40 mi. of deaerated water. The solution immediately turns red, and after a few seconds small glittering red crystals begin to precipitate. After overnight standing, these are filtered through fine fritted glass, washed five times with 10-ml. portions of water, dried with air-free CaCl₂, and stored under N₂. Yield: about 6 g.

Other means of obtaining chromium (II) salt solutions may be used instead of direct solution of the chromium used, provided the product solutions contain no foreign substances which would affect the precipitation of the acetate.

PROPERTIES:

Dark-red crystals, slightly soluble in water and alcohol. Insoluble in ether. When dry, stable in air for a few hours; stable indefinitely under N_2 . Drying over P_2O_5 at 100°C results in loss of the complexed water, change of color to brown, and increased sensitivity to air.

REFERENCES:

S. Vanino. Handb. d. präp. Chemie [Handbook of Preparative Chemistry], Inorg. Section, Stuttgart, 1925, p. 710; E. Zintl and G. Rienäcker. Z. anorg. allg. Chem. <u>161</u>, 378 (1927); M. R. Hatfield in: L. F. Audrieth, Inorg. Syntheses, Vol. III, New York-Toronto-London, 1950, p. 149; K. H. Zapp. Unpublisbed, Freiburg i. Br.; S. Herzog. Unpublished, Jena; M. Kranz and A. Witkowska. Przemysl Chem. <u>37</u>, 470 (1958); Inorg. Syntheses, Vol. VI, 1960, p. 144.

Chromium (II) Oxalate

CrCtO4 2HtO

 $\begin{array}{rrr} CrSO_4 \cdot 5 H_2O + Na_3C_2O_4 = CrC_2O_4 \cdot 2 H_2O + Na_2SO_4 + 3 H_2O \\ 238.2 & 134.0 & 176.1 & 142.1 & 54.9 \end{array}$

A dry mixture of 14 g. of $CrSO_4 \cdot 5$ H₂O. 8 g. of $Na_3C_3O_4$, and 0.25 g. of H₂C₂O₄ · 2 H₂O is covered with about 150 ml. of O₂-free H₂O under a protective blanket of N₂. This mixture is shaken vigorously. After some time, $CrC_3O_4 \cdot 2$ H₂O separates as a fine, crystalline, green precipitate. It is filtered, washed with cold H₂O₄

and dried over CaCl₂, giving a yellowish-green powder. The yield is 80-85%.

Alternate method: Reaction of solid $Na_2C_2O_4$ with concentrated solutions of chromium (II) salt obtained electrolytically (method if Walz).

REFERENCES:

H. Lux and G. Illmann. Chem. Ber, <u>91</u>, 2143 (1958); H. Walz. M.S. thesis, Univ. of Freiburg i. Br., 1958.

Hexaaquochromium (III) Acetate

[Cr(OH₁)₄](CH₁COO)₄

$Cr(OH)_{3} \cdot 3 H_{2}O + 3 CH_{5}COOH = [Cr(H_{2}O)_{5}](CH_{5}COO)_{3}$ 157.1 180.2 337.2

I. Excess glacial acetic acid is added to the light blue-green Achromium (III) hydroxide (for preparation see p. 1345). The reaction proceeds with appreciable evolution of heat. The crystals (which precipitate after a few hours) are separated from the mother liquor, washed thoroughly with acetone and ether, and dried over H_2SO_4 .

II. Alternate method: From chrome alum via the readily obtained dihydroxotetraaquochromium (III) sulfate.

PROPERTIES:

Needle-shaped blue-violet crystals, readily soluble in water; solvolyzed by alcohol.

REFERENCES:

I. A. Hantzsch and E. Torke. Z. anorg. allg. Chem. 209, 78 (1932). II. A. Werner. Ber. dtsch. chem. Ges. 41, 3452 (1908).

Dihydroxahexaacetatotrichromium (III) Acetate and Chloride

[Crs(OH)s(CH2COO)s](CH2COO) n H2O, [Crs(OH)s(CH2COO)s]Cl+8H2O

Prepared from CrO₃, glacial acetic acid and alcohol. a) A two-liter round-bottom flask fitted with a reflux condenser is used. It is charged with 200 g. of CrO₃ (sulfuric acid in the second seco

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which is then covered with 400 ml. of commercial glacial acetic acid. The reaction is induced by careful heating on a water bath which is held below the boil. Since pure CrO_3 does not react with very pure glacial acetic acid even at the boil, the reaction may be started by addition of some alcohol. If the reaction becomes too vigorous, the flask is cooled. When the evolution of CO_3 begins to subside, the flask contents are refluxed for about 2 hours on a rapidly boiling water (or steam) bath. The thick, brown contents of the flask, which consist of hexaacetatotrichromium chromates, are allowed to cool somewhat. To complete the reduction of any chromic acid still present, first 50% alcohol and then 96% alcohol (about 100 ml. of alcohol in all) is added in small portions through the condenser. The flask is now heated for one hour on a steam bath, and the green liquid is then concentrated on a water bath. The green diacetate powder has the formula

 $[C_{r_3}OH(H_2O)(CH_3COO)_4](CH_3COO)_2 \cdot H_2O.$

The monoacetate hexahydrate is obtained by dissolving the powder in some water and allowing evaporation to take place over H_3SO_4 . The monoacetate tetrahydrate crystallizes in long prisms when an aqueous solution of the diacetate is treated with acetone.

PROPERTIES:

Formula weight 675.41 (4 H₃O), 711.45 (6 H₃O). Green, watersoluble crystals.

b) Evaporation of a solution of the diacetate in dilute HCl over H_3SO_4 yields $[Cr_3(OH)_2(CH_3COO)_6]$ Cl · 8 H_2O .

PROPERTIES;

Formula weight 723.90. Dark green prisms, may be recrystallized from water.

REFERENCES:

R. F. Weinland and E. Büttner. Z. anorg. allg. Chem. 75, 329, Anm. 1 (1912); R. Weinland and P. Dinkelacker. Ber. dtsch. chem. Ges. <u>42</u>, 3010, 3012 (1909).

Potassium Trioxalatochromate (11)

$K_1[Cr(C_2O_4)_3] \cdot 3H_1O$

Prepared by treatment of oxalic acid and potassium oxalate with $K_2Cr_2O_7$.

A concentrated aqueous solution containing 12 g. $K_3Cr_3O_7$ is added dropwise with stirring to a solution containing 27 g. of onalis acid dihydrate and 12 g. of neutral potassium oxalate monohydrate. The mixture is then evaporated to a small volume and slowly cooled to bring about crystallization.

SYNONYM:

Potassium chromium oxalate.

PROPERTIES:

Formula weight 485.4. Black-green, monoclinic scales with transparent blue edges. Readily soluble in water.

REFERENCE:

H. Hecht. Präparative anorg. Chemie [Preparative inorganic Chemistry], Berlin-Göttingen-Heidelberg, 1951, p. 158.

Potossium Hexacyanochromate (III)

K₄[Cr(CN)₄]

$C_{r}(CH_{s}COO)_{s} + 8 KCN \rightarrow K_{s}[Cr(CN)_{s}] + 3 CH_{s}COOK$

Seventeen grams of CrO3 or 25 g. of K2Cr2O7 is treated with 70 ml. of HCl (45 ml. of conc. HCl + 25 ml. of water) and reduced while hot by addition of a total of 25 ml, of ethanol in small portions, A very slight excess of ammonia is added to the boiling solution. The precipitate of Cr(OH)a is filtered bot through a fluted filter paper, washed several times with hot water, and finally dissolved in some dilute acetic acid. This solution is evaporated almost to dryness in order to remove the excess acetic acid. The residue is taken up in 150 ml. of water, filtered, and poured into a boiling solution of 100 g. of KCN in 200 ml. of water (use a hood!). The very dark-red solution thus formed is evaporated on a steam bath. A brownish-black solid usually separates; this is removed by filtration. On further concentration, bright-yellow crystals deposit on the walls. The mother liquor also yields additional fractions. The product is recrystallized two or three times from water a dried over H2SO4. The yield is 38 g. (70%).

PROPERTIES:

Formula weight 325.41. d 1.71. Bright yellow, monoclinic crystals, isomorphous with $K_3[Fe(CN)_6]$; decomposes above 150 for Solubility at 20°C: 30.96 g./100 g. water; insoluble in alcohological

Aqueous solutions tend to decompose, especially in light or on heating, separating $Cr(OH)_3$.

REFERENCES:

F. V. D. Cruser and E. H. Miller. J. Amer. Chem. Soc. <u>28</u>, 1138 (1906); O. T. Christensen. J. prakt. Chem. [2] <u>31</u>, 163 (1885); see also J. H. Bigelow in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 203.

Potassium Hexathiocyanatochromate (II)

K_z[Cr(SCN)_t] · 4 H_tO

| KCr(SO ₄) ₂ ·† | 6 KSCN | $\simeq K_{4}[Cr(SCN)_{*}]$ | + 2 K ₂ SO ₄ |
|---------------------------------------|--------|-----------------------------|------------------------------------|
| 12 H.O | | 4 H ₂ O | |
| 499.4 | 583.0 | 569.8 | |

A moderately concentrated aqueous solution of 6 parts of KSCN and 5 parts of chrome alum is heated for 2 hours on a steam bath, and is then concentrated in a dish until the cooled residual liquid solidifies to a mass of red crystals. This solid is extracted with absolute alcohol, in which the $K_3[Cr(SCN)_6]$ dissolves very readily while K_3SO_4 remains as a residue. After evaporation of the filtered alcohol extract, the salt is recrystallized once more from alcohol.

The analogous ammonium salt $(NH_4)_3[Cr(SCN)_6] \cdot 4 H_3O$ is obtained in the same manner, except that reaction in the solution of NH₄SCN and chromium ammonium alum takes place only after a brief period of bolling.

SYNONYM:

Potassium chromium thiocyanate.

PROPERTIES.

Lustrous crystals; dark red-violet in reflected light and garnet red in transmitted light. The salt remains unchanged in air or over H_2SO_4 ; it loses its water of crystallization only when heated to 110°C. One part dissolves in 0.72 parts of water and in 0.94 parts of alcohol; d¹⁶ 1.711.

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BEFERENCE:

J. Roesler. Liebigs Ann. 141, 185 (1867).

Trilithium Hexaphenylchromate (III)

LisCr(C,H,), 2.5(C,H,),O

ether CrCl_{3} + 6 $\operatorname{Li}(\operatorname{C}_{6}\operatorname{H}_{6}) \xrightarrow{} \operatorname{Li}_{3}\operatorname{Cr}(\operatorname{C}_{4}\operatorname{H}_{5})_{5} \cdot 2.5 (\operatorname{C}_{2}\operatorname{H}_{4})_{2}O$ + 3 LiCl 158.4 504.2 720.5 127.3

All operations are conducted in the absence of air and moisture, using high-purity N_2 as a protective gas.

a) The required solution of phenyllithium is prepared in a 500-ml, three-neck flask fitted with a reflux condenser and Hg seal, a highspeed Hg-sealed mechanical stirrer, a gas inlet tube, and a dropping funnel. The procedure is as follows: Clean, finely cut lithium (6 g.) is covered with 100 ml. of ether that has been freshly distilled over benzophenonesodium (referred to hereafter as ketyl ether). With the stirrer operating at high speed, 64 g. of freshly distilled bromobenzene, dissolved in 200 ml. of ketyl ether, is added dropwise at a rate sufficiently fast to keep the reaction solution boiling vigorously. After all the bromobenzene has been added, the solution is refluxed for one hour. After cooling, it is filtered through fine fritted glass. The clear solution thus obtained has a phenyllithium concentration of about 10%.

b) The preparation of the lithium chromium phenyl complex employs the same apparatus as described in (a). However, the dropping funnel is replaced by a tap-injection bulb containing 10 g. of anhydrous, very finely powdered chromium (III) chloride. With vigorous, high-speed stirring of the lithium phenyl solution in the flask, the chromium chloride is slowly introduced by tapping the bulb. The course of the reaction is monitored by observing the decrease in the number of black particles of chromium chloride. After 10-12 hours, the reaction is discontinued without waiting for complete conversion of the solid chromium chloride. The nascent yellow precipitate is filtered through fine fritted glass. By cooling the black-brown filtrate to -10° C, a portion of the complex is obtained in beautiful crystals. The reaction residue is rinsed back into the three-neck flask with 200 ml. of ketyl ether and again collected on the fritted glass.

The reaction flask is now replaced with a reflux condenser which is attached to the N_3 -generating apparatus (to equalize the pressure). The receiver flask is heated and the ether is distilled through the fritted glass plate and onto the residue; by cooling the receiver flask, the ether is suction-drawn through the residue back into the flask. This operation is repeated until the residue is coloriess. On cooling, most of the complex compound crystallizes in the receiver. The crystal slurry thus obtained is recrystallized from a large quantity of ketyl ether; or it is extracted

with fresh ketyl ether as described above. The mother liquor must be yellow-brown and free of halogens. Yield: about 15 g.

PROPERTIES:

Yellow-orange crystals; soluble in ether, benzene and tetrahydrofuran; sensitive to air and moisture; completely hydrolyzed by water or alcohol.

REFERENCE:

F. Hein and R. Weiss. Z. anorg. allg. Chem. 295, 145 (1958).

Ammonium Tetrathiocyanatodiamminechramate (III)

NH4[Cr(SCN)4(NH4)2] H2O

Prepared by fusion of NH_4SCN with $(NH_4)_2Cr_2O_7$ and extraction with water.

An enamel cooking pot of at least 4-liter capacity is charged with 800 g, (10.5 moles) of NH₄SCN and carefully heated; several small flames are used to provide as uniform heating as possible. The mass is stirred with a glass test tube which contains a thermometer; the heating is continued until the solid is partly melted and the temperature is 145-150°C. Now, an intimate mixture of 170 g. (0,675 mole) of finely powdered (NH₄)₂Cr₂O₇ and 200 g. (2.6 moles) of NH₄SCN is added in portions of 10-12 g, with continuous stirring. A fairly vigorous reaction begins after 10 such portions have been added; NH₃ is evolved and the temperature rises to 160°C. The fiames are now extinguished and the rest of the mixture is added to the melt in such a way as to maintain the temperature at 160°C.

Stirring is continued as the melt cools; the solid product which deposits on the walls of the vessel is scraped away, ground to a fine powder while still warm, and stirred in a large beaker with 750 ml. of ice water. After 15 minutes, the insoluble residue is freed of mother liquor as completely as possible (suction-filtration, no washing). It is then stirred into 2.5 liters of water, preheated to 65° C. The temperature is rapidly restored to 60° C and the solution is filtered all at once through a funnel heated with hot water (heating above 65° causes rapid decomposition, with production of a blue color and generation of HCN).

The hot filtrate is placed overnight in an ice chest, and the separated crystals are then filtered with suction. The mother liquor is used for another extraction of the residue at 60°C, thus affording an additional quantity of crystalline Reinecke salt.

Finally, 12-13 additional grams of product may be obtained by concentrating the mother liquor to 260-300 ml. under reduced pressure at 40-50°C.

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The total yield of air-dry Reinecke salt amounts to 250-275 g. (52-57% of theory).

The insoluble residue from the second extraction (about 130-135 g.) is composed predominantly of Morland salt, i.e., guandium tetrathiocyanatodiamminechromate (III).

USES:

Used for the isolation of amines, amino acids, complex cations and organometallic bases; it forms sparingly soluble saits with all of the above; these salts usually crystallize well. Also used as reagent in quantitative determination of Cu and Hg (procedure of C. Mahr) and of quaternary onium cations (procedure of F. Hein).

SYNONYM:

Reinecke salt.

PROPERTIES:

Formula weight 354.45. Ruby-red, lustrous, light-sensitive leaflets, which lose their water of crystallization on drying at 100°C and form scarlet cubes and rhombododecahedra. Both forms are readily soluble in cold water, alcohol, acetone and moist ethyl acetate, insoluble in benzene. Decomposed by boiling water.

REFERENCES:

H. D. Dakin. Org. Syntheses 15, 74 (1935); Coll. Vol. II, 555 (1943).

Tetrathiocyanatodiamminechromic (III) Acid

H[Cr(SCN)₄(NH₄)₄]

 $\begin{array}{rcl} NH_4[Cr(SCN)_4(NH_3)_2] &+ HCl &= H[Cr(SCN)_4(NH_3)_2] &+ NH_4Cl \\ & (\cdot H_7O) & (\cdot 2H_2O) \\ & 354.5 & 36.5 & 355.4 \end{array}$

A concentrated aqueous solution of $NH_4[Cr(SCN)_4(NH_3)_3] \cdot H_2O$ (see preceding preparation) is treated with a small excess of hydrochloric acid, then extracted thoroughly with ether. The free acid is absorbed in the ether with an intense dark red color; addition of NaCl makes the extraction almost quantitative. Evaporation of the ethereal solution in vacuum over H_2SO_4 and KOH yields a red mass which loses its solubility in ether after standing for a few days. The product is recrystallized from 50°C water, in which it dissolves very readily, except for a small yellow residue. On cooling, small red scales separate; these are again recrystallized from water.

SYNONYM:

Reinecke acid.

PROPERTIES:

Lustrous red leaflets; readily soluble in water, alcohol and acetone. Heating for several days at 70°C renders the acid anhydrous; further heating at 110-115°C imparts a darker color. The undried compound decomposes between 80 and 90°C, puffing up and evolving water.

REFERENCE:

R. Escales and H. Ehrensperger. Ber. dtsch. chem. Ges. <u>36</u>, 2681 (1903).

Ammonium Tetrathiocyanatodianilinochromate (III)

NH4[Cr(SCN)4(C+H4NH2)2] · I'/2 H2O

a) $\begin{array}{rcl} & & & & & & & & & & \\ & & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & & \\$

b)
$$(C_{s}H_{s}NH_{s})_{t}H[Cr(SCN)_{s}(C_{s}H_{s}NH_{s})_{t}] + NH_{3} = \frac{637.8}{17.0}$$

NH_t[Cr(SCN)_t(C_sH_cNH₂)_t] + 2 C_sH_sNH₂
488.6 186.2

a) A mixture of 500 g. of chrome alum, 600 g. of KSCN, and 500 ml. of water is heated for 4 hours on a steam bath. The solution is cooled, 500 ml. of aniline is added, and the mixture is stirred for 3 hours at 60° C on a water bath. It is then again cooled and a mixture of 6 liters of water and 600 ml. of giacial acetic acid is added. After a few hours the precipitate is filtered and dissolved.

in 1.5-2 liters of cold methanol. This solution is filtered, and 6 liters of water is added, whereupon $(C_{\theta}H_{B}NH_{2})_{2}H[Cr(SCN)_{4} + (C_{\theta}H_{S}NH_{2})_{2}]$ precipitates as a thick, violet crystal slurry. After 6 further precipitation from methanol-water, the yield is 330 g. b) Four hundred grams of this anomalous anilinium sait is treated with 600 ml. of methanol and 300 ml. of conc. ammonia. This solution is cooled in ice and 3 liters of water is slowly added; the crude ammonium thiocyanoto-aniline complex precipitates. After filtering with suction, it is treated once more in the same manner with methanol, ammonia and water. Yield: about 200 g.

USE:

Separation of amino acids, especially proline.

SYNONYMS:

Ammonium salt of rhodanilic acid; ammonium rhodanilate.

PROPERTIES:

Violet-red crystals, somewhat soluble in water, very soluble in methanol, acetone and ethyl acetate. The solutions decompose on boiling. Insoluble in ether, benzene and chloroform.

REFERENCE:

M. Bergmann, J. Biol. Chem. 110, 476 (1935).

Potassium Tetrathiocyanatodipyridinochromate (III)

K[Cr(SCN)₄py₁] · 2 H₁O

Prepared from K₃[Cr(SCN)₆] and pyridine.

Ten parts of $K_3[Cr(SCN)_6]$ (for preparation, see p. 1374), dried at 110°C, is heated with 30 parts of anhydrous pyridine in a small flask (4 hours on the water bath, in the absence of moisture). The hot solution is then poured into a crystallizing dish and allowed to chill in an ice ohest. The solid which crystallizes is a mixture of KSCN, $py_2 \cdot H[Cr(SCH)_4py_3]$, and $[Kpy_4][Cr(SCN)_4py_3]$. It is suction-dried and placed on a clay plate. The complex potassium salt deliquesces over a period of 1-2 days, and the KSCN is extracted with water at room temperature, while the K[Cr(SCN)_4py_3] is extracted with hot water. When cooled, the resulting red solutions gradually deposit small, lustrous red crystals of the potassium salt. The residue remaining after the hot water extraotion afferdis pure dipyridinium salt $py_3 \cdot H[Cr(SCN)_4py_3]$. PROPERTIES:

Formula weight 517.66. Small red crystals, which become anhydrous on heating to 110 °C. Almost insoluble in cold water, but somewhat soluble in warm H₂O. Completely insoluble in benzene, chloroform and ether; very soluble in aqueous and absolute ethyl alcohol, methanol, ethyl acetate and pyridine; very readily soluble in acetone.

REFERENCE:

P. Pfeiffer. Ber. dtsch. chem. Ges. 39, 2121, 2123 (1906).

Trichlorotriaquochromium

$[CrCl_1(OH_2)_2]$

 $3[CrCl_{2}(OH_{2})_{4}]Cl = 2[CrCl_{3}(OH_{2})_{5}] + [CrCl_{2}(OH_{2})_{4}]Cl + 2H_{2}O$ 691.3 424.9 266.5

Green chromium chloride hydrate $[CrCl_2(OH_2)_4]Cl \cdot 2 H_2O$ is converted into $[CrCl_2(OH_2)_4]Cl$ on standing for 3 days in a vacuum desiccator over conc. H_2SO_4 . It is then suspended in absolute ether; $[CrCl_3(OH_2)_3]$ is formed by disproportionation and dissolves with a brown-violet color. On evaporation of the ethereal solution in the absence of atmospheric moisture, $[CrCl_3(OH_2)_3]$ is obtained as an amorphous brown powder.

PROPERTIES:

Formula weight 212.43. Brown, amorphous, very hygroscopic powder, rapidly altered by traces of water. Soluble in water with a yellow-green color, which quickly becomes pure green owing to a reaction. Solutions in ether may be stored without change if moisture is absent.

REFERENCES:

A. Recoura. Comptes Rendus Hebd. Séances Acad. Sci. <u>194</u>, 229 (1932); <u>196</u>, 1854 (1933); see also F. Hein. J. prakt. Chem. <u>153</u>, 168 (1939).

Trichlorotriethanolochromium

[CrCi₂(C₂H₄OH)₃]

 $CrCl_{2} + 3C_{2}H_{3}OH = [CrCl_{3}(C_{2}H_{3}OH)_{3}]$ 158.4 138.2 296.6

Dried $CrCl_2$ is refluxed (in the absence of moisture) with **absolute** alcohol and a small piece of zinc (or $CrCl_2$). The $CrCl_5$

dissolves: the solution, which is red when hot and green when coldy is concentrated in a vacuum desiccator over conc. H_3SO_4 . The red crystals which deposit are washed with some absolute alcohol and ether, and stored dry.

PROPERTIES:

Dark red, hygroscopic crystals; soluble in alcohol, acetone and chloroform with a red color which soon becomes green. The aqueous solution decomposes rapidly.

REFERENCE:

I. Koppel. Z. anorg. Chem. 28, 471 (1901).

Trichlorotriamminechromium

[CrCl₁(NH₁)₁]

Prepared from (NH₃)₃CrO₄ and hydrochloric acid.

Five grams of trianminechromium tetroxide (for preparation, see p. 1392) is introduced into 50 ml. of well-cooled conc. HCI (constant stirring). The resulting gray- to blue-green precipitate is filtered off. The neutral complex, which deposits from the filtrate after standing for 1-2 days, is filtered with suction and washed with water until the washings become colorless. It is then dried by washing with alcohol and ether.

PROPERTIES;

Formula weight 209.48. Blue crystals with greenish tinge, insoluble in cold $H_{3}O$. Dissolution in warm $H_{3}O$ causes aquation to [CrCl₃(OH₃)(NH₃)₃]Cl. Presumably trans form.

REFERENCE:

A. Werner. Ber. dtsch. chem. Ges. 43, 2289 (1910).

Trichlorotripyridinechromium

[CrCl_spy₁]

I.

 $CrCl_{3} + 3py = [CrCl_{3}py_{3}]$ 158.4 237.3 395.7

The CrCl₃, in excess of dry pyridine, is refluxed in the presence of a small granule of CrCl₂. The CrCl₃ dissolves completely dress

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some time, giving a green color. The solution is filtered and cooled, whereupon the $[CrCl_3py_3]$ crystallizes out. On distilling the pyridine from the mother liquor, the compound can be obtained in almost quantitative yield.

II. Addition of H_8O to a pyridine solution of green chromium chloride hydrate $[CrCl_3(H_2O)_4]Cl \cdot 2 H_3O$ yields a green powder which consists essentially of a mixture of $[CrCl_3py_3]$ and $[Cr(OH)_8(H_9O)_2py_3]Cl$. When this mixture is treated with HCl, the latter salt goes into solution as $[Cr(H_3O)_4py_3]Cl_3$, giving a deep red color. The residue consists of crude $[CrCl_3py_3]$. This is dissolved in conc. HCl and reprecipitated by pouring the filtered solution into a large amount of water. Finally the $[CrCl_3py_3]$ is recrystallized once more from pyridine.

PROPERTIES:

Green leaflets, readily soluble in pyridine, chloroform, acetone and conc. HCl; sparingly soluble in ethyl alcohol; insoluble in water, ether, benzene and naphtha.

REFERENCES:

P. Pfeiffer. Z, anorg. Chem. 24, 282 (1900); 55, 99 (1907).

Chromium (III) Glycinate

(H2NCH2COO)2Cr

 $CrCl_{2} \cdot 6 H_{2}O + 3 H_{2}NCH_{2}COOH + 3 NaOH$ 266.5 225.2 120.0 $= (H_{2}NCH_{2}COO)_{3}Cr + 3 NaC] + 3 H_{2}O$ 274.3

An aqueous solution of one mole of green chromium chloride hydrate and 3 moles of glycine is boiled while 3 moles of NaOH is added gradually. This gives a dark-red solution from which a violet compound separates. The latter is filtered off while the mixture is still hot. The filtrate, after cooling and standing in vacuum over H_2SO_4 , deposits still more of the violet compound, together with larger red crystals. After suction-filtration and drying, the heavy red crystals are separated from the lighter violet ones by slurrying with alcohol. In this way, both compounds are obtained in analytically pure state.

PROPERTIES:

Red crystals = chromium (III) glycinate, $(H_3NCH_3COO)_3Cr$. Violet crystals = so-called "basic" chromium (III) glycinate, $(NH_3CH_3COO)_3Cr(OH)_2Cr(OOCCH_3NH_3)_3 \cdot H_3O$.

Both compounds are sparingly soluble in water and insoluble in organic solvents.

Chromium (III) α -alaninate can be obtained in an analoguus manner. If the reaction is allowed to take place in conc. solution, the red chromium (III) alaninate separates; the "basic" chromium (III) alaninate is obtained by evaporation of the solution.

REFERENCE:

H. Ley. Ber. dtsch. chem. Ges. 45, 380 (1912).

Chromium (III) Xanthate

[(C₁H₁OCS₂)₃Cr]

 $\begin{array}{rcl} KCr(SO_4)_t &+ & 3C_2H_4OCS_tK &= [(C_4H_8OCS_4)_3Ct] &+ & 2K_4SO_4 \\ (\cdot) & 2H_2O) & & 480.9 & & 415.6 \\ & & 499.4 \end{array}$

A solution of 20 g, of potassium xanthate in some water is treated with a solution of 23 g, of chrome alum. The blue-black compound which precipitates is filtered off with suction and dried on a clay plate. It is dissolved in pyridine, and water is added in drops until a permanent clouding is obtained. The solution is then allowed to stand undisturbed to bring about crystallization. The crystals are separated by filtration and dried in vacuum.

PROPERTIES:

Dark-blue crystalline powder, soluble in organic media, insoluble in water.

REFERENCE:

J. V. Dubsky. J. prakt. Chem. <u>90</u>, 118 (1914).

Chromium (III) Acetylacetonate

(C_tH₇O_t)₄Cr

L $Cr(CH_{s}COO)_{s} + 3C_{s}H_{s}O_{s} = [(C_{s}H_{7}O_{s})_{s}C_{r}] + 3CH_{s}COOH^{***}$ (* 6 H_{s}O) 397.2 300.3 349.3

A mixture of 40 g. of [Cr(OH₂)s](CH₃COO)₃ (for preparation, see p. 1371), 150 ml. of water, 40 g. of acetylacetone and 50 ml. of

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18.

2 N acetic acid is heated until solution is complete and crystallisation of the internal complex begins. Then the solution is boiled for a short time until the Hquid bumps vigorously. It is cooled gradually, then ohilled in ice and filtered. The first crop affords 18 g. of chromium acetylacetonate, which can be recrystal-

affords 18 g. of chromium acetyl lized from chloroform-benzene.

II. $Cr(NO_3)_3 + 3C_3H_4O_2 = [(C_3H_2O_2)_3Cr] + 3HNO_3$ (9 H₄O) 400.2 300.3 349.3

An alcoholic solution of $[Cr(OH_2)_e](NO_3)_3$ is treated with the stoichiometric quantity of acetylacetone and then gently refluxed. The chromium complex crystallizes out after the excess alcohol is distilled off.

REFERENCES:

Red-violet crystals, m.p. 216°; can be sublimed in vacuum. Soluble in alcohol, chloroform and benzene; virtually insoluble in water and petroleum ether.

REFERENCES;

F. Hein. J. prakt. Chem. 153, 169 (1939); F. Gach. Monatsh. Chem. <u>21</u>, 108 (1900).—As far as preparation from chromium chloride hexahydrate and acetylacetone in the presence of urea is concerned, see W.C. Fernelius and F.E. Blanch in: T. Moeller, Inorg. Syntheses, Vol. V, New York-Toronto-London, 1957, p. 130.

Chromyl Chloride

CrO₂Cl₂

L $K_2C_1O_4 + 2 NaC_1 + 2 H_2SO_4 = C_2O_2C_1^2 + NB_2SO_4 + K_2SO_4 + 2 H_2O_194.2$ 116.9 196.2 154.9

A clay crucible is used to fuse 200 g. of K_3CrO_4 with 122 g. of NaCl at a temperature which should not be excessive. The melt is poured onto a sheet of iron and broken up into coarse pieces. These are placed in a 2-liter ground-joint flask and covered with 200 ml. of 100% H_3SO_4 . A distilling condenser is connected to the flask at once, and a ground-joint receiving flask with a gas outlet table is attached to the lower end of that condenser. When the initially vigorous reaction becomes moderate, the reaction flask is

heated gently until no further $CrO_{3}Cl_{3}$ distills. The crude product is purified by a second distillation in a dry ground-glass apparatus; the pure $CrO_{3}Cl_{3}$ is collected in dry glass ampoules, which are then melt-sealed.

II.
$$K_2Cr_2O_7 + 4 \operatorname{NaCl} + 3 H_2SO_4 = 2 \operatorname{Cr}O_2Cl_2 + K_3SO_4 + 2 \operatorname{Na}_2SO_4 + 3 H_2O_294.2 = 118.9 = 294.2 = 309.8$$

It is possible to omit the fusion step. Thus, 150 g. of fuming H_2SO_4 is added in portions to a mixture of 50 g. of NaCl and 80 g. of $K_2Cr_2O_7$ (both thoroughly dried). Further procedure is the same as in method I. The yield is approximately 50%, based on $K_2Cr_3O_7$.

III.
$$CrO_{2} + 2HCl = CrO_{3}Cl_{1} + H_{1}O$$

100.0 72.9 154.9

A solution of 50 g, of CrO_3 in 170 ml. of cone. HCl is prepared, and 100 ml. of cone. H_2SO_4 is added in 20-ml. portions while cooling the flask in ice. The fluid mixture is poured into a separatory funnel, and after 20 minutes the lower CrO_2Cl_3 layer is drained into a small ground-joint flask. Dry air is bubbled through it for several minutes and the crude CrO_2Cl_3 is distilled as in method I.

PROPERTIES:

Deep-red liquid; fumes copiously in moist air. Should be stored in the dark and in sealed glass containers. M.p. -96.5 °C, b.p. 117 °C; $d^{\frac{25}{4}}$ 1.9118. Can react explosively with combustible organic and inorganic substances. Soluble in other inorganic acid chlorides and organic liquids, such as POCl₃, CCl₄, CHCl₃ and C_eH₆.

REFERENCES:

I and III. L. Vanino. Handb. d. Prap. Chemie [Handbook of Preparative Chemistry], I, Stuttgart, 1925; p. 718.

II. E. Moles and L. Gomez. Z. phys. Chem. 80, 513 (1912)! See also H. H. Sisler. Inorg. Syntheses, Vol. II, New York-London;

1946, p. 205.

Chromium Trioxide-Pyridine

CrO₁ · 2 py

$2C_{s}H_{s}N + CrO_{s} = 2C_{s}H_{s}N \cdot CrO_{s}$

Four grams of CrO₃ (0.04 mole) is dried in vacuum for four hours at 110°C and then chilled in ice-sait mixture. Fifty mixed

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pyridine (0.63 mole) is similarly chilled in a 300-ml. Erlenmeyer flask. The pyridine flask is agitated vigorously while situated in a cold bath, and the CrO_3 is slowly added. The flask is then stoppered and shaken further until solution is complete (solution is hastened by the use of a large excess of pyridine). The cooling is necessary to prevent oxidation of the pyridine. The excess solvent is then removed in vacuum. The product is sensitive to light. Slow evaporation favors the formation of large crystals. Yield: 10.3 g. (100%).

PROPERTIES:

Yellow to dark-red crystals. Soluble in pyridine; insoluble in CCl₄, benzene and ether. Hygroscopic. Decomposes slowly at 100°C; at higher temperatures, burns to give voluminous green chromium oxide. Hydrolyzes at once with water. Stable indefinitely in the dark. Stored in sealed containers at room temperature.

REFERENCES:

H. H. Sisler, J. D. Bush and O. E. Accountius. J. Amer. Chem. Soc. <u>70</u>, 3827 (1948); O. E. Accountius, J. D. Bush and H. H. Sisler in: J. C. Bailar, Inorg. Syntheses, Vol. IV, New York-London-Toronto, 1953, p. 94.

Chromyl Nitrote

$CrO_2(NO_1)_2$

$$CrO_3 + N_2O_3 = CrO_3(NO_3)_2$$

100.0 108.0 208.0

A powder funnel is used to rapidly pour 8.3 g. of N_3O_5 into a 50-ml. ground-joint flask precharged with 7 g. of CrO_3 and a few (vacuum) boiling stones. The flask is attached to a distillation apparatus whose joints are lubricated with silicone grease and which is protected against entry of atmospheric moisture by means of a P_3O_5 tube. The reaction begins after a short time, with fusion of the solids. The reaction mixture should be left standing overnight at room temperature.

The dark-red liquid product is distilled in aspirator vacuum. A liquid-nitrogen-cooled trap is interposed between the apparatus and the aspirator to prevent access of moisture and to condense the NO₃ and N₂O₅ which distill off. The $CrO_2(NO_3)_2$ distills at a bath temperature of about 75°C (partial decomposition). The receiver then contains 5.8 g, of pure $CrO_2(NO_3)_2$.

PROPERTIES:

Dark-red liquid, sensitive to moisture. M.p. -27°C, b.p. (10⁻³ mm.) 28°C; (17 mm.) 67°C. Decomposes at about 120°C.

REFERENCES

M. Schmeisser and D. Lützow. Angew. Chem. <u>66</u>, 230 (1954); D. Lützow. Thesis, Univ. München, 1955.

Chromyl Perchlorate

CrO₄(ClO₄),

 $CrO_3 + 2 Cl_2O_3 = CrO_2(ClO_4)_2 + 2 ClO_2 + 1/2 O_3$ 100.0 333.8 282.9 134.9

A two-neck flask is used; then, at -50° C, 5 g. of Cl₂O₅, followed by 3 g. of CrO₃, is added through one neck. This neck is then closed off either with a ground stopper lubricated with fluorinated hydrocarbon grease (see under Cl₃O, p. 299 f.), or by sealing off. The other neck leads to a manifold carrying sealable ampoules and a second, similar flask. The open end of the manifold is closed off with a P₃O₅ tube.

The cold bath is now replaced with a bath at $+6^{\circ}$ C. The Cl₃O₆ melts, and the two components react vigorously. The reactor is allowed to stand at 0°C for several hours (preferably overnight). After this, no further gases are evolved.

The reactor is now cooled with liquid nitrogen and the entire system evacuated to about 0.1 mm. The cold bath is removed and the second flask (at the manifold) is cooled; within a few minutes, Cl_3 and ClO_3 distill with foaming. To remove these gases completely, the vessel is immersed in a bath at +20°C for one half hour and vacuum is applied. As soon as no further volatiles distill, the bath temperature is raised to about 35-36°C. The $CrO_3(ClO_4)_3$ now distills into the manifold and flows into the first ampoule (transparent red liquid). The manifold with the ampoules should be somewhat inclined. When sufficient compound has collected in the first ampoule, the latter is sealed off. Additional distilled product collects in the stub left from the first ampoule, and is driven into the next ampoule by heating with a hot-air blower.

PROPERTIES:

Red liquid, very sensitive to moisture. M.p. -1° C, b.p. (extrapolated) (760 mm.) 174.7°C; (0.08 mm.) 35°C; (0.8 mm.) 45°C. Powerful oxidant; dissolves in CCl₄. May be stored for months in the dark at Dry ice temperature. Often explodes at +80°C.

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REFERENCES:

M. Schmeisser. Angew. Chem. <u>67</u>, 493 (1955); D. Lützow. Thesis, Univ. München, 1955.

Rubidium Chromate

Rb_zCrO₄

I.

 $Rb_{1}CO_{2} + CrO_{2} \simeq Rb_{2}CrO_{4} + CO_{2}$ 231.0 100.0 287.0

Obtained by evaporation of an aqueous solution of CrO_3 which has been neutralized with Rb_2CO_3 (or RbOH).

The by-product $Rb_2Cr_3O_7$ forms at even a very small excess of CrO_3 ; therefore somewhat more than the stoichiometric quantity of Rb_2CO_3 should be used.

II. Preparation analogous to that of Cs_2CrO_4 .

PROPERTIES:

Yellow, rhombic crystals, isomorphous with K_3CrO_4 and K_3SO_4 . Readily soluble in water (42% at 20°C).

REFERENCES:

L. Grandeau. Ann. Chim. Phys. (3) <u>67</u>, 228 (1863); J. W. Retgers. Z. phys. Chem. <u>8</u>, 39 (1891); Abeggs Handbuch der anorg. Chemie [Abegg's Handbook of Inorganic Chemistry], IV, 1, p. 362 (1921).

Rubidium Dichromate

Rb₁Cr₂O₇

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 $Rb_2CO_3 + 2 CrO_3 = Rb_2Cr_2O_7 + CO_2$ 231.0 200.0 387.0

Obtained by evaporation of stoichiometric mixtures of Rb_2CO_3 (or RbOH) and CrO_3 .

II. Preparation analogous to that of Cs₂Cr₂O₇.

PROPERTIES:

Trimorphic; forms A and B deposit together from solution above 35°C. Orange-colored monoclinic or red triclinic crystals. Moderately soluble in water (5% at 18°C).

24. CHROMIUM, MOLYSDENUM, TUNGSTEN, URANIÚM

REFERENCES:

L. Grandeau. Ann. Chim. Phys. (3), <u>67</u>, 227 (1863); Abeggs Handbuck der anorg. Chemie IV, 1, p. 362 (1921).

and the second

Cesium Chromote

Cs_tCrO₄

 $\begin{array}{rcl} Cs_2 Cr_2 O_7 &+ Ba(OH)_2 &= BaCrO_4 &+ Cs_3 CrO_4 &+ H_4 O\\ 481.8 & 171.4 & 233.4 & 284.9 \end{array}$

A small excess of $Ba(OH)_2$ is added to a warm solution of $Cs_2Cr_2O_7$. The sparingly soluble $BaCrO_4$ is filtered off and the solution is concentrated until crystallization occurs.

PROPERTIES:

Yellow hexagonal or rhombic crystals, readily soluble in water.

REFERENCE:

J. H. de Boer, J. Broos and H. Emmens. Z. anorg. alig. Chem. 191, 113 (1930).

Cesium Dichromate

Cs₂Cr₂O₇

 $(NH_4)_2Cr_2O_7 + 2CsCl = Cs_2Cr_2O_7 + 2NH_4Cl$ 252.1 336.7 461.8

Reaction of warm solutions of $(NH_4)_3Cr_2O_7$ and CsCl, followed by cooling, yields orange-red crystals of $Cs_2Cr_2O_7$, which are given contaminated with about 5% of $(NH_4)_3Cr_2O_7$. To decompose the ammonium salt, the product is calcined at a low temperature Recrystallization gives an excellent yield of pure $Cs_2Cr_3O_7$.

PROPERTIES:

Orange-red triclinic crystals; sparingly soluble to coldiversity soluble in hot water. REFERENCE:

J. H. de Boer, J. Broos and H. Emmens. Z. anorg. allg. Chem. 191, 113 (1930).

Potassium Fluorochromote

K[CrO₃F]

 $K_2C_{r_2}O_7 + 2 HF = 2 K[CrO_3F] + H_2O$ 294.2 40.0 316.2

Powdered $K_2Cr_2O_7$ is heated in a Pt dish with excess of conc. HF until solution is complete. On cooling, $K[CrO_3F]$ separates as red crystals.

PROPERTIES:

Formula weight 158.11. Ruby-red bipyramids, readily soluble in water. Etches glass vessels in which it is stored. Crystal structure; tetragonal (space group C_{4b}^{6}).

REFERENCES:

П.

A. Streng. Liebigs Ann. <u>129</u>, 227 (1864); J. A. A. Ketelaar and E. Wegerif. Recueil Trav. Chim. Pays-Bas <u>57</u>, 1269 (1938).

Potassium Chlorochromate

K[CrO_sCl]

 $\begin{array}{rcl} K_{t}Cr_{t}O_{7} \ + \ 2 \ HCl \ = \ 2 \ K[CrO_{3}Cl] \ + \ H_{2}O \\ 294.2 & 72.9 & 349.1 \end{array}$

I. Fifty grams of fine $K_2Cr_2O_7$ powder is dissolved in a mixture of 65 ml. of conc. HCI and 50 ml. of water (by heating to 70 °C). The solution is filtered through a jacketed funnel heated with hot water. After 1-2 days, the nascent crystals are filtered off with suction, recrystallized from glacial acetic acid, and dried in a vacuum desiccator over H_2SO_4 .

 $K_2CrO_4 + C_rO_4Cl_2 = 2 K[CrO_3Cl]$ 194.2 154.9 349.1

A three-neck flask is fitted with a stirrer, a thermometer, a dropping funnel, and a gas outlet tube. A solution of 75 g. of

 K_3CrO_4 in 125 ml. of hot water is placed in the flask, and **36 g.** of CrO_2Cl_3 is added dropwise with stirring. The temperature is held at 90-100°C by means of a Bunsen burner. Stirring is continued for 1 hour at the same temperature and the flask contents are then poured into a beaker. After 18 hours the nascent crystals are filtered off with suction and pressed together firmly to remove the mother liquor as thoroughly as possible without washing. The product is then placed on a clay plate, covered with a watch glass, and allowed to stand for 10 hours. Yield: 109 g. (81%, based on K_2CrO_4).

The mother liquor, cooled at 0° C for 1.5 hours, yields about 16 g. of less pure K[CrO₃Cl]. To purify this, 30 g. of the impure product is dissolved in 100 ml. of acetone, filtered, and 700-800 ml. of CCl₄ is added slowly with stirring; 16-17 g. of pure K[CrO₃Cl] is thus obtained.

PROPERTIES:

Formula weight 174.56; d 2.497. Sparkling, orange-colored crystalline needles, soluble in glacial acetic acid and acetone. Undergoes hydrolytic cleavage in water. Heating the salt to 100°C causes loss of chlorine.

REFERENCES:

- I. L. Vanino. Handb. d. Präp. Chemie [Handbook of Preparative Chemistry], I, Stuttgart, 925, p. 321.
- H. H. H. Sisler in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 208.

Potassium Tetraperoxochromate (V)

K,CrO,

Prepared from KOH, CrO₃ and H_3O_3 . A mixture of 25 ml. of 50% CrO₃ solution, 100 ml. of 25% KOH, and 100 ml. of H_3O is cooled in a cold bath until ice begins to form. Now, 30 ml. of 30% H_3O_3 is added dropwise (with shaking), care 3 being taken to keep the solution temperature from rising above 0°C. The initially red-yellow solution scon acquires a black-brown 0°C. The salt which drops to the bottom of the vessel after 1-2 color. The salt which drops to the bottom of the vessel after 1-2 color. The salt which drops to the bottom of the vessel after 1-2 washings are colorless, then with ether, and stored in a stopper of vessel. The yield is about 50%, based on the H_2O_3 used.

PROPERTIES:

Formula weight 297.30. Red-brown crystals, which may be stored for months without decomposition. Moderately soluble in cold water, insoluble in alcohol and ether.

REFERENCE:

E. H. Riesenfeld, H. E. Wohlers and W. A. Kutsch. Ber. dtsch. chem. Ges. <u>38</u>, 1887 (1905).

Ammonium Pentaperoxodichromote

(NH₄)₂Cr₂O₁₂ ¹ 2 H₂O

Prepared from NH₄Cl, CrO₃ and H₂O₂.

The procedure for the blue ammonium sait is the same as that used for K_3CrO_{θ} (see above). The quantities used are: 100 mL of H_2O , 5 mL of conc. HCl, 10 g. of NH₄Cl, 10 mL of 50% CrO₃ solution, and 25 mL of 30% H_3O_2 . At the end, the product is washed only briefly with 90% alcohol.

PROPERTIES:

Formula weight 386.13. Violet-black crystalline powder consisting of flat prisms which show strong pleochroism (bright redbrown and dark blue-violet). May be stored for a few days in a cold desiccator; transforms completely to $(NH_4)_2CrO_4$ on 24-hour exposure in the air; decomposes explosively at 50°C to Cr_2O_3 . Soluble in ice water (violet-brown color).

REFERENCES:

E. H. Riesenfeld, H. E. Wohlers and W. A. Kutsch. Ber. dtsch. chem. Ges. <u>38</u>, 1888 (1905); O. F. Wiede, Ber. dtsch. chem. Ges. <u>31</u>, 518 (1898); R. Schwarz and H. Giese. Ber. dtsch. chem. Ges. <u>66</u>, 310 (1933).

Diperoxotriamminechromium (IV)

(NH₁)₂CrO₄

Prepared from ammonia, CrO3 and H 2O2.

A mixture of 25 ml, of 10% ammonia and 5 ml, of 50% CrQs solution is treated dropwise at 0°C with 5 ml, of 30% H₂O₂. The

resultant solution is first allowed to stand for one hour in a cooling mixture, and is then heated (together with the copious precipitate of $(NH_4)_3Cr_3O_7$ contained therein) to about 50°C until the vigorous evolution of gas ceases and the salt dissolves almost completely. Finally, the solution is filtered and cooled once more to 0°C. The $(NH_3)_3CrO_4$ which crystallizes is filtered off with suction, washed with absolute alcohol and ether, and dried in a desiccator over KOH. Yield: about 0.3 g.

SYNONYMS:

Chromium tetroxide triammine or triamminechromium tetroxide.

PROPERTIES:

Formula weight 167.11; d^{15.8} 1.964. Light-brown needles, soluble in dilute ammonia and water (partial decomposition). Insoluble in other solvents. The product should be protected from moisture, but because of the danger of explosion, storage ampoules other than the type sealed by fusion of the outlet should be used.

REFERENCES:

E. H. Riesenfeld. Ber. dtsch. chem. Ges. <u>38</u>, 4070 (1905); O. F. Wiede. Ber. dtsch. chem. Ges. <u>30</u>, 2160 (1897); for discussion of valence state, see S. S. Bhatnagar, B. Prakash and A. Hamid. J. Chem. Soc. (London) <u>1938</u>, 1432.

Barium Orthochromate (IV)

BasCrO₄

 $BaCrO_4 + Cr_2O_3 + 5 Ba(OH)_2 = 3 Ba_2CrO_4 + 5 H_2O_253.4 152.0 858.9 1172.2$

Stoichiometric quantities of the starting materials, which must be very pure and anhydrous, are thoroughly mixed. (However, a very small excess of $Ba(OH)_a$, i.e., 0.03-0.06 moles BaO/atom CT must be provided. Any larger excess of the base will give rise, in the heating which follows, to partial or sometimes complete formation of tribarium chromate (IV), Ba_sCrO_s . The latter is a heavy, blackish-green, glittering crystalline powder which appears olive-brown under the microscope.)

About 4 g. of the mixture is then heated in a sintered alumination boat in an O_8 -free nitrogen stream (2 hours at 900-950°G).

PROPERTIES:

Microcrystalline, heavy emerald green powder. Readily soluble in dilute HCl or HClO₄, even in the cold, with brownish yellow color. Water causes hydrolysis. Stable to methanol.

REFERENCE:

R. Scholder and G. Sperka. Z. anorg. allg. Chem. 285, 49 (1956).

Barium Chromate (V)

Ba₂(CrO₄)₂

 $2 B_{3}CrO_{4} + B_{3}CO_{3} = B_{3}(CrO_{4})_{2} + CO_{2} + \frac{1}{2}O_{2}$ 506.7 197.4 644.1

An intimate mixture of 1 mole of $BaCrO_4$ and 0.50 moles of $BaCO_3$ is heated in an O_2 -free nitrogen stream at 1000 °C. Four hours of heating suffices for about 2 g, of reactants. The $Ba_3(CrO_4)_2$ product is of excellent purity.

PROPERTIES:

Black-green microcrystalline powder. Water causes gradual decomposition. Completely soluble in dilute acids, with disproportionation to Cr (III) and Cr (VI).

REFERENCE:

R. Scholder and W. Klemm. Angew. Chem. 66, 463 (1954).

Sodium Thiochromite

NaCrS₂

Prepared by reaction of K₂CrO₄ with a soda-sulfur melt.

An intimate mixture of 1 part of K_3CrO_4 with 30 parts of KNaCOs and 30 parts of sulfur is heated for 30-60 minutes in a covered sintered alumina crucible; the latter is placed in an electric furnace. The temperature is 750-850°C. After heating, the crucible is allowed to cool slowly. The cold melt is slurried in water, then washed by decantation several times with dilute NaOH. The thiochromite is filtered off and thoroughly washed, first with dilute alcoholic. NaOH, then with pure alcohol, and finally with ether. The product is free of potassium despite the use of K salts.

. 3

PROPERTIES:

Formula weight 139.13; d 3.2. Crystalline gray-black aggregate with a greenish luster. Well-formed hexagonal leaflets are produced above 800°C; these appear garnet-red by transmitted light. When moist, rapidly darkens and decomposes on exposure to air.

REFERENCES:

W. Rüdorff and K. Stegemann. Z. anorg. allg. Chem. <u>251</u>, 379 (1943); R. Schneider. J. prakt. Chem. <u>56</u>, 415 (1897).

Dibenzenechromium (0)

(C₁H₄)₃Ca

 $\begin{array}{r} \text{AlCl}_{1} \\ 3 \text{ CrCl}_{2} + 2 \text{ Al} + \text{AlCl}_{3} + 6 \text{ C}_{4}\text{H}_{3} \rightarrow 3 [\text{Cr}(\text{C}_{6}\text{H}_{6})_{2}][\text{AlCl}_{4}] \\ 475.1 \\ 53.9 \\ 133.3 \\ 468.6 \\ 2 [\text{Cr}(\text{C}_{6}\text{H}_{6})_{2}]^{+} + S_{2}\text{O}_{4}^{3-} + 4 \text{ OH}^{-} \rightarrow 2 \text{ Cr}(\text{C}_{6}\text{H}_{6})_{2} + 2 \text{ SO}_{3}^{3-} + 2 \text{ H}_{8}\text{O} \\ 416.5 \end{array}$

A 250-ml. three-neck flask is used, and 25 g. (0.16 moles) of anhydrous $CrCl_3$, 3.5 g. (0.13 moles) of dry Ai powder, and 60 g. (0.45 moles) of sublimed and rapidly ground AiCl₃ are weighed in. The flask is evacuated several times with an aspirator and refilled with dry, O_2 -free nitrogen. Then, 150 ml. of absolute benzene is introduced in a countercurrent stream of inert gas. The flask is again evacuated for several minutes to remove traces of NCl, (with the evaporating benzene). Then, 10 drops (0.3 ml.) of mesitylene are added under protection of the N₂ blanket. The flask is now fitted with a reflux condenser carrying a mercury pressurerelief valve. A high-speed Hg-seal stirrer and a stopper are placed on the other necks.

The N_2 stream is cut off and the mixture is refluxed for 35-40 hours with vigorous stirring. The flask contents are cooled, then decomposed by pouring slowly (under N_2) into 200 mi. of CH_aOH contained in a 4-liter three-neck flask. The latter is cooled in icsi two of the necks are fitted with stopcocks and the third carries a high-speed Hg-seal stirrer. Then 200 ml. of H₂O is also added. When hydrolysis is complete, 2 liters of benzene is added, then a solution of 220 g. of KOH in 500 ml. of H₃O. Finally, 220 g. of solid sodium dithionite is rapidly introduced. After 2 hours of high-speed stirring, the dark-brown solution is carefully filtered with suction (in the absence of air) into an evacuated 3-liter flasts.

which carries an N₂ inlet tube. The solution is dried with solid KOH. It is then transferred (under N₂) to a distillation apparatus, and the solvent is removed thoroughly on a hot water bath. The solid black residue is washed 3 times with absolute ether (under N₂) and then sublimed in high vacuum at 160°C. Yield: 29.5 g. (90% of theoretical).

PROPERTIES:

Black, diamagnetic crystals, sensitive to air. M.p. 284-285°C. Slightly soluble in ether and petroleum ether, giving a brown color; moderately soluble in benzene.

REFERENCES:

E. O. Fischer and W. Hafner. Z. Naturforsch. <u>10b</u>, 665 (1955); Z. anorg. allg. Chem. <u>286</u>, 146 (1956); E. O. Fischer, W. Hafner and J. Seeholzer, Private communication.

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Bis{diphenyl}chromium {0}
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{C₁₂H₁₃},Cr

$\begin{array}{c} S_2O_1{}^{t-} \\ \left\{ (\mathbf{C}_{12}\mathbf{H}_{10})_{\sharp}\mathbf{C}\mathbf{r} \right\}^+ \twoheadrightarrow (\mathbf{C}_{1\sharp}\mathbf{H}_{10})_{\sharp}\mathbf{C}\mathbf{r} \end{array}$

The melt is prepared and hydrolyzed in the same manner as described below for bis(diphenyl)chromium (I) iodide. The first filtrate is rejected.

An excess of alkaline sodium dithionite solution is added under N_2 to the later, pure orange-red filtrates, whereupon the bis(diphenyl)chromium (I) cation is reduced instantly and precipitates as bis(diphenyl)chromium (0). After standing for one half hour the precipitate is filtered off on a large, fine fritted-glass funnel and then dried for 1-2 days over P_2O_5 . It is then extracted with ether or pentane in the absence of air; the bis(diphenyl)chromium separates from the solvent in beautiful small crystals. These are filtered off, dried in vacuum, and stored under N_2 . Yield: 10 to 12 g.

PROPERTIES:

Crystals with brasslike luster. M.p. (not sharp) at 112°C. Soluble in ether, alcohol, benzene, etc.; diamagnetic. Limited stability in air when dry. Dibenzenechromium (0) and diphenylbenzenechromium (0) can be prepared from the corresponding chromium (1) saits in esentially the same way.

REFERENCES:

E. O. Fischer and D. Seus. Chem. Ber. <u>89</u>, 1814 (1956); F. Hein and W. Kleinwächter. Private unpublished communication.

Dibenzenechromium (|) lodide

[(C_sH_s)_zC₇]1

Ten grams (0.05 moles) of $Cr(C_8H_8)_2$ fine powder is shaken with 200 ml. of benzene and 100 ml. of H_3O in a separatory funnel, while air is passed through, until all the solid dissolves and the benzene phase becomes virtually colorless. The yellow-brown aqueous layer is filtered and treated with saturated aqueous KI solution (stirring) until no further yellow precipitate separates out. After cooling in ice, the precipitate is filtered off, washed 3 times with some C_3H_5OH , and finally with ether. It is then dried in vacuum. Yield: 10.5 g., or 65% based on $Cr(C_8H_6)_{22}$

PROPERTIES;

Egg-yellow, stable in air, moderately soluble in H_BO.

REFERENCES:

E. O. Fischer and W. Hafner. Z. anorg. allg. Chem. <u>286</u>, 146 (1956); E. O. Fischer. Private communication.

Bis(diphenyl)chromium (|} lodide

[Cr(C₁₃H₁₀)₁]I

Ten grams of sieved, anhydrous $CrCl_3$ dust, 8 g. of Al powder, 27 g. of sublimed diphenyl, and 30 g. of $AlCl_3$ (powdered in a mortar) are separately dried for one half hour in an oven at 110°C. Then, the $CrCl_3$ is mixed intimately with the Al powder, and the biphenyl with the $AlCl_3$. The two mixtures are then blended thoroughly with each other in a 150-ml. beaker placed in a drying oven. Finally, the total mixture is covered with a layer of pure biphenyl (3-4 g.), and the beaker is covered with a watch glass. The beaker is now placed in a silicone oil bath preheated to 100°C, and the bath temperature is slowly raised to 110°C. As soon as the reaction begins (110-120°C, melting of the mass, followed by puffing up and evolution of HCl vapors), the heating of the oil bath is discontinued. The heat of reaction causes the

temperature of the mixture to rise spontaneously to 140-150°C. After 10 minutes the melt is stirred vigorously with a thermometer, care being taken to keep the temperature from rising above 160°C. The reaction is allowed to complete itself in one half hour. During this time, the oil bath temperature is kept at 120°C. Careful conduct of the melt reaction is most important in this preparation.

The beaker with the melt is now cooled to room temperature. The melt is added with a spatula to 100 ml. of methanol (addition in portions) in an 800-ml. beaker placed in an ice bath. An orange-red to brown solution forms; cold, saturated NaCl solution is then added with stirring. This yields an easily filtered product which is separated once on a 15-cm. Buchner funnel. Then about 3 g. of solid KI is added to the acidic, darkbrown filtrate: this causes precipitation of the bis(diphenyl)chromium (I) cation present. However, most of the product is in the filtration residue, and is obtained by leaching the residue several times (on the funnel) with 100-ml, portions of water, followed by suction-drying. Before each leaching, a fast stream of air is drawn through the filter cake for 10-15 minutes, in order to oxidize any remaining chromium (0) to the monovalent state. The leaching is discontinued when the wash water becomes almost coloriess. The bis(diphenyl)chromium (I) iodide is reprecipitated by stirring about 8-10 g, of solid KI into the filtrate. It is filtered off with suction and washed with water, then 10 ml. of alcohol and two 10-ml, portions of ether, Yield: 22-25 g. The crude product is already very pure; it can be recrystallized from alcohol.

PROPERTIES:

Formula weight 487.33; m.p. 157°C. Depending on size, orange to reddish black crystals. Soluble in pyridine, alcohol, chloroform, acetone; almost insoluble in benzene and water; insoluble in ether and naphtha. Not sensitive to dilute hydrochloric acid.

REFERENCES:

F. Hein. Ber. dtsch. chem. Ges. <u>54</u>, 2716 (1921); E. O. Fischer and D. Seus. Chem. Ber. <u>89</u>, 1814 (1956); F. Hein and W. Kleinwächter. Unpublished private communication.

(Diphenyll(benzene)chromium (1) lodide

[(C₁₁H₁₀)Cr(C₁H₄)]]

All operations are conducted under pure N_2 in the absence of moisture,

A Grignard solution is prepared from 37 g. of magnesium, 235 g. of bromobenzene and 900 ml. of absolute ether. After the

-1

end of the reaction, the solution is decanted from the unreacted Mg into a 1.5-liter sulfonation flask, which is provided with a stirrer, a thermometer, a tap-injection bulb from which solid reagents can be added, and inlet and outlet tubes for $N_{\rm S}$.

The solution is cooled to -15 to -18 °C. Vigorous stirring and good cooling are provided, and 40 g. of sublimed CrCl₃ is tapped from the bulb into the flask at a uniform rate; total addition time: 2 to 3 hours. (The CrCl₃ is preextracted with boiling HCl, washed, dried, and sieved through a U.S. standard 60-mesh screen.) The reaction temperature should not rise above -12°C. The mixture becomes black-brown. After the addition of CrCl3, stirring is continued 2 to 3 hours. After standing overnight in an ice chest, the mixture is stirred thoroughly and decomposed by pouring it slowly onto an ice-H2SO4 mixture (750 g. of ice, 25 ml. of conc. H₂SO₄) contained in a 4-liter breaker. The addition proceeds in air and with constant stirring while the beaker is immersed in an ice-salt bath. The yellow-red ethereal emulsion is rapidly decanted into a dish and the ether is driven off. The aqueous layer is filtered through a suction funnel with the largest possible filtering surface.

The residue from the ethereal layer is stirred with approximately 50 ml. of 50% KI and 50 ml. of saturated Na₂SO₃ solution, and is then thoroughly extracted with chloroform (shaking in a separatory funnel) until the solvent is only slightly yellow. The aqueous solution, which contains KI, is combined with the filtrate from the aqueous layer and similarly extracted with chloroform. The residue from the filtration of the aqueous layer, the filter paper, the funnel, and all vessels are also extracted with chloroform. The combined orange-colored chloroform extracts (which contain the crude iodide) are washed twice, each time with 15 ml. of KI and 10 ml. of Na₂SO₃ solutions, then once with 25 ml. of H₂O, and dried for 24 hours over anhydrous potassium carbonate. The filtered chloroform solution is concentrated, under anhydrous conditions, in aspirator vacuum at a bath temperature of 25 to 30°C. The residual viscous mass is rinsed into a dish with a minimum amount of chloroform. To remove diphenyl, the material is triturated, first with 100-ml. portions and later with 30-ml. portions of absolute ether, until a sample of extract shows almost no residue on evaporation. A total of 1.5 to 2 liters of absolute ether is required. The viscous, red-orange, crude iodide hardens and becomes powdery as the extraction of diphenyl progresses. It is dried over P₂O₅ in vacuum. It may be kept for months if stored in a cool place away from light. Yield: 35-40 g. of crude iodide. It is composed of bis(diphenyl)chromium (I) iodide, (diphenyl)(benzene)chromium (I) iodide (the principal constituent), and a very small percentage of dibenzenechromium (I) iodide.

To obtain pure (diphenyl)(benzene)chromium (I) iodide, the procedure is as follows: 39 g. of crude iodide is dissolved in 900 ml. of methanol, treated with 300 ml. of water, and passed through an anion exchange column (e.g., OH form of Wofatit L 150 or Amberlite IRA 410; 150 g. of dry material in 70% methanol) at a rate of 3 ml./min. The column is then eluted with 70% alcohol and the yellow to orange fraction of the filtrate is collected in the absence of CO_2 . This fraction is concentrated in aspirator vacuum at a bath temperature of 30-35 °C until a methanol-free solution remains. This is filtered to remove a slight cloudiness (diphenyl). The clear, filtered solution is diluted to 300 ml, with water and treated with a solution of 18 g. of anthranilic acid (m.p. 145°C) and 12 g. of KOH in 60 ml. of H₂O while cooling the flask in ice; this treatment causes the (C12H10)2Cr (I) anthranilate to deposit as an orange-yellow, amorphous precipitate. After standing for 3 hours, the precipitate is removed by filtration through a very fine fritted-glass funnel. The filtrate is treated with 20 g, of solid KI in a separatory funnel. The (C12H10)-(C_sH_e)CrI separates at once as an oil. The oil is extracted with chloroform until the latter is only slightly yellow. The combined chloroform extracts are thoroughly shaken with some 20% KI solution, and then with a very small quantity of water; the extracts are then dried for several hours over potassium carbonate. The filtered solutions are concentrated by distilling off the chloroform in vacuum (under anhydrous conditions) at a bath temperature of 30-35°C. Finally, about a 10-fold quantity of absolute ether is added, causing an orange-red oil to separate; this gradually solidifies and can be ground under ether. The supernatant ether layer is replaced 2 or 3 times to remove the chloroform. The powder is filtered off under anhydrous conditions, washed several times with ether, and dried in a drying pistol at 2 mm. and 55-60°C (using acetone as the heating medium). The product is recrystal-lized by dissolving in absolute alcohol at 60-70°C (anhydrous conditions), filtering through a very fine fritted-glass funnel while still bot, and storing overnight at -20°C. This yields massive orange-red crystals. The (C12H10)(CeHe)CrI can also crystallize in goldenyellow hexagonal leaflets, but these transform into the orange-red crystals after standing for several days in the mother liquor.

Since the $(C_{12}H_{10})(C_{e}H_{e})Crl$ often separates as an oil, seeding the solution may be helpful. The precipitation can be completed by very slow addition of a 3- to 5-fold quantity of ether. The precipitate is filtered off under anhydrous conditions, washed twice with some 1:1 absolute ether/absolute ethanol, twice with absolute ether, and then dried to a constant weight in a drying pistol at 2 mm. and 55-60°C (using acetone as the heating medium). This drying quantitatively removes the ether, which otherwise adheres tenaciously. Yield: 26 g. of $(C_{12}H_{10})(C_{e}H_{e})Crl$. The (diphenyl)(benzene)chromium (l) iodide can also be prepared by a reductive Friedel-Crafts reaction, starting with an appropriate mixture of benzene, diphenyl, $CrCl_3$, $AlCl_3$ and Alpowder. The reaction can be carried out under reflux at atmospheric pressure, but again affords (diphenyl)(benzene)chromium in a mixture with dibenzenechromium and bis(diphenyl)chromium. After conversion to the iodides, they must be separated from each other in a manner analogous to that given above.

The yield in this method, even under the most favorable conditions, is lower than that of the Grignard procedure.

PROPERTIES:

Formula weight 411.33. Red-orange, massive, somewhat lightsensitive crystals. M.p. approximately 160°C (decomp.). Can be stored in vacuum or under N_3 in the dark. Readily soluble in pyridine; soluble in chloroform, alcohol and acetone; less soluble in water; insoluble in ether, benzene and petroleum ether.

REFERENCES:

F. Hein. Ber. dtsch. chem. Ges. <u>54</u>, 2741 (1921); F. Hein and H. Meininger. Z. anorg, allg. Chem. <u>145</u>, 115 (1925); F. Hein and E. Markert. Ber. dtsch. chem. Ges. <u>61</u>, 2261 (1928); F. Hein, P. Kleinert and E. Kurras, Z. anorg, allg. Chem. <u>289</u>, 229 (1957); H. H. Zeiss and M. Tsutsui, J. Amer. Chem. Soc. <u>79</u>, 3062 (1957); F. Hein and K. Eisfeld. Z. anorg, allg. Chem. <u>292</u>, 162 (1957).

Molybdenum

Мо

Ι.

 $M_0O_3 + 3H_2 = M_0 + 3H_1O_144.0$ 67.31. 98.0 54.1

The MoO_3 is obtained by heating ammonium molybdate. Since MoO_3 is volatile at higher temperatures, it is prereduced in a stream of hydrogen at about 500°C to the nonvolatile lower oxides. The oxides are then reduced to the metal at about 1000°C. The product is allowed to cool in an H₂ stream, and the metal is obtained as a gray-black powder.

II.
$$3 M_0 O_4 + 4 A I = 3 M_0 + 2 A J_2 O_4$$

333.9 107.9 237.9 203.0

Because of the volatility of MoO_3 , the starting material is MoO_3 , which is obtained by reduction of MoO_3 with H_3 at

dark-red heat. A clay orucible embedded in dry sand is used, and a **mixture of 80 g.** of MoO_2 and 21 g. of Al powder (or, better, Al **grapules the** size of grains of sand) is placed in it. The mixture is **grapules the** size of grains of an ignition mixture. * After cooling the **crucible** is broken up, and the solid melt of MO, weighing about 50 g. (about 90% yield), is solated. If 60 g. or 40 g. of MoO_2 is charged, the yield drops to 70-80%. The metal contains 98-98.5% Mo as well as some Si, Fe and Al.

PROPERTIES:

Solid Mo is bright, with a silvery luster. Powder is light- to black-gray, depending on particle size. M.p. 2620°C; d 10.23; hardness 5.5. Attacked (with difficulty) by nonoxidizing acids and aqueous alkalies. Crystal structure; A 2 type.

REFERENCES:

H. Funk. Darst. der Metalle im Laboratorium [Preparation of Metals in the Laboratory], Stuttgart, 1938, p. 69 f.; H. Biltz and R. Gärtner. Ber. dtsch. chem. Ges. <u>39</u>, 3370 (1906).

Dibenzenemolybdenum (0)

(C,H,),Mo

An intimate mixture of 4 g. (0.015 moles) of MoCl₅, 3 g. (0.023 moles) of anhydrous fine AlCl₃ powder and 1 g. (0.04 g.-atoms) of Al powder is placed in a glass combustion tube of about 75-ml. capacity. About 30 ml. of absolute benzene is then added. The tube is evacuated, sealed, placed in an iron protective tube, and heated in a horizontal position for 15 hours at 120°C.

After cooling, the tube is carefully opened and the dark-colored contents are decomposed with 20 ml. of methanol (cooling) and then treated with 75 ml. of water. The residue is filtered off on a

[•]Ignition mixture (German "Zündgemisch" or "Zündkirsche"ignition cherry) is made from 15 parts by weight of barium peroxide and 2 parts of powdered magnesium metal, intimately mixed and held together with collodion. The whole is wrapped with magnesium ribbon, a piece of the ribbon serving as the fuse. Magnesium burns with the evolution of much heat; the barium peroxide furnishes the large amounts of oxygen needed for such forced combustion (H. Blücher, Ausiamftsbuch für die chemische Industrie [Data Book for the Chemical Industry], 18th ed., de Gruyter, Berlin, 1954, p. 1314).

fritted-glass funnel. The dark-colored filtrate is transferred to a 500-ml. three-neck flask, carefully prepurged with N₃. The solution is covered with 200 ml, of benzene, and 10 g. of potassium diaminomethanedisulfinate $(NH_2)_2C(SO_2K)_2$ (or the same amount of formamidinesulfinic acid $(NH_2)_2CSO_2$) is added with vigorous stirring. Next, 60 ml. of conc. ammonia is added (under a protective nitrogen atmosphere). This gives rise to a green color in the nascent suspension, as well as in the benzene. After two hours of stirring, the green benzene solution is decanted (in the absence of air) into a fairly large Schlenk tube (see Part I, p. 75) which has been carefully prepurged with N₂; it is then dried with solid KOH.

A green crystalline residue remains after vacuum removal of the benzene. This is transferred to a sublimation vessel (complete exclusion of air) and sublimed in high vacuum at 100-105 °C.

Yield: with $(NH_2)_2C(SO_2K)_2$, 1 g.; with $(NH_3)_2CSO_3$, 0.7 g.; or 27 and 20% of theoretical, respectively (based on MoCl₃).

PROPERTIES:

Green crystals, extremely sensitive to air; decomp. 115°C. Soluble in organic media such as benzene, ether and petroleum ether. Insoluble in water. Very sensitive to oxidation.

REFERENCE:

E. O. Fischer and H. O. Stahl. Chem. Ber. 89, 1805 (1956).

Molybdenum (II) Chloride

MosCl

l.

 $8 \text{ MoCl}_3 = \text{Mo}_3 \text{Cl}_1 + 3 \text{MoCl}_4$ 1213.9 500.8 713.3

Heating of 20 g. of pure $MoCl_3$ to red heat in a small boat placed in an O_2 -free nitrogen stream gives bright yellow, analytically pure Mo_3Cl_6 (93% yield).

ĬI.

 $3 M_0 + 3 COCl_2 = Mo_8Cl_3 + 3 CO$ 288.0 298.8 500.6

A stream of $COCl_2$ (3 bubbles/sec.) is allowed to react with 8 g. of very pure Mo in a Vycor tube (30 minutes at about 610°C). Yield is 90%; 0.5% is lost in the form of side products; the remainder is unreacted Mo. Heating is carried out with a thermostatically controlled electric furnace precalibrated to 610°C.

The sintered reaction mass is finely ground and extracted several times with a mixture of 95 parts of ether and 5 parts of alcohol (reflux). The filtered, golden-yellow solution gives (in vacuum) a scalelike residue which crumbles to a light-yellow dust when ground. This compound corresponds to the formula $Mo_3Cl_8 \cdot C_2H_3OH$; the alcohol cannot be removed without decomposing the product.

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PROPERTIES:

Amorphous, dull-yellow powder, stable in air. Infusible, non-volatile; d^{2} 3.714. Insoluble in water, glacial acetic acid, toluene and naphtha. Soluble in alcohols, acetone and pyridine.

REFERENCES:

- W. Biltz and C. Fendius. Z. anorg. alig. Chem. <u>172</u>, 384 (1928);
 S. Senderoff and A. Brenner. J. Elektrochem. Soc. <u>101</u>, 28 (1954).
- H. K. Lindner, E. Haller and H. Helwig. Z. anorg, allg. Chem. 130, 210 (1923).

Molybdenum (III) Chloride

MoCl₃

 $M_0Cl_5 + H_2 = M_0Cl_3 + 2 HCl_{273.2} + 22.4 i. = 202.3$

The reaction tube shown in Fig. 320 is used both for the preparation of $MoCl_5$ (see p. 1405) and the subsequent reduction to $MoCl_{3*}$

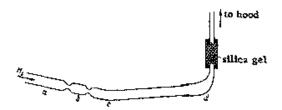


Fig. 320. Preparation of molybdenum (III) chloride. The lengths of the individual tube sections are: a 32 cm., b 8 cm., c 60-75 cm. The LD. is 2-2.5 cm., 1-1.2 cm. at the constrictions.

24, CHROMIUM, MOLYBOENUM, TUNGSTEN, URANIUM

1465

Six grams of Mo powder is placed at a, and MoCl₅ is prepared from it (see next preparation); the product is then sublimed into band c by means of a Cl₃ stream. After cooling, the Cl₃ is displaced with CO₂, and this, in turn, with dry, O₂-free hydrogen. The left end (near its lowest part) of zone c is now heated to about 250°C, so that a 5- to 10-cm. section of the tube is filled with red vapor. After some time, a white mist of HCl appears at the tube end adjacent to the moisture-retaining silica gel tube. Continued volatilization of the MoCl₅ (which keeps dropping into the lowest section of the tube) results in a copper-red coating.

The heat source is gradually shifted to the right, until all the $MoCl_5$ is transformed into $MoCl_3$. Overheating should be scrupulously avoided. The reaction requires 2-3 hours. At the end, the H₂ is replaced by dry CO_3 , and the remaining $MoCl_5$ is distilled from section b so that none of it remains in the $MoCl_3$. The excess $MoCl_5$ is driven into adapter d (this tube is attached to the reactor by means of an asbestos seal). After cooling, the reactor tube is cut into several pieces and the crystals are pushed out with a glass rod. Yield: 4-6 g.

PROPERTIES:

Copper- to brown-red powder; d_{5}^{45} 3.578, Stable in air; sparingly soluble in pyridine; insoluble in water, alcohol and ether. Forms a blue solution with conc. $H_{2}SO_{4}$.

REFERENCES;

H. Biltz and W. Biltz. Übungsbeispiele aus der unorganischen Experimentalchemie [Excercises in Inorganic Experimental Chemistry], 3rd and 4th eds., 1920; W. Biltz and C. Fendius, Z. anorg, allg. Chem. <u>172</u>, 389 (1928); L. P. Liechti and B. Kempe. Liebigs Ann. <u>169</u>, 344 (1873); see also A. Rosenbeim, G. Abel and R. Lewy, Z. anorg, allg. Chem. <u>197</u>, 200 (1931).

Molybdenum (V) Chloride

MoCle

$2 M_0 + 5 Cl_1 = 2 M_0 Cl_1$ 191.9 110.01. 540.5

The apparatus shown in Fig. 321 is used for the chlorination of the Mo. During the experiment, an additional large-diameter piece of glass tubing is attached at c by means of a large-diameter rubber hose. This glass tube is pointed upward. The left section of reaction tube a-b is charged with 6-10 g. of Mo (for preparation, see p. 1401). Then CO₃ and H₂ (both free of oxygen and very dry) are passed through the tube until the air is completely displaced from a wash bottle which is connected in series. The CO₃ flow is now shut off, and the Mo heated in the hydrogen stream for 1-2 hours (the temperature should be as high as possible). The water (which forms via reduction of the surface oxide layer) is driven off via the open end c by means of a burner and the tube is allowed to cool in the H₂ stream.

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The oxide layer may also be reduced in an alternate procedure, whereby the Mo is heated in a dry HCl stream until no further wooly sublimate ($MoO_3 \cdot 2$ HCl) is formed. The sublimate can be driven into the above mentioned glass tube by gentle warming (use a hood!). It is recommended that a drying tube or a wash bottle with conc. H_2SO_4 be attached at the end of the reaction tube to maintain anhydrous conditions. The outlet gases should pass through the drying arrangement before entering the hood.

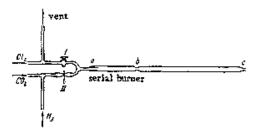


Fig. 321. Preparation of molybdenum (V) chloride. Overall length of reaction tube about 1 m.; part a-b 30 cm.; J.D. 2-2.5 cm. and 1-1.2 cm. at the constrictions.

Before chlorination, the tube is cooled, the attached wash bottle (conc. H_2SO_4) purged of air with Cl_3 , and the H_2 (or HCl) displaced from the tube with Cl_3 ; during this operation, pinchcock II remains closed. The reaction between Mo and Cl_3 either starts spontaneously or at most needs only very gentle heating with a serial burner for initiation. The reaction is accompanied by the appearance of streams of deep dull-red vapor which condense beyond the constriction b. By gentle heating of the Mo with a serial burner, as well as occasional heating of constriction b by fanning with a Bunsen flame, the MoCl₆ is collected in b-c, where beating must be avoided. At the end, only a few small gray flakes remain at the left of b.

24. CHROMIUM, MOLYBOENUM, TUNGSTEN, URANIUM

The tube contents are allowed to cool in a CO_a stream, c is closed off with a cork, and bis sealed off with a torch. The crystale are loosened by tapping, and transferred to a CO_a -filled, 35-cm long storage tube of the same diameter as the combustion tube (the storage tube is slipped over constriction c). The storage tube is, then sealed off.

PROPERTIES:

Blue-black, extremely hygroscopic crystals; dark green if oxychloride is present. M.p. 194°, b.p. 268°; d^{25} 2.927₅. Soluble in water and alcohol (solvolysis); soluble without decomposition in organic solvents such as ether, CHCl₃, CCl₄ and CS₂.

REFERENCES:

H. Biltz and W. Biltz. Übungsbeispiele aus der unorganischen Experimentalchemie [Exercises in Inorganic Experimental Chemistry], 3rd and 4th eds., 1920, p. 216; W. Biltz and A. Voigt. Z. anorg. allg. Chem. 133, 299 (1924); P. Liechti and B. Kempe. Liebigs Ann. 169, 345 (1873); E. R. Epperson et al. Inorg. Syntheses 7, 163 (1963).

Molybdenum (III) Bromide

MoBr₁

 $2 M_0 + 3 Br_2 = 2 M_0 Br_3$ 191.9 479.5 671.4

Obtained (75% yield) by heating Mo in a stream of Br_3 at 350°C. Separated from by-products by washing in cold, HBr-saturated water.

PROPERTIES:

Formula weight 335.70. Black, densely matted crystalline needles, which decompose to Mo_3Br_3 and Br_3 when calcined in the absence of air. Insoluble in water and acids, readily soluble boiling anhydrous pyridine, forming [MoBr₃py₃].

REFERENCE:

A. Rosenheim, G. Abel and R. Lewy. Z. anorganig. Chems 194, 200 (1931).

Tribromotripyridinemolybdenum

[MoBr.pys]

 $MoBr_{s} + 3 py = [MoBr_{s}py_{s}]$ 335.7 237.3 573.0

Five grams of MoBr₃ (see preceding preparation) is refluxed at 120°C with 20g, of anhydrous pyridine (frequent swirling necessary). The hot pyridine solution is rapidly filtered (suction) to remove a small amount of residue and is then treated with conc, HCl until a weak acid reaction is obtained. The brown-yellow precipitate which forms is filtered off and washed with alcohol and ether. For purification the compound is extracted with chloroform in a Soxhlet apparatus. Crystal clusters consisting of small octahedra separate upon slow evaporation of the solution.

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PROPERTIES:

Brownish-yellow needles; crystallize in octahedra from chloroform; soluble in pyridine; sparingly soluble in chloroform; insoluble in water, dilute acids, alcohol and ethyl acetate.

REFERENCE

A. Rosenheim, G. Abel and R. Lewy, Z. anorg. allg. Chem. 197, 201 (1931).

Potassium Hexachloromolybdate (III)

K₁MoCl₁

 $2 \text{ MoO}_{s} + 6 \text{ HOI} + 6 \text{ KOI} + 6 e \rightarrow 2 \text{ K}_{s}\text{MoOI}_{s}$ (-2 H₂O) 360.0 447.3 652.0

L A solution of 20 g. of $H_2MoO_4 \cdot H_2O$ in 150 ml. of conc. HCl and 50 ml. of distilled water is electrolyzed for several hours at about 0.06-0.12 amp./in.³; the electrolysis vessel is water cooled and CO₂ is bubbled through the solution. The solution is thus reduced to the red, trivalent state.

Smooth Pt. Hg or amalgamated Pb may be used for the oathode. The carbon anode, immersed in 15% HCl, is separated from the cathodic electrolyte by a clay cell diaphragm.

The reduced solution is evaporated as rapidly as possible over a free flame until its volume is about 90 ml.; it is then saturated

24. CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM

with hydrogen chloride and treated with a deaerated 10% solution of 15-20 g. of KCl in distilled water. It is then concentrated at 70°C and reduced pressure until crystals begin to separate, filtered and resaturated with hydrogen chloride while cooling in ice. The crystals are suction-filtered, washed with conc. HCl, with alcoholic HCl and finally with alcohol; they are then dried in vacuum.

II. Potassium molybdate is dissolved in HCl and reduced at a cathode immersed in a clay cell. Gaseous HCl is bubbled through the cathode liquor to precipitate the K_3MoCl_6 .

PROPERTIES:

Formula weight 425.98. d¹⁹ 2.54. Brick-red crystals, readily soluble in water.

REFERENCES:

- W. R. Bucknall, S. R. Carter and W. Wardlaw, J. Chem. Soc. (London) <u>1927</u>, 513; A. Rosenheim and W. Braun. Z. anorg. Chem. <u>46</u>, 320 (1905).
- H. S. Senderoff and A. Brenner. J. Electrochem. Soc. <u>101</u>, 28 (1954); see also K. H. Lohmann and R. C. Young in; J. C. Bailar, Inorg. Syntheses, Vol. IV, New York-London-Toronto, 1953, p. 97.

Molybdenum (IV) Oxide

MoO₂

I.

 $M_0O_3 + H_2 = M_0O_2 + H_2O_144.0 = 22.4 l_1 = 128.0 = 18.0$

Molybdenum (VI) oxide is reduced for 5-7 hours in a stream of H_2 at 450°C; the oxide mixture is then calcined at dark-red heat in a porcelain boat while a stream of HCl is passed over it; this causes any remaining MoO₃ to volatilize as MoO₃ - 2 HCl. Finally the product is allowed to cool under H_2 .

II. MELT REDUCTION OF MOO3 WITH NH3

The following method is useful for preparing pure MoO₂: Eight grams of dehydrated commercial ammonium molybdate, 7 g. of purified molybdic acid, 14 g. of calcined K_2CO_3 , and 7 g. of H3BO₃ are fused together in a large-capacity, covered Pt crueible and kept in the molten state for several hours. Cooling yields a

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F. HEIN AND S. HERZOG

brittle cake, permeated with beautiful MoO_2 crystals; this is easily **removed from** the crucible. The pure crystals are readily separated by a simple extraction of the melt with boiling water.

III. A mixture of MoO_3 and Mo (2:1 mole ratio) is heated for 40 hours at 700°C in the absence of air.

PROPERTIES:

Brown-violet powder or crystals, insoluble in water; d_{4}^{28} 4.696. Crystal structure: C 4 (rutile) type.

REFERENCES:

- L. C. Friedheim and M. K. Hoffmann. Ber. dtsch. chem. Ges. 35, 792 (1902).
- II. W. Muthmann, Liebigs Ann. 238, 116 (1887).
- IIL A. Magnéli, G. Andersson, B. Blomberg and L. Kihlborg. Analyt. Chem. 24, 1998 (1952).

y-Molybdenum Oxide

Mo.Ou

 $11 \text{ MeO}_{5} + \text{ Me} = 3 \text{ Me}_{4}\text{O}_{13}$ 1593.5 96.0 , 1679.4

Very pure molybdenum powder and sublimed MoO_3 are intimately mixed and charged into a preignited alumina crucible, which is placed at the sealed end of a quartz tube. The mixture is degassed in high vacuum, purged frequently with O_3 -free argon, and then heated for 3 days at 580°C under an argon pressure of 150 mm. The product is allowed to cool, the material is reground to a fine powder, and reheated for 3 days in the same manner.

PROPERTIES:

Formula weight 559.80. Violet crystalline powder. Relatively stable to acids and alkalies. Concentrated HNO₃ causes slow oxidation to MoO₃. Semiconductor material. d_{4}^{20} 4.18. Orthorhombic crystals (space group D_{45}^{25}).

REPERENCES:

 G. Hägg and A. Magnéli. Ark. Kem. Mineral., Geol. <u>19 A</u>, 1 (1944);
 O. Glemser and G. Lutz. Z. anorg. alig. Chem. <u>263</u>, 2 (1950);
 A. Magnéli, G. Andersson, B. Blomberg and L. Kihlborg. Analyt. Chem. <u>24</u>, 1998 (1952).

Lower Molybdenum Hydroxides

MOLYBDENUM BLUE, ModOu(OH),

Obtained by reaction of nascent hydrogen with MoOa.

Fifty ml. of distilled water and 10 ml. of conc. HCl, followed by 3 g. of analytically pure zinc granules, are added to 10 g. of MoO₃. The mixture is left standing overnight; the blue precipitate is then filtered off, washed until no chloride reaction is evident, and dried over P_3O_5 .

Alternate methods: a) Reduction with SnCl₂ · 2 H₂O in HCl solution.

b) Synthesis from MoO₃ and Mo powder (O. Glemser and G. Lutz, see below).

Other molybdenum blue compounds: See O. Glemser and G. Lutz (below).

PROPERTIES:

Formula weight 477.82. Blue crystalline powder. In air, oxidizes very slowly to MoO_3 . Stable to NH_3 and alkalies. Good electrical conductivity.

REFERENCE:

O. Glemser and G. Lutz. Z. anorg. allg. Chem. 264, 17 (1951).

Mo_bO₆(OH)₁₀

This olive-colored hydroxide is obtained by the action of zinc granules on molybdenum trioxide in conc. HCl.

An Erlenmeyer flask is fitted with a water-filled valve to exclude air (Contat-Göckel attachment), whereupon 1 g of MoO₃ is charged; 100 ml, of conc. HCl is then added, followed by about 50 g, of zinc granules. The solid phase first becomes blue [formation of $Mo_4O_{10}(OH)_3$ and $Mo_2O_4(OH)_3$], then red $[Mo_5O_7(OH)_6]$, and after about one hour green $[MO_5O_5(OH)_{10}]$. It is desirable to cool the flask with ice during the reduction. The $Mo_5O_5(OH)_{10}$ is extremely sensitive to air; the latter must therefore be excluded during washing with water. The compound is dried with O_3 -free nitrogen and stored in sealed tubes.

PROPERTIES:

Oxidizes instantly in air, evolving heat. Evolves hydrogen on thermal decomposition in vacuum, forming Bordeaux red $Mo_5O_7(OH)_8$. This is also the main product obtained in the reaction of aerated water with $MO_8O_8(OH)_{10}$.

REFERENCE:

O. Glemser, G. Lutz and G. Meyer. Z. anorg. allg. Chem. 285, 173 (1956).

Molybdenum (VI) Oxide

MoOs.

Prepared from ammonium molybdate and nitric acid.

Prepared from animatic acid is added to a boiling solution of pure, Boiling conc. nitric acid is added to a boiling solution of pure, Boiling conc. marine molybdate, thus precipitating H₃MnO4. recrystantized annuolity and hours, the granular precipitate is Alter standing for a Buchner funnel, washed and dried for 16-20 hours at above 150°C, whereupon it dehydrates to MoO₃. The MoO₃ may be purified by sublimation in a quartz tube at 780°C.

SYNONYMS:

Molybdenum trioxide; molybdic anhydride.

PROPERTIES:

Formula weight 143.95. White powder, turning yellow on heating and reverting to white on cooling. The sublimed product consists of sparkling, colorless crystalline flakes. M.p. 795 °C, b.p. 1155 °C; d²² 4.696. Solubility at 28°C: 0.490 g. MoO₃/liter H₂O. Crystal form: rhombic. Space group V¹⁶.

REFERENCES:

W. C. Schumb and W. H. Hartford. J. Amer. Chem. Soc. 56, 2613 (1934); O. Honigschmid and G. Wittmann. Z. anorg. allg. Chem. 229, 66 (1936).

Molybdic Acid

H-MoO, H,O

Prepared from ammonium molybdate and nitric acid. An aqueous solution of ammonium molybdate (150 g./liter) poured into I liter of 30% nitric acid [360 ml. of conc. Hist (d 1.42) per liter] at room temperature (vigorous stirring). The 200 g. of solid NHANOa is dissolved in the clear liquid, which then seeded with a few granules of $H_3MoO_4 \cdot H_3O$. On standing

8-10 days H_2MoO_4 · H_2O separates in almost theoretical yield. The acid is washed for several days by repeated decantation with ice water.

PROPERTIES:

Formula weight 179.98. Transparent canary-yellow crystals, very sparingly soluble in water. Loses 1 mole of H_2O by standing for about 2 weeks in vacuum over H_2SO_4 . d¹⁸ 3.124. Monoclinic-prismatic crystals.

REFERENCE:

A. Rosenheim. Z. anorg. Chem. 50, 320 (1906).

Ammonium Oxopentachtoromolybdate (V) (NH4);[MeOCI;]

A) PREPARATION OF MoO₃ SOLUTION

The MoO_3 (100 g.) is dissolved in HCl (d 1.16, 500 ml.) by heating. The solution is concentrated to 250 ml., filtered and made up to 500 ml. with HCl.

B) ELECTROLYTIC REDUCTION

The above-prepared solution (75 ml.) is diluted with an equal volume of H_{3O} and electrolyzed at a platinized Pt cathode (surface = 5 cm.²) at 2.5 amp. until hydrogen evolves. The anode is made of smooth Pt sheet; it is immersed in 5 N HCl, which is separated from the cathode space by means of a clay cell.

The resulting red-brown solution is vacuum-concentrated to 50 ml. and treated with a solution of 9 g. of NH₂Cl in 30 ml of water; the mixture is heated for about one minute.

Hydrogen chloride is introduced while cooling the flask and emerald-green crystals are precipitated. These are recrystallized by dissolving in a minimum quantity of water at 80°C and saturating the solution with HCl while cooling. The crystals are washed with conc. HCl and dried in vacuum over KOH.

PROPERTIES:

Formula weight 325.32. Emerald-green octahedral crystals, which dissolve in water with hydrolysis and development of brown color.

1.

REFERENCES:

R. G. James and W. Wardlaw, J. Chem. Soc. (London) 1927, 2146; F. Foerster and R. Fricke. Z. angew. Chem. <u>36</u>, 458 (1923).

Potassium Hydrogen Diperaxamonomolybdate

KHM0Os 2 HrO

Potassium molybdate solutions rich in H₂O₂ are treated with one equivalent of mineral acid per mole of molybdate, whereupon KHMoOe · 2 H₂O crystallizes.

PROPERTIES:

Formula weight 268.09. Long, pale yellow, crystalline needles.

REFERENCES:

K. F. Jahr. Ber. Ges. Freunde TH. Berlin 1939, 91; K. F. Jahr. Naturforsch, u. Medizin in Deutschland [Scientific Research and Medicine in Germany] 1939-1946 (FIAT Review) 25. III. 189.

Tetraamminezinc Tetraperoxomolybdate (VI)

[Zn(NH₃)₄]MoO₄

Prepared from ammonium molybdate, NH4OH and ZnSO4 by addition of H₂O₂.

A mixture of 100 ml. of water, 100 ml. of conc. ammonia (d 0.91), and 20 ml, of an ammonium molybdate solution containing 1 g.-atom of Mo per liter is cooled to -12 °C in an ice-salt mixture. Lower temperatures cannot be used, since water is frozen out (ice) at -14°C. Then 30 ml. of Perhydrol (30% H₂O₂) is added, followed by 20 ml. of 1 M ZnSO4 solution (brief but thorough stirring). The solution is allowed to stand undisturbed for 1.5 hours at -12°C. After one half hour it is examined for signs of incipient crystallization. If none is observed, crystal formation is induced by careful rubbing of the flask walls with a glass rod. The orystals are filtered off, washed twice with ice-cold 96% alcohol and then twice with ice-cold ether. Yield: about 3 g.

PROPERTIES:

Formula weight 357.46. Deep red-brown, lustrous crystals; soluble in water (decomposition). Ammoniacal solutions are more

stable. Insoluble in organic solvents. Appreciably more stable than the corresponding potassium salt and barely explosive. However, it is not advisable to seal it into ampoules. May be stored in a desiccator over KOH and under NH_3 for about 1 week.

REFERENCE:

K. Gleu. Z. anorg. alig. Chem. 204, 73 (1932).

Molybdenum (IV) Sulfide

MoS₂

I.

 $MoO_2 + 3S = MoS_2 + SO_1$ 128.0 98.2 160.1

A mixture of 150 g. of K_2CO_3 , 310 g. of S, and 200 g. of MoO_3 is heated at red heat for one half hour. After cooling and extracting with water, the residue is 80 g. of MoS_3 . It is also possible to start with 200 g. of ammonium molybdate, 150 g. of K_2CO_3 , and 280 g. of S; this affords a more crystalline product, although in lower yield. According to Bell and Herfert, one may also start with MoO_3 , K_2CO_3 and S.

11.

 $Mo + 2S = MoS_2$ 96.0 64.1 160.1

Stoichiometric quantities of Mo and S are heated in an iron tube. The MoS_{2} thus obtained has the crystal lattice of natural molybdenite.

SYNONYM:

Molybdenum disulfide.

PROPERTIES:

Opaque, gray-blue leaflets with a greasy feel, or graphite-like powder. Sublimes at 450°C; d^{15} 5.06. Soluble (decomposition) in aqua regia. Decomposed by H_2SO_4 to MoO₃. Electrical conductor whose conductivity increases with illumination. Diamagnetic, Crystal structure; C 7 type.

REFERENCES:

 M. Guichard, Comptes Rendus Hebd. Séances Acad. Sci. <u>129</u>, 1239 (1899); Ann. Chim. Phys. 7, <u>29</u>, 552 (1901); R. E. Bell and R. E. Herfert, J. Amer. Chem. Soc. <u>79</u>, 3351 (1967).

II. A. E. van Arkel. Recueil Trav. Chim. Pays Bas 45, 442 (1926)

Ammonium Tetrathiomolybdate

(NH4)+Mo54

Prepared by treating an ammoniacal ammonium molybdate solution with H_2S .

A solution of 5 g. of $(NH_4) \cdot MO_7O_{34} \cdot 4 H_2O$ in 15 ml. of water is prepared and treated with 50 ml. of ammonia (d 0.94). Then H₂S is introduced. The solution first turns yellow, later deep red, and after half an hour a copious quantity of crystals, some of them well-formed, precipitates suddenly. The crystals are washed with cold water, then with alcohol, and dried in vacuum.

PROPERTIES:

Formula weight 260.27. Blood-red crystals with metallic surface luster, readily soluble in water, very sparingly soluble in alcohol.

REFERENCE:

G. Krüss. Liebigs Ann. 225, 29 (1884).

Potassium Octacyanomolybdate (iV)

K₄[Mo(CN)₈] · 2 H₂O

L A solution of Mo (III) obtained by electrolytic reduction is oxidized to the quadrivalent state with a stoichiometric quantity of MoO_3 and is then treated with NH_4SCN and pyridine. The precipitate is converted to $K_4[Mo(CN)_8] \cdot 2 H_2Oby$ reaction with KCN.

A solution of 15 g. of pure McO_3 in 150 ml. of 8 N HCl is reduced to the trivalent state at a lead cathode (5-10 amp.) while cooling the cathode cell (porous clay) with water and bubbling CO_3 through the solution. A graphite rod immersed in 15% HCl serves as the anode.

The reduced solution is treated with a solution of 7.5 g. of MoO_3 in 75 ml. of 8 N HCl; the solution thereby changes from red to green. The Mo (IV) salt solution thus obtained is poured into a concentrated solution of 95 g. of NH₄SCN; 60 g. of pyridine is added, and the solution is made weakly alkaline with ammonia. These reactions are best carried out under CO_3 in the absence of air.

A black oil separates during the neutralization; this solidifies to a solid black tar on cooling with ice. The supernatant liquid is decanted; the tar is washed with water and added slowly to a hot, saturated 10 M KCN solution. The reaction mixture is concentrated antil crystals begin to deposit; it is then cooled in ice and filtered with suction.

The mother liquor is further concentrated and the cyano complex is precipitated with alcohol (rapid stirring). The crude product is dissolved in some water, the solution heated for some time with activated charcoal, filtered, concentrated by evaporation, and finally treated with alcohol. The precipitate of $K_4[Mo(CN)_8]$ • 2 H₂O is fairly pure except for traces of thiocyanate, which can be removed by an additional recrystallization. Yield: about 55 g.

Alternate methods:

II. The product of the reaction of MoO_3 with HSCN and pyridine is treated with KCN. The yield is low. (See original reference for details.)

III. Via the following intermediates:

HCl, H₂O KSCN pyridine MoO₃ \rightarrow H₂MoO₄ \rightarrow Mo(OH)₂(SCN)₃ \rightarrow KCN Mo(OH)₂(SCN)₅ · 2 py \rightarrow K₄[Mo(CN)₉] · 2 H₂O

PROPERTIES:

Formula weight 496.50 (dihydrate). Golden or bright-yellow tablet-shaped crystals (rhombic bipyramidal); gives up its water of crystallization at 105-110°C. Very readily soluble in water, insoluble in ether. Solubility in absolute alcohol at 20°C: 0.017 g. per liter. $d^{2\frac{5}{4}}$ (anhydrous salt) 2.337.

REFERENCES:

- I. H. H. Willard and R. C. Thielke. J. Amer. Chem. Soc. <u>57</u>, 2610 (1935).
- II. A. Rosenheim, Z. anorg. Chem. <u>54</u>, 97 (1907); see also W. Biltz, E. Eschweiler and A. Bodensiek. Z. anorg. allg. Chem. 170, 168 (1928).
- III. N. H. Furman and C. O. Miller in: L. F. Audrich, Inorg. Syntheses, Vol. III, New York-Toronto-London, 1950, p. 160.

Tungsten

W

$$WO_4 + 3H_2 = W + 3H_4O$$

231.9 67.31, 183.9 54.1

Pure ignited WO₃ is placed in a porcelain or, better, a nickel boat, which is then inserted into a tube of unglazed porcelain or other refractory material. The tube is heated by means of an electric furnace while passing through a stream of pure, dry H_2 . The initial temperature is 800°C (maintained for some time), the initial temperature is 800°C (maintained for some time), later 1000-1200°C. The reduction proceeds fairly rapidly and is complete when no further H_2O vapor evolves. The tube is allowed complete when no further H_2O wapor evolves. The tube is allowed to occl in the H_2 stream. Gray metal powder is the product.

Other authors report that the reduction with very pure H₂ may even be completed at 800°C (3 hours of heating).

a very coarse powder results from reduction with moist H₂ above
a very coarse powder is pure if the starting WO₃.

Alternate method:

$WO_3 = 3 Zn = W + 3 ZnO$ 231.9 1961 183.9 244.1

Pure, freshly ignited WO3 is cooled and mixed with 1.5 times the theoretical quantity of dry Zn dust. This mixture is compressed in a crucible and overlaid with another 3- to 5-mm, layer of Zn dust, which is similarly compressed. The crucible is then closed off with a well-fitting cover and heated briefly to red heat. A vigorous reaction ensues after about 5 minutes, as shown by a cloud of evolving ZnO. The crucible is then allowed to cool completely while still covered. The light-gray top layer, composed principally of ZnO, is removed. The black crucible contents are crushed and thoroughly boiled with dil. HCl to remove ZnO and any Zn still present. The black residue is allowed to settle for a moment and the acid is decanted. The metal powder is washed by decantation with water once or twice, filtered rapidly with suction, and rewashed with water. In this operation the powder must always be covered with liquid. Finally the metal is washed with alcohol, suction-filtered, and dried in air. Careful preparation should yield a black powder containing at least 99.8% W.

SYNONYM:

Wolfram.

PROPERTIES:

Tungsten powder is gray to black, depending on particle size; the solid exhibits a light gray, lustrous surface. M.p. ~ 3650 °C, h.p. > 5000 °C (calculated from the vapor pressure curve); d 19.3. Hardness 4.5-8, depending on the history. Crystal structure: A 2 type.

REFERENCES:

H. Funk. Darstellung der Metalle im Laboratorium [Preparation of Metals in the Laboratory], Stuttgart, 1938, p. 72 f.; O. Ruff. Angew. Chem. 25, 1892 (1912); O. Glemser and H. Sauer. Z. anorg. allg. Chem. 252, 145 (1943); M. Delépine. Comptes Rendus Hebd. Séances Acad. Sci. 131, 184 (1900); L. Weiss and A. Martin. Z. anorg. allg. Chem. 65, 308 (1910).

Tungsten (V) Chloride

WCI,

WCl₀ + $\frac{1}{2}$ H₂ = WCl₅ + HCl 396.7 11.21, 361.2

Reduction of WCl₅ vapor with H_2 for too short a period of heating and at too low a temperature results in hexachloride-containing WCl₅. Too high a temperature affects the yield adversely, since considerable amounts of lower chlorides form.

A tube of high-melting glass (Fig. 322) is used. The WCla produced in section a is distilled into the 50-cm.-long section bin a stream of H₂. Section b is heated to the reduction temperature, which lies somewhat above the boiling point of WCl₈ (350-400°C, electric furnace). The WCl₅ is distilled into storage tube c in a stream of N₂, thereby separating it from the lower chlorides; tube c is then sealed off at both ends.



Fig. 322. Preparation of tungsten (V) chloride.

PROPERTIES:

Black, crystalline solid with somewhat greenish luster. Extremely hygroscopic, M, p. 248°C; d^{26}_{4} 3.875. Water causes immediate decomposition; somewhat soluble in dry CS₂.

REFERENCES:

H. E. Roscoe, Liebigs Ann. <u>162</u>, 356 (1872); W. Biltz and A. Voigt.
 Z. anorg. allg. Chem. <u>133</u>, 301 (1924); W. Biltz and C. Fendius.
 Ibid. <u>172</u>, 385 (1928); W. Klemm and H. Steinberg. Ibid. <u>227</u>, 193 (1936).

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Tungsten (VI) Chloride

WCI.

 $W + 3 Cl_{2} = WCl_{6}$ 183.9 66.01. 396.7

Prepared in a Vycor tube with several constrictions (Fig. 323). A quartz tube is even better and the special apparatus described by Hönigschmid and Menn is the best.



Fig. 323. Preparation of tungsten (VI) chloride.

A procelain or quartz boat containing W powder is placed in section a and is heated for 1-2 hours in a stream of H₂ (700-1000°C). After cooling, the H₂ flow is discontinued, the H₂ displaced by N₂; after about 30 minutes, air-free Cl₂ (see p. 272 for preparation) is introduced.

The tube area containing the boat is gradually heated to 600°C. The first product is a small amount of red oxychloride; later products consist only of blue-black hexachloride, which deposits in section *a* (beyond the heated boat) in the form of sparkling crystals. The tube constrictions are kept at 350-400°C during the chlorination, which requires 2-3 hours. Next the red oxychloride forerun is driven into *e*; then the WCl₈ collected in *a* is sublimed into *b* at 350-400°C, while an additional forerun deposits in *c*. For further purification, the WCl₈ can be sublimed into *c* (the oxychloride is moved into *d* prior to this sublimation). Finally, the WCl₈ is fused in a stream of Cl₂; on resolidification, the mass bursts into small crystals with a loud crackling noise. After cooling, the Cl₂ is displaced with dry, O₂-free nitrogen and the tube section containing the purified WCl₈ is sealed off at both ends.

L

 $WO_3 + 3 CCl_4 = WCl_4 + 3 COCl_2$ 231.9 461.5 398.7 298.8

The chief requirements in this method are the presence of an excess of CCl_4 , completely anhydrous conditions, and thorough completion of the reaction; if these conditions are not observed, red by-product WOCl₄ forms readily. Moreover, the WOCl₄ has the undesirable property of catalyzing the hydrolysis of WCl₈ in moist air.

A dry glass bomb tube about 50 cm. long is charged with 0.5 g. of WO₃ and 11 g. of CCl₄ (the WO₃ must be completely dehydrated by previous ignition, after which it should be pure yellow; the CCl₄

1420

I.

is predried by long standing over granular CaCl₂ or P₂O₅ and is saturated with Cl₂). The tube is then sealed. The water vapor from the torch flame should not be allowed to enter the tube. The tube is placed in a protective iron jacket and slowly heated (1.5-2 hours) to about 450 °C; it is kept at this temperature for 7-8 hours. After slow cooling, the tube is very carefully transferred to a welldrawing hood without removing it from its protective iron tube. The latter is inclined and clamped to a support. The sealed tip of the glass tube is then heated at low hood vacuum until the phospene. present in the tube under high pressure, blows the tip away. The phosgene is driven out by vacuum as far possible, the CCl₄ poured off, the residual solid washed once with fresh CCl₄, and the reactor tube connected to an aspirator via a CaCl, drying tower. All the CCl4 is volatilized and the tube is resealed since the beautiful, almost black crystals of WCls hydrolyze in air to yellowred WOCl4 and yellow WO2Cl2. Proper procedure yields an almost black solid with no red or yellow spots.

PROPERTIES:

Blue-black, moisture-sensitive crystals. M.p. 275°C, b.p. 347°C; d² $\frac{5}{4}$ 3.520. Indefinitely stable if stored in a dark desiccator over H₂SO₄. Very slightly soluble but decomposed in water; the purer the WCl₆, the lower the decomposition rate. Very readily soluble in alcohol (with yellow color), CHCl₃, CCl₄ (with red and dark-brown color, respectively). CS₂, ether, benzene, ligroin and acetone. These solutions decompose on long standing in air, and very rapidly on heating or addition of water. Good crystals are obtained by heating WCl₆ in CCl₄ to 100°C in a sealed tube, followed by slow cooling (rectangular tablets and four-sided prisms). Crystallizes in space group C³₃₁.

REFERENCES:

- L. O. Hönigschmid and W. Menn. Z. anorg. alig. Chem. <u>229</u>, 58 (1936); see also M. H. Lietzke and M. L. Holt in: L. F. Audrieth, Inorg. Syntheses, Vol. III, New York-Toronto-London, 1950, p. 163.
- II. W. Jander. Lehrbuch für das anorganisch-chemische Praktikum [Lab. Text for Inorg. Chemistry], 5thed., Leipzig, 1944, p. 403.

Tungsten (IV) Oxide

WO:

$$WO_3 + H_2 = WO_2 + H_2O_3$$

 $931.9 \quad 22.41, \quad 215.9 \quad 18.0$

Stable at 900°C in a gaseous atmosphere composed of 40-55% H_3 and 45-60% H_3O .

÷,

2. Pure H₀ is subjected to an additional purification over silica gol and is then slowly passed through a water-filled flask to saturate it with water vapor. The flask is held in an 85 °C thermostat. To avoid condensation of the water vapor thus taken up, the tube which connects the flask to the reactor is wrapped with electric heating tape and heated to about 100 °C. The H_2/H_2O mixture then flows over a boat with WO₂ set in a porcelain or a quartz reactor tube surrounded by a tubular electric furnace and beated to 800-900 °C. The reduction is complete in 2 hours. The product is allowed to cool in an O₂-free nitrogen stream. The nitrogen is admitted through a 3-way stopcock located between the water flask and the reactor.

II. A mixture of WO_3 and W (corresponding to the formula $WO_{2,00}$) is heated for 40 hours at 950°C in a small evacuated and sealed quartz tube.

PROPERTIES:

Brown crystalline powder. M.p. 1500-1600°C under N₂, b.p. 1730°C; appreciably volatile above 1050°C; d^{25}_{4} 11.05. Hardness 5-5.5. Crystal structure: C 4 (rutile) type.

REFERENCES:

- L. O. Glemser and H. Sauer. Z. anorg. allg. Chem. 252, 151 (1943);
 J. A. M. van Liempt. Ibid. <u>126</u>, 184 (1923); L. Wöhler and
 R. Günther. Z. Elektrochem. <u>29</u>, 281 (1923).
- II. A. Magnéli, G. Andersson, B. Blomberg and L. Kihlborg. Analyt. Chem. 24, 1998 (1952).

y-Tungsten Oxide

W₂₀O₄₁

 $\begin{array}{rrrr} 49 \, WO_{9} \ + \ 5 \, W \ = \ 3 \, W_{10}O_{49} \\ 1/10 \ 1364.1 \ 92.0 \ 1436.1 \end{array}$

Very pure W powder and very pure WO_3 are intimately mixed in the prescribed ratio of $WO_{3.72}$ and heated for 6 hours at 800°C in a small evacuated and scaled quartz tube. The product is ground and treated again for 24 hours at 800°C in the same manner.

PROPERTIES:

Formula weight 4853.47. Red-violet crystalline powder; semiconductor, d_{4}^{20} 7.72, Deformed D0₉ type.

REFERENCES:

O. Glemser and H. Sauer, Z. anorg. alig. Chem. 252, 144 (1943); A. Magnéli, Ark. Kem. <u>1</u>, 223 (1949); A. Magnéli, G. Andersson, B. Blomberg and L. Kihlborg. Anal. Chem. <u>24</u>, 1998 (1952).

Tungsten Blue

H. WO1

produced by reaction of nascent hydrogen with WO2.

Fine WO₃ powder is slurried with distilled water in an Erlenmeyer flask, conc. HCl and analytically pure Zn granules are added, and the flask is closed with a valve which excludes air (Contat-Göckel attachment). When the Zn is consumed, the supernatant liquid is rapidly decanted and fresh conc. HCl and Zn granules are added. This is repeated until the reaction product is brown. Washing, drying and transfer of the product to a storage vessel must be carried out in the absence of oxygen.

PROPERTIES:

Formula weight 232.42. Brown to violet powder; d_{2}^{20} 7.35. Very readily oxidized. Evolves H₃ along with H₂O on thermal decomposition. Oxidized by water with H₃ evolution. Slow oxidation affords blue H_{0.33}WO₃ and H_{0.1}WO₃. D0₉ type with tetragonal distortion.

REFERENCE:

L

O. Glemser and C. Naumann. Z. anorg. allg. Chem. 265, 288 (1951).

Tungsten (VI) Oxide

WO₁

The yellow WO_3 is obtained by slow dropwise addition of a warm, saturated solution of Na_3WO_4 to 2-3 times its volume of boiling conc. HCl, followed by additional heating (for 4 heat) on a steam bath. The precipitate is allowed to settle, washed with

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8 B.A. 8

5% NH₄NO₃ solution until no further Cl⁻ reaction is obtained, and dried, first at 120°C and finally at 600°C.

PROPERTIES:

Lemon-yellow powder. M.p. about 1470°C, b.p. about 1700°C; d³7 7.27. Crystals triclinic, pseudomonoclinic. Space group C₁.

REFERENCE:

W. Reinders and A. W. Vervloet. Receuil Trav. Chim. Pay-Bas 42, 627 (1923).

Yellow Tungstic Acid

H,WO4

L

 $C_{a}WO_{4} + 2 HX = H_{2}WO_{4} + CaX_{2}$ 258.0 249.9

A boiling mixture of 50 ml. of H_2O , 40 ml. of conc. HCl, and 40 ml. of HNO₃ is treated with 20 g. of pure CaWO₄. The resulting yellow precipitate is washed 8 times by decantation with slightly acidified water, and dissolved in 50 ml. of conc. ammonia. The clear filtrate is heated to boiling and treated with acid (60 ml. of H_3O , 50 ml. of HNO₃ and 10 ml. of HCl) to precipitate yellow tungstic acid, which is washed several times by decantation with pure H_3O , filtered through a leaf filter and slurried in pure H_3O . The suspension settles on standing for 14 days, during which an electric current is occasionally passed through it (Pt electrodes); the clear supernatant liquid is siphoned off; the residue is concentrated on a steam bath and then thoroughly dried in a desiccator over solid NaOH. The tungstic acid product is free of HCl and has the composition WO₃ - 1.13 H_3O .

11. A boiling solution of 200 g, of ammonium tungstate (composition 2 $(NH_4)_{2}O$, 0.5 WO₃, 3 H₂O] in 4.48 liters of H₃O is poured into 2 liters of boiling 35.4% HCl. The deep-yellow precipitate is filtered off and purified by a nine-day dialysis (until the wash water is free of Cl⁻ and the pH has reached a constant value of 4.4). Air drying of the residue gives a 55% yield of tungstic acid of composition WO₃ · 1.18 H₂O; it still contains traces of NH_a and Cl⁻.

PROPERTIES:

Yellow powder, which appears amorphous under the microscope; it is claimed that its x-ray pattern is crystalline.

5.

REFERENCES:

L. G. F. Hüttig and B. Kurbe, Z. anorg, allg, Chem. <u>122</u>, 45 (1922). II. A. M. Morley, J. Chem. Soc (London) <u>1930</u>, 1990.

Tungsten Oxytetrachloride

WOCL

$WO_a + 2 SOCI_a = WOCI_4 + 2 SO_2$

L A mixture of WO₃ with 4 times its weight of SOCl₃ is heated in a sealed tube for 6-12 hours at 200°C. The reaction proceeds to completion only if the SO₂ is vented by opening the sealed tube for a brief time. The red WOCl₄ crystallizes from the excess SOCl₂ in long, well-formed needles, and is purified by removing the SOCl₂ in vacuum.

II. A sealed tube is used to heat the WO_3 with a solution of CI_3 in CCI_4 (3 hours at 200°C). The tube is cooled and opened (caution: phosgene is present!); the WOCI₄ is washed in the tube with dry CCI_4 ; and the tube and its contents are heated to 160°C and immediately placed in a desiccator.

PROPERTIES:

Long, lustrous, red needles, yellow in transmitted light. M.p. 209°C. b.p. 232°C. Decomposed at once by water, more slowly by atmospheric moisture, forming tungstic acid.

REFERENCES:

- I. H. Hecht, G. Jander and H. Schlapmann, Z. anorg, allg. Chem. 254, 261 (1947).
- II. A. Michael and A. Murphy. Amer. Chem. J. 44, 382 (1910).

Tungsten (IV) Sulfide

WS_z

I.

$W + 2S = WS_{2}$ 183.9 64.1 248.0

A stoichiometric mixture of W and S is heated at 800°C under very pure N₂ in a scaled quartz tube for 24 hours.

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F. HEIN AND S. HERZOG

B.
$$2 WO_1 + 7 S = 2 WS_2 + 3 SO_2$$

468.8 224.4 496.1 192.2

An intimate mixture of 33 g. of WO₃, 40 g. of sulfur and 15 g. of K_2CO_3 is placed in a tubular crucible of unglazed porcelain (190 mm. long, 35 mm. I.D.) which is closed off with a perforated asbestos lid. The crucible is heated in a vertical tubular furnace at 600-700°C until the reaction is complete and the excess S has burned off. It is then heated for an additional 15 hours at 1400°C while H_2S is passed through. Large crystals of pure sublimed WS₂ are thus obtained.

Finely crystalline WS_2 is obtained from 92 g. of W powder and 35 g. of sulfur by following the above directions but heating only for 7 hours at 1450°C in a stream of H_2S .

PROPERTIES:

Blue-gray crystals with a metallic luster, insoluble in water; d_{0}^{10} 7.5. Crystal structure: C 7 type. Exhibits catalytic and radio-detector properties.

REFERENCES:

- O. Glemser, H. Sauer and P. König. Z. anorg. Chem. <u>257</u>, 241 (1948).
- IL E. Tiede and H. Lemke. Ber. dtsch. chem. Ges. 71, 584 (1938).

Tungsten Hexaphenoxide

W(OC₄H₃)₄

$$WCl_{a} + 6 HOC_{a}H_{5} = W(OC_{a}H_{5})_{a} + 6 HCl$$

366.7 554.7 955.3

One wt. part of WCl_e and about 10 parts of phenol are heated in a long, large test tube. Vigorous evolution of HCl begins as soon as the phenol melts. The tube is now heated over a small flame until the phenol boils. After some time the melt (which initially is brown-black even in thin layers) becomes deep red. Boiling is continued (or a short time; the tube is then cooled while rotating it to distribute the melt on the walls of the vessel. The cooled melt is treated with some alcohol while crushing with a glass rod. The excess phenol dissolves in the alcohol and the product separates as a brick-red powder. It is filtered off latter.

SYNONYM:

Tungston hexaphenolate.

PROPERTIES:

Dark-red needles or leaflets. M.p. 98°C. Readily soluble in CCl_4 , CS_2 , C_8H_8 , etc. Relatively poorly soluble in cold alcohol.

REFERENCE:

H. Funk and W. Baumann. Z. anorg. allg. Chem. 231, 265 (1937).

Potassium Enneachlaraditungstate (HI) K.W.CL

Prepared by electrolytic reduction of a KCl-containing solution of WO $_3$ in conc. hydrochloric acid.

A solution of 10 g. of $WO_3 \cdot H_3O$ in a conc. solution of 7.5 g. of K_3CO_3 is prepared. This solution (volume of about 15 mL) is added in 2 or 3 portions to 260 mL of conc. HCl (40°C); the hydrate, which precipitates after each addition, is allowed to redissolve before the next portion is introduced. After complete solution is finally obtained, the liquid is quickly cooled to 0°C. The crystalline precipitate thus obtained is composed for the most part of KCl. The solution, filtered through a fritted glass funnel, contains 3-4% WO₃ as H[WO₃Cl₃], and is used in electrolysis.

The cathode vessel is a porous clay cell of about 6.5 cm. I.D. and 21 cm. high; this is set in a heavy-wall 12.5-cm.-I.D. and 20-cm.-high glass cylinder and centered with the aid of a rubber stopper. The rubber stopper contains five holes: two for the symmetrically placed carbon anodes, two for glass tubes used for passing CO_a through the anodic electrolyte (so as to decrease the Cl_a concentration in the latter), and a fifth hole through which the electrolyte is introduced. A drain is provided at the bottom of the anode vessel to permit rapid emptying at the end of the run. The clay cell is closed off hermetically with a rubber stopper, which carries a gas-tight stirrer (Hg seal), the cathode lead, and an opening for removal of samples during the electrolysis. The anodic liquor is conc. hydrochloric acid, while the clay cell is charged with 450 ml. of the W (VI) solution described above. The latter is reduced at 40°C and a current density of 0.4 amp./in.² until it turns yellow-green and the consumption of permanganate becomes constant.

The cathode is a 140-cm.² Pb sheet, which may be amalgamated if necessary. Runs with amalgamated electrodes require a longer time (up to 2 hours) than do those with pure Pb cathodes (80-90 min.), but the product solution is free of Pb.

To obtain reproducible results with Pb cathodes, the latter must be formed by alternating anodic and cathodic polarization in $2 N H_2SO_4$; this is unnecessary with the amalgamated electrodes (because of the purely chemical reducing action of the cathodic metal, it is best to admit the cathodic liquid only after the voltage has been applied). The Pb, which initially goes into solution and later reprecipitates, causes no problem either during electrolysis or in the later workup of the solution.

After the completion of the reduction, the cathode is carefully removed from the solution, the anode vessel rapidly emptied, and the cathodic liquid containing the precipitated crystals poured into an Erlenmeyer flask, where it is then saturated with HCl while chilling in ice-salt mixture. After 1-2 days, the crystalline precipitate is collected on a frifted-glass funnel, washed with some conc. hydrochloric acid, then with alcohol and ether, and dried in a stream of air. The yield is about 60% based on the $WO_3 \cdot H_2O$ used.

For purification, $K_3W_2Cl_9$ is reprecipitated with a readily soluble potassium salt. For example, 25 g. of $K_3W_2Cl_9$ is dissolved in 175 ml. of boiled cold water; the solution is filtered into an Erlenmeyer flask which contains 150-175 g. of solid KSCN. The flask is then shaken. A copious quantity of deep green to yellow-green crystals separates even during the filtration; the solution meanwhile turns red. After one hour of standing in the cold, the crystals are suction-filtered, washed a few times with very concentrated KSCN solution, then with hot 80% alcohol, and dried in air. The product is fairly stable and can be stored for months in dry air over H_3SO_4 .

SYNONYM:

Potassium nonachloroditungstate (III).

PROPERTIES:

Formula weight 804.24. Small, dark-green tablets, yellow in transmitted light. Soluble in water, giving a dark-green color; very slightly soluble in alcohol. The aqueous solution oxidizes in air; the crystalline compound also oxidizes but more slowly.

REFERENCES:

O. Collenberg and A. Guthe. Z. anorg. allg. Chem. <u>134</u>, 317 (1924);
O. Collenberg and K. Sandved. Ibid. <u>130</u>, 9 (1923); O. Olson-Collenberg. Ibid. <u>88</u>, 50 (1914); W. Biltz. Ibid. <u>170</u>, 164 (1928);
H. B. Jonassen, A. R. Tarsey, S. Cantor and G. F. Heifrich in: Th. Moeller, Inorg. Syntheses, Vol. V, New York-Toronto-London, 1957, p. 139.

24. CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM

Hexachlorotripyridineditungstate (III)

W₂Cl₁py₂

 $K_3W_2Cl_s$ + 3 py = 3 KCl + $W_2Cl_9py_s$ 804.3 237.3 223.7 817.9

Ten grams of freshly recrystallized $K_3W_3Cl_9$ is refluxed in 150 ml. of dry pyridine for 6 hours (N₂ atmosphere). The red solution is filtered to remove the brown precipitate and treated with a large excess (10 volumes) of ether. This precipitates the dark-brown complex salt; it may be recrystallized from pyridine.

PROPERTIES:

Insoluble in water, somewhat soluble in ether and beazene. Diamagnetic. A corresponding aniline complex exists.

REFERENCE:

H. B. Jonassen, S. Cantor and A. R. Tarsey. J. Amer. Chem. Soc. <u>78</u>, 271 (1956).

Potassium Octacyanotungstate (IV)

K₄[W(CN)₅] · 2 H₂O

Prepared from K₃W₂Cl₂ and KCN.

A solution of 20 g, of $K_3W_3Cl_9$ in 150 ml, of cold, boiled water is prepared and treated on a water bath with 65 g, of KCN powder; this causes oxidation to W (IV), and the green color of the solution changes to red. The KCN should be added very carefully (shaking) over a period of 5 to 10 minutes.

The solution is now heated about two hours on the water bath, filtered (decolorizing charcoal being added if required) and evaporated until crystals begin to deposit. The first crystal fraction, consisting predominantly of KCl, is filtered off and discarded. The filtrate is diluted to 130 ml. and treated, while still warm, with 20-25 ml. of 95% alcohol. The $K_4[W(CN)_8] \cdot 2 H_8 \dot{O}$ separates in lustrous, bright-yellow plates on sharp cooling in a freezing mixture. After one hour, 15 additional ml. of alcohol is added. The mixture is suction-filtered after standing for 12 hours in the cold. The product is washed with hot 80% alcohol. Yield: 60-70%, based on tungsten. For purification, the compound is first precipitated twice from 50% aqueous solution by adding an equal volume of alcohol. It is then dissolved in 16% KCN solution and, after concentrating, allowed to stand at 0° C until crystallization is complete. The product is again reprecipitated with water and alcohol to remove traces of KCN.

PROPERTIES:

Formula weight 584.5. d^{25} 1,989. Bright-yellow crystalline powder; slow evaporation of a KCN solution affords large, yellowred crystals. Very readily soluble in water (about 19-14 g./10 ml. H₂O at 18°C). Insoluble in alcohol and ether.

REFERENCE

O. Olsson-Collenberg. Z. anorg. allg. Chem. <u>88</u>, 50 (1914); H. Baadsgaard and W. D. Treadwell, Helv. Chim. Acta <u>38</u>, 1669 (1955).

Potassium Octacyanotungstate (V)

K₄[W(CN)₆] · H₂O

A solution of $K_4[W(CN)_8] \cdot 2 H_2O$ (11.69 g. = 0.05 moles) in 125 ml, of water (acidified with 2 ml, of conc. HNO₃ and titrated with permanganate to a permanent red color) is prepared. The silver salt is then precipitated by addition of 0.21 g. (0.08 moles) of AgNO₃ dissolved in 50 ml, of water. The solid is washed with dil. HNO₃, dissolved in the minimum amount of ammonia, and reprecipitated with some dil. HNO₃. After thorough washing with water, the salt is suspended in 50 ml, of water and converted to the potassium salt by addition of 0.11 g. (0.07 moles) of KCl. The AgCl precipitate is removed by filtration, and the filtrate is treated with alcohol until the $K_3[W(CN)_6] \cdot H_3O$ precipitates. It is filtered and dried over CaCl₂. The yield can be as high as 91%, based on the starting tungstate (IV).

PROPERTIES:

Formula weight 527.4. Small lemon-yellow crystals, readily soluble in water.

REFERENCES:

Olsson-Collenberg. Z. anorg. allg. Chem. <u>88</u>, 50 (1914);
 H. Baadagard and W. D. Treadwell. Helv. Chim. Acta <u>38</u>, 1669 (1955).

U

The preparation of the pure metal is rendered difficult by its great tendency to combine with O, N, C, etc., and to alloy with many metals.

Basically, the following preparative methods are available:

a) Reduction of uranium oxides or halides with suitable metals, such as Na, Mg, Ca (methods I to IV).

b) Electrolysis (method V).

I. In the Jander method, UO3 is reduced with metallic Ca:

 $UO_2 + 2Ca = U + 2CaO$ 270.1 80.2 238.4 112.2

The reactor is an iron crucible about 13 cm. high, 1.6 cm. I.D., with a 0.1-cm. wall. This is charged with the reactant mixture, consisting of 7 g. of UO₂ and 11 g. of Ca turnings (the latter should be as freshly distilled as possible). The crucible cover is then welded on and the reactor heated for one hour at 1000-1100°C (the crucible should be embedded in charcoal powder to protect it from oxidation). The crucible is then completely cooled, opened, and the contents are covered with 90% alcohol saturated with NH₄Cl. Aqueous NH₄Cl solution is then added. The material is washed with water and then with alcohol. The product consists of four different fractions:

a) a very finely divided oxide-containing uranium, which can be separated by slurrying;

b) iron metal particles with a small uranium content, which can be removed after drying by means of a magnet;

c) nonmagnetic metal flakes (uranium with a high content of iron), which can be separated on a 140-170 U.S. standard sieve;

d) a very fine gray-brown powder, containing about 97% U and 2-3% Fe, but only very small amounts of O. The yield of this fraction is 66%.

The presence of iron impurity in the product can be avoided by coating the inner surface of the iron crucible with caloium carbonate, but the shrinkage of this lining during drying and its fragility necessitate considerable care in handling. A reactor lined with calcium carbonate is capable of producing material containing 99.9% U, although the yield is appreciably lower than in the above-described procedure.

II. Very pure uranium is obtained by reduction of U_2O_2 with ireship distilled Ca in high vacuum. The mixture is heated above

the melting point of Ca, and the U is obtained as a fine gray powder which can be separated from the by-product CaO by sieving. Any unused Ca (which is present in excess) sublimes out from the product at the reaction temperature. The product analyzes as 99,95% U.

III. Both of the above procedures may be improved by adding to the reactant mixtures a mixture of scrupulously predried and prefused $CaCl_2$ and $BaCl_2$. The salt mixture serves as a flux and at high temperatures dissolves both the CaO and Ca metal. It is further recommended that the product be reduced a second time under the same conditions; this is because the first reduction normally goes to equilibrium and no further.

IV. Many variations of the reaction of uranium chlorides with metallic Na in sealed iron vessels have been described. The products range in purity from 99 to 100% U. The preparative method described below is based on the earlier procedures and attempts to overcome some of their shortcomings; however, it affords a uranium whose x-ray diffraction pattern still clearly shows UO₂ lines. For this reason one must question the assertions of earlier authors who claimed that this procedure gives a completely pure product.

 $UCl_{*} + 4 Na = U + 4 NaCl$

 379.9 = 92.0 = 208.1

 $UCl_{*} + 5 Na = U + 5 NaCl$

 415.4 = 115.0 = 239.1

An alumina tube closed at one end (a so-called Tammann crucible), 12 cm, high and 2 cm. I.D., is charged successively with 5 g. of NaCl, 13 g. of uranium chloride (for preparation, see p. 1436 under UCl., method 1), and 4.5 g, of Na metal (freshly cut under ether). The materials must be added as rapidly as possible and then ocvered with NaCl up to 1 cm. below the top edge of the crucible. The filled tube is placed inside an only slightly larger iron crucible (3-mm, wall thickness) and the lid of the latter is welded on (see also Part III, Intermetallic Compounds, preparation of alloys by fusion of components). Two thick wires or bars are welded onto the outside of the iron crucible so that it may be suspended in a vertical tubular electric furnace. The reactor is gradually heated to 1150°C (2 hours), held for 15 minutes at this temperature, and then allowed to cool. The crucible is opened, and the contents of the alumina tube are treated with HCI-saturated methanol to remove unreacted Na, then with hot water to dissolve away the NaCl. Yellow Na 2U207 may appear

during this operation, even if the chloride reactant contained only a small percentage of UO_3Cl_3 . However, the $Na_3U_2O_7$ may be separated completely from the U metal residue by repeated slurrying with water and decantation. The residue is then washed several times with HCl-saturated methanol and with water. Finally, light-gray metallic pellets are obtained.

V. ELECTROLYTIC PREPARATION

Very pure uranium is obtained by electrolysis of KUF_5 in an NaCl-CaCl₂ melt. A cylindrical graphite crucible serves both as the electrolysis vessel and the anode. It has an I.D. of 6 cm., a height of 15 cm. and walls 1-2 cm. thick. The electrical connection is made with a strip of Ni sheet wrapped around the upper part of the outside wall. The cathode is a strip of Mo sheet, 0.5 mm. thick and 1 cm. wide, which is immersed in the melt so that its lower end is 2.5 cm. above the bottom of the crucible. The latter stands in a suitable refractory vessel, around which a heating wire is wound. The entire apparatus is placed in a large-diameter lead vessel filled with thermal insulation.

A mixture of 250 g. of NaCl and 250 g. of anhydrous CaCl₂ is first fused together, and the melt temperature is adjusted as exactly as possible to 775°C. When the mixture is thoroughly melted, the cathode is inserted and the current is turned on (30 amp., potential drop between the electrodes about 5 v.). The current density should be 10 amp./in.².

Now, 30 g. of KUF_5 is added in small portions so that it melts as rapidly as possible. After addition of the KUF_5 is completed, a deposit of U begins to form on the cathode, where it appears in the form of a metallic tree; this reaches a thickness of about 2.5 cm. in 45 minutes. The old cathode is then slowly withdrawn from the melt, a new one is introduced, and the electrolysis is continued as before, while fresh salts are added to the melt as needed,

The material adhering to the cathode consists of a gray, spongy mass, which is permeated and surrounded by solidified melt. The melt protects the material from oxidation during cooling. After thorough cooling, the solids are stripped off the cathode and treated with water. Most of the salts dissolve quite easily, while the residue of heavy U powder can be readily and completely freed from traces of CaF₂, etc., by slurrying with water. The fraction consisting of very fine particles should be separated at the same time, since this material oxidizes very easily. The residue then comprises pure, fairly coarse particles of gray metal. The latter is washed with 5% acetic acid, followed by alcohol and ether; it is dried in vacuum and stored in air-tight vessels. This material is not pyrophoric. However, if the fise metal powder is not removed the dry product may ignite in air under some circumstances.

PROPERTIES:

Light-gray pellets or black powder. M.p. 1689°; d 18.685. May be distilled using an electric furnace. Dissolves in dil. HCl and H₂SO₄ (slowly in cold acids but rapidly in warm ones), evolving H₂.

REFERENCES:

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 - I. W. Jander. Z. anorg. allg. Chem. 138, 321 (1924).
- IL E. Botolfsen. Bull. Soc. Chim. France 45, 626 (1929).
- III. W. Kroll. Z. Metallkunde 28, 30 (1936).
- IV. J. Zimmermann. Liebigs Ann. <u>216</u>, 16 (1883); A. Fischer. Z. anorg. Chem. <u>81</u>, 170 (1913); A. Roderburg. Ibid. <u>81</u>, 122 (1913); D. Lely and L. Hamburger. Z. anorg. allg. Chem. <u>87</u>, 220 (1914); H. Haag and G. Brauer. Data from the Chem. Lab. of the Univ. of Freiburg i. Br., 1950.
- V. F. H. Driggs and W. C. Lilliendahl. Ind. Eng. Chem. 22, 516 (1930).

Uranium Hydride

UH,

 $U + 3/2 H_2 = UH_3$ 238.1 33.6 L 241.1

This procedure is successful only when very pure uranium metal is employed.

Uranium (10 g.) is freed of the adherent oxide layer by brief treatment with dil. nitric acid, washing with water, and drying over P_2O_5 . The metal is then coarsely ground and placed in a porcelain boat, which should be large enough to accommodate the increase in volume which accompanies the hydride formation. Hydrogen is then passed over it at 250°C. [The pretreatment of the H₂ includes passage through a copper column heated to 650-700°C, a drying agent (magnesium perchlorate), and uranium powder heated to 700-750°C.] The reaction is complete after 20-30 minutes; the yield is quantitative.

See also Part II, Section I, p. 113 f.

24. CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM

PROPERTIES:

Fine, black, pyrophoric powder. Loses H_2 when heated in vacuum above 250 °C, forming a uranium of high chemical activity. Powerful reducing agent; reacts vigorously with water according to: 2 UH₃ + 4 H₂O = 2 UO₂ + 7 H₂.

REFERENCES:

F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. W. Nottorf, J. B. Johns and A. H. Daane, Nucleonics 4, 4 (1949).

Uranium (III) Chloride

ÜCI,

 $UCl_4 + \frac{1}{2}H_2 = UCl_3 + HCl_379.9$ 11.21, 344.4 38.5

1. Completely pure UCl₄ is reduced with H_2 in the same tube in which it is prepared. The reduction proceeds below red heat and then at dull-red heat, until the off-gases are free of HCL. Absolutely pure H_2 must be used. The dull-brown, very hygroscopic UCl₃ adheres strongly to glass. Thus, when the mechanically separated product is dissolved, some brown to brick-red U (IV) silicate is always obtained as a residue.

II. Uranium is reacted with dry HCl at 250-300°C.

PROPERTIES:

Lustrous, dark-red, very hygroscopic needles; d^{25} 5.440. Very readily soluble in water, giving a purple-red liquid which becomes green within a few seconds as H₂ is evolved and a red precipitate forms. Insoluble in anhydrous alcohol, acetic acid, CCl₄, CHCl₅, acetone and pyridine.

REFERENCES:

- I. A. Rosenheim and H. Leobel. Z. anorg. Chem. <u>67</u>, 235 (1908);
 W. Biltz and C. Fendius. Z. anorg. alig. Chem. <u>172</u>, 386 (1928);
 J. F. Suttle in: Th. Moeller, Inorg. Syntheses, Vol. V. New York-Toronto-London, 1957, p. 145.
- II. E. Staritzky, Analyt, Chem. 28, 1055 (1956).

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Uranium (IV) Chloride

UCL

1. The preparation of completely pure UCl_4 (or UCl_5) is difficult since under normal conditions there exists an equilibrium: 2 UCl_4 + $Cl_2 = 2 UCl_5$. However, for many purposes, especially for the subsequent reduction to metallic U, any mixture of the two uranium chlorides is adequate. Such a mixture is prepared rapidly and conveniently by the following method.

 $UO_{z} + C_{z} + 2V_{z}Cl_{z} (2Cl_{z}) = UCl_{z} (UCl_{z}) \div CO_{z}$ 270.1 12.0 415.4 (379.9)

A quartz tube 40 cm. long and 2 cm. I.D., both ends of which carry ground joints, is charged with a mixture of 20 g. of UO_2 and 7 g. of carbon black, distributed along the entire length of the tube. One end of the reactor tube is connected to a wash bottle containing H₂SO₄; the latter, in turn, is connected to a U tube filled with P_2O_5 , which is attached to a Cl_2 cylinder. The other end of the reactor is connected to two ground-joint Erlenmeyer flasks in series (do not use round-bottom flasks; these are not as well suited for the precipitation operation), which in turn are attached to a wash bottle with H₂SO₄ (the latter is connected backward and serves as a trap for atmospheric moisture). All joints are lubricated with vitreous phosphoric acid. A very fast stream of CI2 is passed through this apparatus. When all the air is displaced, the reactor is heated with two rosette burners, beginning at the Cl_ inlet. Within a short time the uranium chloride begins to sublime into the cooler part of the tube, largely as a brown vapor. By shifting the burners to the next zone of the tube as the reaction is completed in the preceding one, it is possible to sublime most of the uranium chloride into the two Erlenmeyer flasks. The yield is almost quantitative. It takes one hour to obtain about 13 g. of uranium chloride from 20 g, of UO2.

Chlorination of U_3O_8 under identical conditions, sometimes recommended in the literature, gives chlorides greatly contaminated with UO_2Cl_3 .

II. UCl₄ may be obtained by heating a mixture of 20 g. of UO₂ and about 6 g. of sugar-derived charcoal, covered with some additional sugar charcoal powder. The reactants are in an unglazed boat and a stream of Cl₂ is passed over the latter (the air is first displaced by evacuation and several purgings with Cl₂). The reaction begins at 450°C and is completed at 600-700°C. The UCl₄ is driven into a spherical receiver sealed onto the reactor tube to be a CO₂ stream into a second receiver sealed onto the first. 24. CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM

ш.

 $UO_{2} + 2 SOCl_{2} = UCl_{4} + 2 SO_{2}$ 270.1 237.9 379.9 128.1

A bomb tube of ~ 1.5 cm. I.D. is charged with 5.6 g. of pure UO₂ and 10 ml. of SOCI₂ (freshly distilled in vacuum); these are then thoroughly mixed. The scaled tube is heated for 7 days at 200°C; the time required for completion of the reaction may be somewhat reduced if the tube is briefly cooled at regular intervals and the SO₂ formed is permitted to escape.

The product consists of UCl₄, partially dissolved in SOCl₂ and partially present as green crystals. The lower part of the bomb tube is cut off, the entire contents rinsed rapidly with some SOCl₂ into a 100-mi. ground-joint flask and distilled under reduced pressure (e.g., 140 mm.) in a stream of dry N₂ (or CO₂) to remove the SOCl₂. Finally, the brown adduct of SOCl₂ and UCl₄ is decomposed by heating at about 150°C until a pure green residue of UCl₄ is obtained (half an hour is required). Yield: about 7.5 g. (95%).

IV. Analogous to Hönigschmid's method for UBr. (see p. 1440 f.). The product has the composition indicated by the formula. The procedure is somewhat tedious because of numerous precautionary measures necessary. Useful only for small quantities.

V. Chlorination of UCl₃ at 250°C.

PROPERTIES:

Formula weight 379.90. Light-green needles or dark-green octahedra, which sublime at red heat as a red vapor. M.p. 567°, b.p. 618° ; d^{2} 4.73-4.97. The aqueous solution gives a strongly acidic reaction because of hydrolysis. Soluble in ethyl acetate and benzoate; insoluble in ether, chloroform and benzene.

REFERENCES:

- I. H. Haag and G. Brauer. Experiments at chemical laboratories of the University of Freiburg i. Br., 1950.
- II. A. Voigt and W. Biltz. Z. anorg. allg. Chem. 133, 281 (1924).
- III. H. Hecht, G. Jander and H. Schlapmann. Ibid. 254, 255 (1947); checked at chemical laboratories of the University of Freiburg i. Br., 1951.
- IV. O. Hönigschmid and W. E. Schilz, Z. anorg. allg. Chem. <u>170</u>, 148 (1928); O. Hönigschmid and F. Wittner, Ibid. <u>226</u>, 296 (1936).
 - V. E. Staritzky. Analyt. Chem. 28, 1056 (1956). See also J. A. Hermann and J. F. Suttle in: Th. Moeller, morg. Syntheses, Vol. V, New York-Toronto-London, 1957, p. 143.

1437

Щ.,

Uranium (V) Chloride

UCI,

 $UCl_{*} + \frac{1}{2}Cl_{*} = UCl_{5}$ 379.9 11.01, 415.4

A very clean hard-glass tube a-h, bent as shown in Fig. 324, is charged at location b with a mixture of UCl₄ and finely divided wood charcoal, and attached immediately to a Cl₂-generating apparatus via joint a. The reactants and the glass tube are carefully dried by heating in the Cl₂ stream, which is predried over P_2O_5 . When stronger heating is applied at b, a mixture of UCl₄ and UCl₅ distills toward d. To completely convert this chloride mixture into UCl₅, a sufficient quantity of Cl₂ is first frozen in f by cooling the latter; the tube is then sealed off at c and (after evacuation via joint h) at g. The solid Cl₂ at f is brought to 0°C. This results in a vapor pressure of about 3.6 atm, Then heating the tip of tube dcauses sublimation of pure UCl₅ from the heated zone; it forms a dark-brown deposit at c.

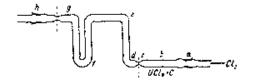


Fig. 324. Preparation of uranium (V) chloride.

Alternate method: Chlorination of U_3O_8 with CCl_4 in a sealed tube at 250°C (Michael and Murphy).

PROPERTIES:

Deep-brown, crystalline, very hygroscopic sublimate. Dissociates slowly, even at room temperature, to UCl₄ and Cl₂ (equihibrium partial pressure of Cl₂ at 20°C is at least 10^{-2} mm.); must therefore be stored in sealed vessels filled with Cl₂. Soluble in water with fizzing and evolution of HCl; soluble in absolute alcohol and acetone; the best solvents are ethyl acetate and benzonitrile.

REFERENCES:

H. Martin and K. H. Eldau, Z. anorg. allg. Chem. <u>251</u>, 295 (1943);
 O. Ruff and A. Heinzelmann, Ber. dtsch. chem. Ges. <u>42</u>, 495 (1909);
 A. Michael and A. Murphy. J. Amer. Chem. Soc. <u>44</u>, 365 (1910).

Uranyl Chloride

UO₂Cl₂

 $\begin{array}{rll} UO_{2}SO_{4} \cdot 3 \ H_{2}O &+ \ BaCl_{2} &= \ UO_{2}Cl_{2} &+ \ BaSO_{4} &+ \ 3 \ H_{2}O \\ & 420.2 & 208.3 & 341.0 \\ & UO_{4} &+ \ 2 \ HCl &= \ UO_{2}Cl_{2} &+ \ H_{2}O \\ & 286.1 & 72.9 & 341.0 \\ & U_{3}O_{8} &+ \ 6 \ HCl &+ \ H_{2}O_{2} &= \ 3 \ UO_{2}Cl_{3} &+ \ 4 \ H_{4}O \\ & 842.2 & 218.8 & 34.0 & 10^{2}3.0 \end{array}$

An aqueous solution of uranyl chloride is prepared by (a) dropwise addition of a BaCl₂ solution to a conc. solution of UO_2SO_4 . 3 H₂O [for preparation, see p. 1447 under uranium (IV) sulfate] until all of the SO_4^{2-} ion is precipitated (no excess of BaCl₂), followed by filtration; or (b) by thoroughly boiling UO_3 with water to give a yellow powder of H₃UO₄, which is then dissolved in dil. HCl; or (c) by slurrying U_3O_6 in conc. HCl, followed by dropwise addition of 30% H₂O₂; the U₃O₆ is thus dissolved as UO_2Cl_3 , although the reaction is slow.

Careful evaporation of any of the UO_2Cl_2 solutions on a water bath and then in a vacuum desiccator over conc. H_2SO_4 affords a crystalline mass of composition $UO_3Cl_2 \cdot H_3O$. To obtain $UO_2Cl_3 \cdot$ $3 H_2O$, a small portion of the residue is beated with some conc. HCl, the resulting solution is allowed to evaporate in a desiccator, and the small crystals which separate are added to a conc. solution of the main body of the monohydrate, whereupon they grow into large, uniform prismatic crystals,

The $UO_2Cl_2 \cdot H_BO$ and $UO_2Cl_2 \cdot 3 H_BO$ can be dehydrated without decomposition by the following method. The uranyl chloride is first dried over P_2O_5 , placed in flat porcelain boats, and slowly heated in a dry HCl/Cl₂ stream to about 450°C over a period of 4-5 hours. Under these conditions no decomposition to the oxide takes place and only the water of crystallization is removed. If any $UO_3(OH)Cl$ is present, it is converted to UO_3Cl_3 by reaction with the HCl, liberating water.

Alternate methods: a) repeated evaporation of uranyl nitrate or acetate with conc. HCl yields UO_3Cl_2 solutions, which are crystallized in a vacuum desiccator over KOH. The amount of water of crystallization present in the product depends on the duration of the drying period.

b) Oxidation of UCl4 with O2 (Leary and Suttle).

PROPERTIES:

UO₂Cl₂

Golden-yellow when completely anhydrous: hydrated UO₂Ol₃ exhibits a greenish luster.

i.

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UO_pCl₂ · 3 H₂O

Formula weight 395.03. Yellow-green, fluorescent, obliqueangled prisms, deliquescent in air; extremely soluble in water, alcohol and ether. At 18°C, 7.35 wt. parts of $UO_2 Cl_2 \cdot 3 H_2O$ dissolve in 1 part of H_2O ; the saturated solution is very viscous.

REFERENCES:

F. Mylius and R. Dietz. Ber. dtsch. chem. Ges. <u>34</u>, 2774 (1901);
W. Oechsner de Coninck. Comptes Rendus Hebd. Séances Acad. Sci. <u>148</u>, 1769 (1909); L. Ochs and F. Strassmann. Z. Naturforsch. <u>7 b</u>, 637 (1952); H. A. Leary and J. F. Suttle in; Th. Moeller, Inorg. Syntheses, Vol. V, New York-Toronto-London, 1957, p. 148.

Uranium (IV) Bromide

UBr4

Prepared by brominating a mixture of UO₂ and charcoal.

The apparatus used by Hönigschmid (Fig. 325) consists essentially of two parts: the glass section A and the quartz tube B with receiver C. Section A serves to hold the weighing tube and its stopper, and is attached to the quartz tube B by means of a large flange joint. Section B has a sacklike protuberance on one side, of the same LD, as the quartz tube itself.

System D, comprising 3 quartz tubes connected by ground joints, is inserted into tube B. The side view of this system is shown separately in the figure, and is also reproduced in the main drawing. Tube $a \cdot d$, constricted in the middle, carries a quartz boat containing the oxide-charcoal mixture. Tube b, which will be stored later in the weighing tube mentioned above, serves as a receiver for the pure, fused UBr₄. Tube c leads the uncondensed bromide vapors into the receiver.

The quartz boat is charged with a mixture of 1 part of sugarderived charcoal and 4 parts of uranium oxide, intimately ground together in an agate mortar. The boat is then inserted into tube a. The flanged joint and all stopcocks which will come in contact with bromine vapor are greased with sirupy metaphosphoric acid. The flanged connection is held together with strong metal springs. The apparatus is heated with small electric tube furnaces which can be shifted along the level action.

shifted along the length of the quartz tube as far as the protuberance. The apparatus is first filled with N_2 , and the quartz tube is heated along its entire length (beginning at the protuberance) in order to dry the material. Then a Br₂-saturated stream of N_2 is

introduced and the furnaces are shifted in such a manner that the entire system of tubes can be heated as far as part d. The temperature is raised to yellow heat; the UBr₄ begins to form and condenses in d. Tubes b and c remain completely free of material and only a small amount of UBr₄ collects in receiver C. About 5 g. of UBr₄ forms in one hour. The furnaces are now shifted in such a way that the preweighed tube b remains cold, yet the sublimate in d is heated to yellow heat. The second sublimation (from d into b) is carried out either in bromine vapor or in pure N₂.

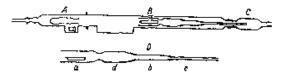


Fig. 325. Preparation of uranium (IV) bromide.

The melting of the UBr₄ should be accomplished without a loss, if possible, and without too long an exposure to high temperature. Thus, after completion of the sublimation, the entire system of tubes is pushed toward the protuberance by means of a quartz rod inserted through receiver C, while all furnaces are still at their maximum temperature. In this way the small tube b with the UBr₄ is shifted into the hottest part of the apparatus. The sublimate fuses in a few moments; the furnaces are now shut down and removed at once. Unnecessary overheating of the UBr₄ is thus avoided.

The apparatus is allowed to cool in a stream of N_B , and are then filled with dry air. In disassembling the tube system, receiver C is removed first and the individual joints are loosened with a long glass rod provided with a small hook, while a steady, fast stream of air is passed through. Tube a is pushed up to the protuberance and is allowed to glide into the latter by gently turning the whole apparatus. Then tube b with the fused sublimate is pushed into the previously prepared weighing tube, which is then closed in the usual manner. The length of the run from the beginning of heating to the disassembly of the apparatus is 3 hours or less.

PROPERTIES:

Formula weight 557.73. d_{4}^{21} 4.838. Lustrous, brown to black leaflets, sublimable in a Br_2-N_2 stream; in N_2 alone, dissociates partially to UBr_3 and Br_2 . Dissolves in H_2O with fizzing and formation of a green liquid.

REFERENCES:

O. Hönigschmid. Monatsh. Chem. <u>36</u>, 59 (1915): O. Hönigschmid and F. Wittner. Z. anorg. allg. Chem. <u>226</u>, 296 (1936).

Uranium (IV) Oxide

UO,

L $U_3O_8 + 2H_2 = 3UO_2 + 2H_2O_3$ 842.2 44.81. 810.2 96.0

The starting U_3O_8 is prepared by heating pure uranyl nitrate, oxalate or peroxide (or ammonium diuranate) to 700-800°C; it is then reduced with H₂ at 900°C and allowed to cool in the stream of H₂.

 $\Pi_{s} \qquad \qquad UO_{s}C_{s}O_{s} - 3H_{z}O = UO_{z} + 2CO_{s} + 3H_{z}O$ $= 412.1 \qquad \qquad 270.1$

Precipitation of a hot cone. solution of uranyl nitrate with oxalic acid yields a yellow powder of $UO_2C_2O_4 \cdot 3 H_3O$; this is converted to black, very fine, pyrophoric UO_3 powder in a stream of H_3 even below red beat.

REFERENCES:

Formula weight 270.1. Brown powder. M.p. 2176° under N₂; d^{25} 10.8. Crystal structure: C 1 (fluorite) type.

REFERENCES:

I. W. Biltz and H. Müller, Z. anorg. allg. Chem. <u>163</u>, 261 (1927).
II. W. Jander. Ibid. <u>136</u>, 321 (1924).

Uranium (VI) Oxide

UO₁

Pure UO₃ is difficult to prepare because the thermal cleavage of uranyl compounds does not free the product of traces of volatile components, while at high temperatures dissociation into U_3O_3 and O_2 becomes objectionable. To circumvent these drawbacks it is desirable to use O_3 at a pressure above atmospheric.

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$$\frac{UO_4 \cdot 2H_2O}{338.1} = \frac{UO_3}{286.1} + \frac{1}{2}O_2 + 2H_2O$$

A weighing tube is charged with 5-10 g, of the dry peroxide and placed (unstoppered) in an electric crucible furnace preheated to 350°C. A fast stream of O_2 is admitted through the opening in the

furnace lid. The temperature is initially held for 3-5 hours at 350°C and then for one half to one hour at 400°C. The weighing tube is then stoppered and allowed to cool in a desiccator.

II. Uranyl nitrate is heated in O₂ to 500°C; however, the product still contains traces of water.

| ш. | $U_sO_s + 1/_sO_s$ | - 300, |
|----|--------------------|--------|
| | 842 2 | 858.2 |

Figure 326 shows the apparatus in which rather large quantities of U_3O_9 can be converted to UO_9 at an oxygen pressure higher than atmospheric. The reactor r consists of an Inconel (a Cr-Ni alloy) tube which is screwed into a brass flange plate. This plate also carries a seal seat groove with a neoprene gasket. The upper, blind flange plate, also made of brass, carries the seal tongue and is drilled for a welded-on brass cross. The latter is connected to two high-pressure diaphragm valves and a pressure gage. A removable quartz insert q facilitates replacement of reactants. Manometer m is arranged in such a way that it also serves as a pressure-relief valve. The graduated tube g is for the liquid oxygen; it must contain sufficient oxygen to generate the desired pressure in the reactor.

Pure U_3O_8 (or UO_3 prepared as in method I) is placed in the quartz insert tube g and the reactor assembled to the flanges. The entire system is purged with O_2 , beginning at stopcock h_{1i} the O_2 may be discharged at the pressure gage. Then stopcock h_1 is closed and the apparatus is evacuated by opening stopcocks ha and h_3 ; in this operation, value v_4 is open and v_6 closed. The U₃O₆ is completely dried by heating reactor r for one hour at 850°C while maintaining the vacuum. A McLeod gage is used to ascertain when the apparatus is completely evacuated; the vacuum connection at stopcock h_2 is then closed, as are stopcock h_3 and value v_4 . Trap is filled with liquid O₂ by immersing it in liquid N₂ and opening h1. The amount of O2 condensed in the trap should exceed by 10% that required to bring the pressure in the reactor to 27 atm. gage. This O₂ quantity can be estimated more exactly after the apparatus has been used once. When sufficient Og is condensed in the trap, stopcock h_1 is closed. Now the graduated tube g is immersed in a Dewar flask filled with liquid N2 and stopcock h3 is opened. The exact quantity of O₂ which is needed to attain the required gage pressure is measured into g and stopcock ha is then closed. The reactor is cooled in liquid Ng and valve v4 is opened. Tube g is then immersed in liquid Og in order to establish an inside pressure of about 1 atm.; this causes the O2 to distill over into the reactor. Next, value v_4 is closed and the reactor τ is brought very gradually to room temperature in order to avoid scattering of the UsOs by

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the evaporating O₂. The best procedure for doing this is to replace the liquid-Ng-filled Dewar flask with an empty one. The reactor the in placed in an electric furnace and heated for 40 hours at 600-700°C. If too much O₂ is condensed in the reactor, the excess can be discharged through valve v_8 . The liquid O_2 remaining in trap f can be removed by vacuum, or allowed to escape (slowly) through the manometer while the trap is in a Dewar flask containing gradually evaporating liquid N2-

According to x-ray diffraction data, this procedure yields pure UO3-

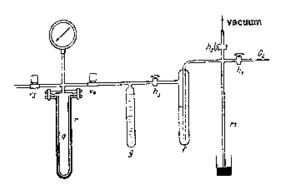


Fig. 326. Preparation of uranium (VI) oxide. r Inconel reactor; q quartz insert tube; g graduated condensation trap; f condensation trap; m manometer and pressure-relief valve; v valves.

PROPERTIES:

Bright crange-yellow, very hygroscopic, amorphous powder or hexagonal crystals; d²⁵ 7.368. Soluble in mineral acids, forming uranyi salts. In water, it hydrates in 24 hours at room temperature to give UO₃ · H_aO.

A red, hexagonal modification, which is less stable, forms at 450-500°C; its crystal structure resembles that of U₃O₈,

REFERENCES:

- L W. Biltz and H. Müller. Z. anorg, ailg. Chem. 163, 258 (1927).
- I. G. F. Huttig and E. v. Schroeder. Ibid. 121, 250 (1922); S. S. Lu. Sci. Technol. China 1, 12 (1948), abstr. in Chem. Zentr. 1949, II, 951,
- III. J. Sheft, S. Fried and N. Davidson. J. Amer. Chem. Soc. 72 2172 (1950).

24. CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM

Alkali Uranotes (VI)

LisUO, NasUO, KsUO

 $UO_3 + Li_2CO_3(Ne_2CO_3, K_2CO_3) = Li_2UO_4(Ne_3UO_4, K_2UO_4) + CO_3$ 286.1 73.9 (106.0, 138.2) 316.0 (348.1, 380.3)

Alkali carbonate and UO₃ (1:1 mole ratio) are intimately ground, placed in a large-diameter crucible, and gradually heated in an electric furnace to 800°C while O₂ is slowly passed through. The process is interrupted several times to regrind the reactants. The end of the reaction is recognized by the failure of a sample to evolve CO₂ on dissolution in dil. hydrochloric acid (2-3 days required to reach this point).

PROPERTIES:

Light orange when finely divided. Aqueous slurries show a distinctly alkaline reaction within a few minutes. Soluble in dilute hydrochloric acid and sulfuric acid, as well as in 2 N acetic acid (except for potassium uranate).

REPERENCE:

W. Rüdorff and H. Leutner. Z. anorg. allg. Chem. 292, 193 (1957).

Alkali Uranates (V)

LIUO₅, NaUO₂

 $L_{12}UO_4(Na_2UO_4) + UO_2 = 2 LiUO_3(NaUO_3)$ 315.9 (348.0) 270.1 596.0 (618.1)

A mixture of alkali uranate $\langle VI \rangle$ and UO_{e} (1:1 mole ratio) is heated in evacuated, sealed quartz ampoules at 650-750°C. The ampoules are opened at intervals of 10-20 hours, the reaction product is reground to a fine powder, and the heating is resumed using a new ampoule. The reaction is complete in 75-100 hours; the lithium compound forms in a somewhat shorter time and at a somewhat lower temperature.

PROPERTIES:

Formula weights: $LiUO_3$ 293.0; NaUO_3 309.1. $LiUO_3$ is dark violet, NaUO_3 brown-violet. Both are very stable. Much more resistant to acids than the corresponding uranates (VI). Dilute hydrochloric and sulfuric acids have no effect in the cold. Dissolve is dil. nitric acid.

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BEFERENCE:

W. Rudorff and H. Leutner. Z. anorg. allg. Chem. 292, 193 (1957).

Uronium Peroxide

UO4 · 2 H2O

Precipitates from uranyl nitrate solutions on addition of H₃O₂.

I. A boiling 10% solution of uranyl nitrate is treated dropwise with 30% H₂O₂. The resulting amorphous, white precipitate is filtered on the finest filter possible (membrane or Millipore filter) and washed thoroughly with boiling water. The peroxide, which is a bright sulfur-yellow after filtration, is first dried in the air on a clay plate, then at 100°C to constant weight, and stored in vacuum over P₂O₅.

II. Reaction of $(NH_4)_2[UO_2(C_2O_4)_2] \cdot 3 H_2O$ with H_2O_2 yields crystalline, nonhygroscopic $UO_4 \cdot 3 H_2O$, which is converted to the dihydrate by storing in vacuum over P_2O_5 .

III. A readily filterable peroxide hydrate is obtained from the reaction of 50 ml. of 30% H₂O₃ with 3 g. of UO₃ (half a day at room temperature).

PROPERTIES:

Formula weight of $UO_4 \cdot 2 H_2O_1$: 338.10. Yellowish-white, amorphous powder or fine needles.

REFERENCES:

I and H. A. Rosenheim and H. Daehr. Z. anorg. allg. Chem. 181, 178, 180 (1929).

III. A. Sieverts and E. Müller. Ibid. 173, 299 (1928).

Uranium (IV) Sulfide

USt

 $UCl_{1} + 2H_{1}S = US_{2} + 4HCl_{379.9} + 4HCl_{379.2}$

L The best starting material for the preparation of US_2 is $Na_2UClein this material is preferable to UCl₄ because its volatility is lower.$

24. CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM

The starting mixture is prepared during the synthesis of UCL- (a) p. 1436, method II); thus, the sealed-on round receiving flash (b) precharged with 10 g. of ignited NaCl. Fusion of the UCL with NaCl yields a green cake. The Cl₂ is removed by evacuation of the reactor tube. Then a stream of dry H₂S (either generated from the liquefied material or made by passing pure, dry H₂ over a boot containing molten S) is passed over the Na₂UCl₈ while heating the latter to 600-700°C; the reaction is continued for 4-5 hours until the off-gases are free of HCl. The US₂ is allowed to cool under H₂S and washed briefly with deaerated ice water, then with alcohol and ether, and dried in vacuum at 140°C.

II. Prepared from U_3O_8 and H_2S at 1150°C (electric furnace); depending on the reaction conditions, either α - or β -US₂ is formed.

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PROPERTIES;

Black leaflets with a metallic luster, altered only by prolonged standing in air; d_{4}^{26} 7.96.

REFERENCES:

- I. E. F. Strotzer, O. Schneider and W. Biltz. Z. anorg. allg. Chem. 243, 307 (1940); A. Colani, Ann. Chim. Phys. (8) 12, 80 (1907); R. Flatt and W. Hess. Helv. Chim. Acta 21, 526 (1938).
- II. M. Picon and J. Flahaut. Comptes Rendus Hebd. Séances Acad. Sci. <u>237</u>, 808 (1953).

Uranium (IV) Sulfate

U(SO₄)_t · 8 H₄O or 4 H₂O

Prepared by cathodic reduction of UO₂SO₄:

| 001301 1 | | - X6 | + U(SO4)2 | |
|--------------------------------|------|------|----------------------------------|--|
| (-3 H ₂ O) 420.2 | 98.1 | | (- 8 H ₂ O) 574.3 | |

The electrolyte consists of an approximately saturated solution of $UO_2(SO_4) \cdot 3 H_3O$ (1 mole) in about twice the stoichiometric quantity (2 moles) of H_3SO_4 . The $UO_2SO_4 \cdot 3 H_3O$ is prepared from $UO_2(NO_3)_2 \cdot 6 H_3O$ by evaporating to dryness with H_3SO_4 and concentrating an aqueous solution of the residue to a strupy consistency, whereupon the $UO_2SO_4 \cdot 3 H_3O$ slowly crystallises. The

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 $UO_{2}SO_{4}-H_{2}SO_{4}$ solution is placed in a cooled glass cylinder which houses the cathode space. A clay cell contains the anode. The best results are obtained with an Hg cathode and a carbon rod anode. The Hg layer is placed on the bottom of the cathode vessel; the electrical connection is made with a copper wire sealed into a glass tube. The reaction proceeds quite rapidly at 3-5 amp. Any material which separates during the electrolysis is redissolved by addition of some water. At the end the cathode liquid becomes dark green with a steel-blue to black-violet fluorescence. If the electrolysis continues beyond the tetravalent state, the reddish brown color (in transmitted light) of trivalent uranium becomes apparent; however, this compound is very unstable and is quickly reoxidized in air to tetravalent uranium.

The concentrated acidic $U(SO_4)_3$ solution thus obtained is very stable and may be kept for weeks, in contrast to the very dilute solution.

Concentration of the solution in vacuum over H_2SO_4 yields $U(SO_4)_3 \cdot 8 H_2O$ as large, dark-green crystals; alternately, the product may be obtained by evaporation in air below 75°C. If the product is precipitated with alcohol in the cold, it is a light-green, fine crystalline powder.

The tetrahydrate $U(SO_4)_2 \cdot 4H_2O$ is prepared by dropwise addition of conc. H_2SO_4 to the reduced solution (high-speed stirring); the H_2SO_4 is added until no further precipitation occurs. During this operation the temperature rises to 40-50 °C.

The salt is washed with alcohol and ether and dried on a clay plate.

PROPERTIES:

 $U(SO_4)_2 \cdot 8 H_4O$: Formula weight 574.32. Dark-green monoclinic prismatic crystals. Hydrolyzes on solution in water, precipitating the basic sulfate $UOSO_4 \cdot 2 H_2O$. Solubility (20°C): 8.78 g./100 g. of solution in 0.1 N H₂SO₄.

 $U(SO_4)_3 \cdot 4 H_2O$: Formula weight 502.26. Whitish-green precipitate composed of needles arranged in a starlike form. Sciuble in water with separation of the basic sulfate; soluble in dilute acids.

REPERENCE:

H. J. Meyer and H. Nachod. Liebigs Ann. <u>440</u>, 186 (1924).

24. CBROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM

Ammonium Uranyi Carbonate

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ietas) Misso

$(NH_i)_i[UO_i(CO_i)_i]$

 $2 UO_4 (NO_3)_2 + 6 NH_4 + 3 H_4 O = (NH_4)_4 U_2 O_7 + 4 NH_4 NO_8$ (· 6 H_4 O)
1004.4 624.2

 $\frac{(NH_4)_2U_2O_7 + 6(NH_4)_2CO_5}{624.2} = 2(NH_4)_4[UO_2(CO_3)_3] + 6NH_3 + 3H_2O_2$

The $(NH_4)_2U_2O_7$ is precipitated from an aqueous solution of 10 g, of $UO_2(NO_3)_2 \cdot 6 H_3O$ by addition of conc. ammonia. The fine yellow powder is suction-filtered, washed with water, and stirred with an excess of conc. $(NH_4)_3CO_3$ solution for about 10 minutes (the flask is on a 70°C water bath). The clear supernatant liquid is decanted and allowed to stand overnight. Yellow crystals precipitate; these are filtered with suction and dried in air. The residue of undissolved $(NH_4)_2U_2O_7$ is treated several times with the mother liquor at 70°C, as described above, until crystals no longer form on cooling. Yield: 5-8 g.

PROPERTIES:

Formula weight 522.26. Well-formed, transparent yellow crystals, monoclinic prismatic; d 2.773. Sparingly soluble in water; insoluble in alcohol and ether; may be recrystallized without decomposition from aqueous $(NH_4)_2CO_3$.

REFERENCE:

Ebelmen, Liebigs Ann. 43, 302 (1842).

Uranium (IV) Oxalate

$U(C_2O_4)_2 \cdot 6 H_2O$

UCl₄ + 2 $H_2C_2O_4$ + 6 H_2O = U(C₃O₄)₂ · 6 H_3O + 4 HCl 180.1 523.2

Five grams (0.012 moles) of $UO_2(CH_3COO)_3 \sim 2 H_2O$ powder is dissolved in 100 ml. of dilute HCl (1:10 in water) preheated to 30%. While stirring, 5 g. (0.024 moles) of Na₂S₂O₄ $\sim 2 H_2O$ powder is

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added in small portions. The initial precipitate is brown, but rapidly changes to whitish-green. Then 5 ml. of conc. HCl is added and the mixture is heated for about 10 minutes on the water bath (until solution is complete). The dark-green solution of uranium (IV) salt is usually somewhat cloudy because of a haze of fine sulfur. It is filtered in the absence of air and treated while still warm (appr. 60° C) with a saturated oxalic acid solution; the latter is added slowly (good stirring). A heavy, solid gray precipitate forms at once. It settles in a few minutes and, after standing for one half bour, exhibits the dark-green color of uranium (IV) oxalate. It is washed 5 times with 100-ml. portions of water. Sulfite and oxalate should be removed completely by this operation. Since uranium (IV) oxalate is completely stable in air, it may be air dried. The yield is almost quantitative (5.7 g.).

PROPERTIES:

Dark-green microcrystals, stable in air (in contrast to solutions of uranium (IV) saits]. May be recrystallized from warm conc. hydrochloric acid. Only slightly soluble in water and dil. acids. Loses 5 moles of H_2O at 110°C, but the sixth mole only at about 200°C.

REFERENCES:

V. Kohlschütter and H. Rossi. Ber. dtsch. chem. Ges. <u>34</u>, 1473, 3630 (1901); E. Marchi in: L. F. Audrieth, Inorg. Syntheses, Vol. III, New York-Toronto-London, 1350, p. 166.

Potassium Tetraoxalatouranate (IV)

K₄[U(C₂O₄)₄] · 5 H₂O

 $\frac{U(C_2O_4)_2 \cdot 6 H_2O}{522.2} + \frac{2 K_2C_2O_4 \cdot H_2O}{368.5} = \frac{K_4[U(C_2O_4)_4] \cdot 5 H_2O}{836.6} + \frac{3 H_2O}{522.2}$

A slurry of 6 g. (0.014 moles) of $U(C_2O_4) \cdot 6 H_2O$ in 50 ml. of water is treated in the absence of air with a solution of 5 g. (0.027 moles) of $K_2C_2O_4 \cdot H_2O$ in 20 ml. of water and allowed to stand on a steam bath for one hour. It is then filtered and the dark-green filtrate is treated dropwise with 200 ml. of absolute alcohol (good stirring). Small light-green crystals precipitate. These are filtered off, washed with absolute alcohol, then with ether, and dried over P_2O_E .

PROPERTIES:

Readily soluble in water (21.7 g. per 100 g. of water at 17°C), but only very slightly soluble in water-alcohol mixtures. Converted to the monohydrate by heating for a few hours at 200°C.

REFERENCES:

 V. Kohlschütter. Ber. dtsch. chem. Ges. <u>34</u>, 1472, 2619 (1901);
 E. Marchi in; L. F. Audrieth, Inorg. Syntheses, Vol. III, New York-Toronto-London, 1950, p. 169.

Uranium (V) Ethoxide

U(OC₅H₄)₅

 $\begin{aligned} & \text{UCl}_{4} + 4 \operatorname{NaOC}_{7} H_{3} = U(\operatorname{OC}_{2} H_{5})_{4} + 4 \operatorname{NaCl} \\ & U(\operatorname{OC}_{6} H_{5})_{4} + \frac{1}{4} \operatorname{Br}_{2} = U(\operatorname{OC}_{2} H_{5})_{4} \operatorname{Br} \\ & U(\operatorname{OC}_{1} H_{5})_{4} \operatorname{Br} + \operatorname{NaOC}_{7} H_{5} = U(\operatorname{OC}_{2} H_{5})_{5} + \operatorname{NaBr} \end{aligned}$

A sodium ethoxide solution is prepared from 800 ml, of absolute ethanol and 46 g. (2 g.-atoms) of Na (use a 1-liter, three-neck flask). Toward the end of the reaction, refluxing and good stirring are needed. The solution is cooled to room temperature. Then. while stirring rapidly, 190 g. (0.5 moles) of fine UCl4 powder is added in portions of about 20 g. (5-minute intervals). The contents of the flask are protected at all times against atmospheric moisture by means of a CaCl₂ tube. The heat of reaction causes the alcohol to boil, and the flask is therefore set in cold water. When all the UCl₄ has been added and the reaction subsides, the flask contents are refluxed on a steam bath for two hours (stirring). They are then cooled to room temperature and a solution of 40 g. (0.5 g.-atoms) of bromine in 20 ml. of dry benzene is added dropwise (rapid stirring) over a period of 15 minutes. The color changes from light green to brown, then gray and, toward the end of the addition, dark green.

While continuing the stirring, a sodium ethoxide solution prepared from 11.5 g. (0.5 g.-atoms) of Na in 200 ml. of absolute alcohol is rapidly added, causing the color to turn brown. The mixture is then distilled under anhydrous conditions to remove the alcohol. To achieve this, about one third of the material is introduced as rapidly as possible into a 500-ml. Claisen flask and the alcohol is distilled off on an oil bath (good stirring). Then the second fraction is added, etc. When the mass becomes solid, the stirrer is removed; the flask is closed off with a stopper and gradually heated to 150°C at 2-3 mm. The completely dry residue, which contains NaCl and U(OC₂H₅)₅, is now heated further on an oil bath at a vacuum of 0.001-0.004 mm. The uranium (V) ethoxide distills at a bath temperature of about 160-240°C. The yield may be as high as 217 g. (94%).

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SYNONYM:

Uranium (V) ethylate.

PROPERTIES:

Dark-brown liquid, B.p. about 123°C at 0.001 mm.; d²⁵ 1.711. Considerably higher thermal stability than UCls. Miscible with ethanol, ether, benzene, chloroform, pyridine, etc. Immediately decomposed in water.

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REFERENCE:

R. G. Jones, E. Bindschadler, G. Karmas, F. A. Yoeman and H. Gilman, J. Amer. Chem. Soc. 78, 4287 (1956).

Uranium (VI) Ethoxide

U(OC₂H₃).

$U(OC_2H_3)_3 + NaOC_2H_3 = NaU(OC_2H_3)_3$

 $2 \operatorname{NaU}(\operatorname{OC}_2H_3)_6 + (\operatorname{C}_6H_3\operatorname{CO})_2\operatorname{O}_2 = 2 \operatorname{U}(\operatorname{OC}_2H_3)_6 + 2 \operatorname{C}_6H_3\operatorname{COONa}$

A 500-ml, three-neck flask is fitted with a gas-tight stirrer and a gas outlet tube. This flask is used to prepare a sodium ethoxide solution from 300 ml. of absolute alcohol and 1, 69 g. (0.074 g.-atoms) of Na. When all of the Na is dissolved, the solution is cooled under No and 20 ml. (34 g., 0.074 moles) of uranium (V) ethoxide (see above for preparation) is added with a pipette. The brown color of the ethoxide disappears, and a clear, light-green solution of NaU(OC₂H₅)₆ is formed. Now, 8,90 g. (0.037 moles) of dry benzoyl peroxide powder is added in three equal portions at about 10-minute intervals while vigorously stirring. The mixture becomes warm, acquiring a red color and forming a gelatinous precipitate of sodium benzoate. After one hour of additional stirring under Na, half of the material is transferred (still under No) to a 250-ml. Claisen flask fitted with a distilling condenser, and the alcohol is distilled out at atmospheric pressure on a steam bath. The second half is then added and the procedure repeated.

The receiver flask is now heated on an oil bath and the contents are subjected to a vacuum distillation. At first, with the bath temperature as high as 140°C and at 5-10 mm., the last of the alcohol is removed; the uranium (VI) ethoxide distills out at the same bath temperature but at a high vacuum (0.003 mm.). Yield: 20 g. Rectification in high vacuum affords the pure product. Yield: 16 g. (43%). The boiling point is 72-74°C at 0.001 mm.

STRONYN:

Uranium (VI) ethylate.

PROPERTIES:

Red, mobile liquid; d 1.563. Monomeric in benzene. Readily soluble in benzene, ether, petroleum ether, etc. Extremely sensitive to moisture; forms uranyl hydroxide when hydrolyzed. Strong oxidizing agent. Readily reduced to uranium (V) ethoxide. Synproportionates with U (IV) ethoxide according:

$$U(OC_2H_3)_0 + U(OC_2H_6)_4 = 2 U(OC_2H_3)_4$$

REFERENCE:

R. G. Jones, E. Bindschadler, D. Blume, G. Karmas, G. A. Martin, J. R. Thirtle, F. A. Yoeman and H. Gilman. J. Amer. Chem. Soc. <u>78</u>, 6030 (1956).

Uranyidibenzoyimethane

UO₂(C₁₃H₁₁O₂)₂

 $UO_2(CH_3COO)_2 + 2 C_{13}H_{12}O_2 = UO_2(C_{13}H_{11}O_2)_2 + 2 CH_3COOH$ (2 H-O) 424.2 448.5 716.6

Methanolic solutions of uranyl acetate and dibenzoylmethane are combined in the cold. An intense reddish-yellow color appears at once, and after a few seconds uranyldibenzoylmethane powder begins to separate; it can be recrystallized from a large amount of hot alcohol. Other solvents may also be used for purification; however, one must bear in mind that uranyldibenzoylmethane forms well-crystallized addition compounds with almost all solvents.

Used analytically for the rapid separation of rare earths produced in the fission of uranium, since these do not form complexes with dibenzoylmethane in the presence of water. The uranium can be rapidly and conveniently separated by extraction (as the UO_2 complex).

PROPERTIES:

Orange-red crystals, which change color at about 180°C and begin to decompose at 245°C. Readily soluble in all ketones and esters and in pyridine; moderately soluble in ethyl alcohol; sparingly soluble in ether; insoluble in hydrocarbons such as benzene, toluene and naphtha. Stable to water, but is decomposed by acids and alkalies (even by ammonia).

REFERENCES:

H. Götte. Z. Naturforsch. 1, 378 (1946). Preparation of dibenzoylmethane: A. Magnani and S. M. McElvain. Org. Syntheses, collective Vol. 3, p. 251, New York-London, 1955.

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SECTION 25

Manganese

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Monganese

Mn

I. BY ELECTROLYSIS

Very pure Mn may be produced by electrolysis under the following conditions:

The electrolysis is performed with anode and cathode spaces separated from each other, using canvas or a ceramic substance as the cell diaphragm. The cathode electrolyte contains 70 g of $MnSO_4 \cdot 4H_3O$ and 200 g of $(NH_4)_3SO_4$ per liter, the anode electrolyte 100 g of $(NH_4)_3SO_4$ per liter. The cathode is a polished stainless steel sheet; the anode is a lead sheet. The cathodic current density is 0.16 amp./in.² and the temperature of the electrolyte should not exceed 40°C. The pH value in the cathode cell should be maintained between 4.5 and 8.5, and the free sulfuric acid content of the anode cell should not exceed 5%. To prevent oxidation of the catholyte and to promote uniform deposition of Mn, a small quantity of a saturated SO_3 solution is added from time to time to the catholyte so that a concentration of about 0.1-1 g. of SO_3 /liter is maintained in it.

The current efficiency is about 50-70%. In addition to impurities, the content of which is a function of the purity of the starting electrolyte, the metal contains up to 0.02% S and some H₂; however, the latter can be readily removed by heating in vacuum. The γ -Mn product is silver-gray, polishes readily and is stable in air. The boundary layer in contact with the cathode shows gradual transition to fine-grained β -Mn and is therefore hard. If performed under different conditions, the electrolysis will produce shiny layers of metal which rapidly turn dark upon exposure to air; in this case the metal should be immersed in a 5% Na₂Cr₂O₇ solution immediately upon removal from the electrolyte; this treatment passivates if and permits it to retain its lustrous surface.

II. BY DISTILLATION

Very pure Mn can be obtained by the distillation of Mn prepared via the aluminothermic or the electrolytic methods. The metal, in a sintered Al₂O₃ boat, is placed in a ceramic tube closed at one end. The tube must be pretested for gas tightness, and a vacuum of at least 0.005 mm. Hg should be established in it. The tube is heated in a Globar furnace to a temperature of 1250 to 1350°C. at which temperature the Mn vapor pressure is 1-2 mm. The distilled metal deposits as small needles on a tubular nickel sleeve cooled by running cold water and located in the vicinity of the boat; the metal can be loosened by slight tapping. The product is extremely reactive and ignites upon exposure to air; all subsequent handling must therefore take place in an Ar atmosphere in the absence of O₂.

Manganese prepared under the same conditions but deposited on an uncooled surface, e.g., an alumina rod, is less reactive. The dense, silvery scales of the crystalline metal are easily stripped off and reduced to powder. This product is the α -modification, which is stable at temperatures below 742°C.

PROPERTIES:

Atomic weight 54.93. M.p. 1212°C, b.p. 2152°C. Electrolytically precipitated Mn: d 7.2, crystal structure y -Mn, A 6 type. Distilled Mn: d 7.44, crystal structure & Mn, A12 type.

REFERENCES:

- I. R. Springer. Die elektrolytische Abscheidung des Mangens [The Electrolytic Deposition of Manganese], Akad. Verlagsges... Leipzig, 1951; S. M. Shelton and M. B. Royer. Trans. Electrochem. Soc. 74, 447 (1938), Chem. Zentr. 1939, I, 2284; I. A. Mendelev, S. I. Orlova and Y. S. Shpichinetskiy. Tsvet. Metal. 16, 53 (1941), Chem. Zentr. 1942, II, 2196; E. Herrmann. Ann. Physik (5] 21, 139 (1934).
- II. R. Schenk and A. Kortengråber, Z. anorg. allg. Chem. 210, 273 (1933); H. Haraldsen and W. Klemm. Ibid. 220, 164 (1934); M. L. V. Gayler. Metallwirtschaft 9, 678 (1930); M. Picon and J. Flahaut. Comptes Rendus, Hebd. Seances Acad. Sci. 237, 569 (1953).

Manganese (II) Oxide

MnO

 $Mn(NO_2)_2 = MnO_2 + 2 NO_3; MnO_2 + H_2 = MnO + H_2O_2$ (·6H.O) 70.9 287.0

The oxide varies from grassy green to light green and may be obtained from any of the oxides (or other suitable salts of

manganese) by reduction with H_2 at temperatures below 1200°C. Thus, for example, $Mn(NO_3)_2 \cdot 6H_2O$ is heated in air to about 300°C; the product (approx. $MnO_{1.95}$) is ground to powder and reduced for 4 hours at 800°C with pure, oxygen-free hydrogen; the reaction rate becomes appreciable about 450°C. With prolonged heating or high temperatures the product turns an increasingly grayish color and finally becomes light gray; in the presence of oxygen, It is brown. A reduction temperature of 800°C is sufficient for hydrated oxides; $MnCO_3$ must be heated to 1000-1100°C for 15-20 minutes.

PROPERTIES:

M. D. 1785°C; d5.18. Crystal structure: B1 (rock salt) type.

REFERENCES:

P. Dubois. Ann. Chimie [11] <u>5</u>, 432; for preparation by heating MnCO₃ or MnC₂O₄ in a high vacuum, see M. LeBlanc and G. Wehner. Z. phys. Chem. A <u>168</u>, 63 (1934); T. E. Moore, M. Ellis and P. W. Selwood. J. Amer. Chem. Soc. <u>72</u>, 856 (1950); for preparation by heating MnCO₃ in flowing N₂, see H. Ulich and H. Siemonsen. Arch. Eisenhüttenwesen <u>14</u>, 27 (1940); Z. Elektrochem. 45, 637 (1939).

Manganese (II) Hydroxide

Mn(OH),

 $MnCl_{2} + 2 KOH = Mn(OH)_{2} + 2 KCl$ (· 4 H₂O) 197.9 112.2 89.0 149.1

In the method of Simon, a solution of 300 g, of analytically pure KOH in 500 ml. of water in a round-bottom flask (see Fig. 327) is heated for about one half hour while a stream of completely O_{2} free hydrogen is passed through; a completely O_{2} -free solution of 15-17 g. of MnCl₂ · 4H₂O in 15 ml. of boiled water is then added from a dropping funnel. The mixture is then heated to 190-200°C (as rapidly as possible) on an oil bath while H₂ is bubbled through. When the amorphous precipitate of Mn(OH)₂ is completely dissolved, the flask is allowed to cool slowly on the oil bath, whereby the compound precipitates out as white flakes of pearly sheen.

After cooling to room temperature, boiled water prepurged with H₂ is added from a dropping funnel until the flask is almost filled; the liquor is then siphoned off by means of a glass tube which

reaches almost to the bottom of the flask (the flow of H_2 should not be interrupted either during this or the preceding operation). The glass tube is connected to a Pyrex glass filter (constantly flushed with a H_2 stream), which in turn is attached to a suction flask; the latter is connected to the suction pump by way of a wash

bottle containing a solution of $CrCl_2$. The addition of small amounts of water (washing operation) to the flask is repeated several times. The crystals are transferred (by shaking the flask) to the glass filter, washed on the filter, first with a large quantity of O_3 -free water (a second dropping funnel is used), then with absolute alcohol through which H₃ is bubbled, and finally with peroxide-free ether. The product, still on the glass filter, is then dried in a desiccator over P_2O_5 while maintaining a high vacuum.

This procedure gives a moderate yield of a well-crystallized product. Larger amounts of the microcrystalline substance are prepared more conveniently by the method of Scholder and Kolb [boiling with concentrated sodium hydroxide to which $(NH_3OH)Cl$ is added].

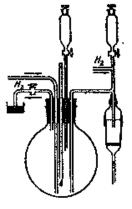


Fig. 327. Preparation of manganese (II) hydroxide.

PROPERTIES:

When free of alkaline hydroxides and amorphous components, the dry product can be kept in an air-filled desiccator for weeks. The crystalline compound occurs in nature as pyrochroite.

Solubility (18°C) 0.0019 g./liter. d 3.258. Crystal structure; type C 6.

REFERENCES:

A. Simon, Z. anorg, alig. Chem. <u>232</u>, 369 (1937); T. E. Moore, M. Ellis and P. W. Selwood. J. Amer. Chem. Soc. <u>72</u>, 858 (1950);
 R. Scholder and A. Kolb. Z. anorg, alig. Chem. <u>264</u>, 211 (1951).

Manganese (III) Oxide

y-Mn₂O₃, y-MnO(OH)

 $\begin{array}{ll} 2 \, MnSO_4 \cdot 4 \, H_2O \, + \, H_2O_3 \, + \, 4 \, NH_3 = 2 \, MnO(OH) \, + \, 2 \, (NH_4)_3 SO_4 \, + \, 6 \, H_2O \\ \\ 446.1 & 34.0 & 88.0 & 175.9 & 264.3 \end{array}$

The method of Marti gives γ -MnO(OH) with a well-defined x-ray pattern. A solution of 2.2 g, of MnSO₄ · 4H₂O (10 mmoles) in 350 ml. of water is treated in a large beaker (very vigorous mechanical agitation) with 34 ml. of a 3% H_3O_2 solution (30 mmoles). With continued very vigorous agitation, 50 ml, of a 0.2 M NHs solution (10 mmoles) is added at once from a graduated cylinder. The dark-brown or black suspension, which is evolving oxygen, is brought to a boil as rapidly as possible. The boiling is continued for about 4 minutes and the solution is filtered, washed with 1.5 liters of hot water, and dried over P_3O_5 in vacuum at temperatures below about 100°C.

Careful dehydration of γ -MnO(OH) (vacuum, 250 °C) yields γ -Mn₂O₃, γ -MnO(OH) occurs in pature as manganite.

REFERENCES:

W. Marti. Uber die Oxidation von Manganhydroxyd und über höherwertige Oxyde und Oxydhydrate des Mangans [The Oxidation of Manganese Hydroxide and the Higher Oxides and Hydrated Oxides of Manganese], Thesis, Univ. of Bern, 1944, p. 83;
W. Feitknecht and W. Marti. Helv. Chim. Acta <u>28</u>, 142 (1945);
T. E. Moore, M. Ellis and P. W. Selwood. J. Amer. Chem. Soc. <u>72</u>, 861 (1950); P. Dubois. Ann. Chimte [11] <u>5</u>, 434 (1936);
A. Simon and S. Fehér. Z. Electrochem. <u>38</u>, 137 (1932);
F. Krull, Z. anorg. allg. Chem. <u>208</u>, 134 (1932); K. L. Orr. J. Amer. Chem. Soc. <u>76</u>, 857 (1954).

Monganese (IV) Oxide

MaO,

$\frac{Mn(NO_{2})_{2} \cdot 6 H_{2}O}{257.0} \approx \frac{MnO_{2} + 2 NO_{2} + 8 H_{2}O}{88.9}$

The starting $Mn(NO_3)_2 \cdot 6H_2O$ is decomposed in air by heating to about 190°C; the product is ground to powder, boiled with nitric acid (conc. HNO₃ diluted 1:6) and heated in air to 450-500°C. The x-ray pattern of the product clearly shows the lines of pyrolusite (β -MnO₂). At atmospheric pressure, oxygen begins to split off above 530°C in air, and above 565°C in oxygen.

Alternate methods: a) From MnCl₂ and $(NH_{2}S_{2}O_{B}$ in aqueous solution (A. Simon and F. Fehér, Z. Elektrochem. <u>38</u>, 137 (1942)].

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b) From NH₄MnO₄ and NH₃ in aqueous solution (A. Harzer, German Patent 713,904, Class 12, Group 3, as well as the references cited below).

c) From Mn₂O₇ [P. Dubois, Ann. Chimie [11] <u>5</u>, 411 (1936);
A. Simon and F. Fehér, Kolloid-Z. <u>54</u>, 50 (1931); A. Simon and
F. Fehér, Z. Elektrochem. <u>38</u>, 137 (1932)].

SYNONYM:

Manganese dioxide.

REFERENCES:

C. Drücker and R. Hüttner. Z. phys. Chem. <u>131</u>, 263 (1928); O. Glemser. Ber. dtsch. chem. Ges. <u>72</u>, 1879 (1939); F. Krüll, Z. anorg. allg. Chem. <u>208</u>, 134 (1932); W. Marti, Thesis, Univ. of Bern, 1944; T. E. Moore, M. Ellis and P. W. Selwood, J. Amer. Chem. Soc. <u>72</u>, 863 (1950); G. Butler and H. R. Thirsk, J. Electrochem. Soc. <u>100</u>, 297 (1953); G. Gattow and O. Glemser, Z. anorg. allg. Chem. <u>309</u>, 121 (1961).

Manganese (VII) Oxide

MagO₇

 $\begin{array}{l} 2 \text{ KMnO}_4 + 2 \text{ } \text{ } \text{H}_2 \text{SO}_4 = 2 \text{ } \text{KHSO}_4 + \text{ } \text{Mn}_2 \text{O}_7 + \text{H}_2 \text{O} \\ 316.1 & 196.2 & 272.3 & 221.9 \end{array}$

Concentrated H_3SO_4 (15 ml., d 1.84) is placed in a dry porcellain mortar precleaned with chromosulfuric acid; then 23 g. of KMnO₄ is carefully added over a period of 10-15 minutes, while constantly stirring with a pestle. To obtain the desired result, the following precautions must be observed: only very pure KMnO₄ crystals, free of dust and organic substances (preferably Merck A.R. quality; do not reduce the crystals to powder), can be used. The reaction slurry should be left standing overnight in a dry spot, protected against dust. Porous pyrolusite is formed during this time, and the Mn₂O₇ oil is very gently kneaded out from it. Proper safety measures must be observed during the preparation and further workup of the material, since it often explodes for no apparent reason (an asbestos face shield with safety glasses and heavy leather gloves should be worn and one should work behind heavy glass plate and a fine wire screen).

Yield: 10 g. (62%). The product is entirely free of K+ and SO2-.

SYNONYMS:

Manganese heptoxide, permanganic acid anhydride.

PROPERTIES:

An oil with green metallic luster in reflected light; dark red in transmitted light; specific odor. M.p. 5.9°C; d2° 2.396; heat

of formation: -177.4 koal (20°C); dissociation at approx. 55°C, detonation at 95°C. In vacuum, rapid and explosive dissociation above 10°C. Forms $a - Mn_2O_3$ during explosive decomposition, $y-MnO_2$ during slow dissociation. Soluble in conc. H_2SO_4 and H_3PO_4 with an olive green color. Hygroscopic; dissociates slowly in humid air to MnO_3 , liberating O_3 -containing O_2 and, occasionally, a red mist of $HMnO_4$. Stable under refrigeration (-10°C) ally, a red mist of $HMnO_4$. Stable under refrigeration (-10°C) with most organic compounds; attacks acetic acid, acetic anhydride and CCl₄ even below room temperature. Dangerous compound ! The impact sensitivity of Mn_3O_7 is equal to that of mercuric fulminate.

REFERENCES:

J. M. Lovén. Ber. dtsch. chem. Ges. <u>25</u>, Ref. 620 (1892); A. Simon and F. Fehér. Z. Elektrochem. <u>38</u>, 138 (1932); O. Glemser and H. Schröder, Z. anorg. allg. Chem. <u>271</u>, 294 (1953).

Sodium Monganate (V)

Na,MpO₄ · 0.25 NaOH · 12 H₂O

 $\begin{array}{rl} 2 \text{ KMnO}_{4} + 2 \text{ Na}_{5}\text{SO}_{3} \cdot 7 \text{ H}_{2}\text{O} + 6 \text{ NaOH} + 4 \text{ H}_{2}\text{O} \\ 316.1 & 504.3 & 240.0 & 72.1 \\ & = 2 \text{ Na}_{5}\text{MnO}_{4} \cdot 10 \text{ H}_{2}\text{O} + 2 \text{ Na}_{2}\text{SO}_{4} + 2 \text{ KOH} \\ & 736.2 & 284.1 & 112.2 \end{array}$

A solution of 2 g. of very fine $KMnO_4$ powder in 50 ml. of 28% sodium hydroxide is triturated in a small Erlenmeyer flask with 3.5 g. of finely divided $Na_3SO_3 + 7H_2O$; the flask stands in an ice bath. The trituration requires about 10 minutes, that is, until a light-blue crystalline slurry is obtained. This is then transported by vacuum onto an ice-cooled glass filter, and the product washed thoroughly with 28% sodium hydroxide at 0°C. The wet preparation is rapidly spread in a thin layer on fresh clay and stored at 0°C in an evacuated desiccator (no drying agent). The salt has the stoichiometric composition and contains, in addition to the hydroxide, about 0.4% SO₃; the preparative procedure should be designed to keep contamination by silicates or aluminates to a minimum.

PROPERTIES:

Formula weight 368.1. The salt, in the form of well-crystallized sky-blue rods, remains stable at 0° C if kept free of H₂O 一般の理

and CO₂. Solubility in 28% NaOH at 0°C is equivalent to 0.06% Mn_2O_5 . A solution of the salt in 50% potassium hydroxide turns grassy green upon heating or dilution; simultaneously, MnO₂ is precipitated according to the equation:

$$2 \operatorname{Na_{3}MnO_{4}} + 2 \operatorname{H_{2}O} = \operatorname{Na_{4}MnO_{4}} + \operatorname{MnO_{4}} + 4 \operatorname{NaOH}.$$

REFERENCES:

H. Lux. Z. Naturforschg. <u>1</u>, 281 (1946) and unpublished work. The preparation of the sulfate-free product is described by R. Scholder, D. Fischer and H. Waterstradt, Z. anorg. allg. Chem. <u>277</u>, 236 (1954).

Potassium Manganate (VI)

K₂MnO₄

$2 \text{ KMnO}_4 + 2 \text{ KOH} = 2 \text{ K}_6 \text{MnO}_4 + \frac{1}{2} \text{ O}_2 + \frac{1}{2} \text{ O}_2 + \frac{1}{2} \text{ O}_2$ 316.1 112.2 394.2

A solution of 30 g. of KOH in 50 ml. of water is prepared; 10 g. of KMnO₄ is added and the mixture is bolled in an open 250-ml. Erlenmeyer flask until a pure green solution is obtained. The water lost by evaporation is then replaced and the flask set in ice. The precipitated black-green crystals, which show a purplish luster, are collected on a Pyrex glass filter, washed (high suction) with some 1 N potassium hydroxide, and dried over P_2O_5 . The salt can be recrystallized by dissolving in dil. potassium hydroxide and evaporating in vacuum.

PROPERTIES:

Formula weight 197.1. Solubility (20°C) in 2N potassium hydroxide 224.7 g./liter, in 10N potassium hydroxide 3.15 g./liter.

REFERENCES;

K. A. Jensen and W. Klemm. Z. anorg. allg. Chem. <u>237</u>, 47 (1938); R. Luboldt. J. prakt. Chem. <u>77</u>, 315 (1859). Preparation of an especially pure, KOH-free product is described by R. Scholder and H. Waterstradt, Z. anorg. allg. Chem. <u>237</u>, 122 (1954).

Barium Manganate (Vil)

Ba(MnO₄)_t

A solution of 100 g. of KMnO₄ and 100 g. of Ba(NO₃)₂ in 1.5 liters of boiling water is prepared and treated with 20 g. of Ba(OH)₂. $8H_2O$. The solution is heated on a water bath with frequent agitation until the evolution of O₂ largely ceases, whereupon another 20 g. of Ba(OH)₂ · $8H_2O$ is added and the water lost by evaporation replaced. The procedure is continued until the liquid becomes colorless. When the sparingly soluble BaMnO₄ settles out (together with some MnO₂ and BaCO₃), the liquid is decanted, the precipitate washed repeatedly with several liters of boiling water, boiled with a dilute solution of Ba(OH)₂, and rewashed thoroughly with bolling water.

The precipitate is then suspended in 1 liter of water and completely decomposed by introducing simultaneously CO_2 and superheated steam. This takes a few hours. The solution is left to settle; the liquor is suction-filtered through glass and concentrated until the almost black crystals appear upon cooling. The yield is 65-80 g. (80 to 100% of theory). Permanganates of all types of metals can be prepared by reacting the $Ba(MnO_4)_2$ with an equivalent quantity of sulfate.

SYNONYM:

Barium permanganate.

PROPERTIES:

Sparingly soluble in water; d 3.77.

REFERENCES;

W. Muthmann. Ber. dtsoh. chem. Ges. <u>26</u>, 1017(1893); H. G. Grimm,
 C. Peters and H. Wolff. Z. anorg. allg. Chem. <u>236</u>, 73 (1938).

25. MANGANESE

1463

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Silver Manganate (VII)

AgMnO₄

 $KMnO_4 + AgNO_5 = AgMnO_4 + KNO_5$ 158.0 189.9 926.8 101.3

A hot (80°C) solution of 5 g. of AgNO₃ in 100 ml. of water is added to a hot (80°C) solution of 4.66 g. of KMnO₄ in 300 ml, of water to which a drop of conc. nitric acid has been added. The mixture is permitted to cool. Since the product still contains some K, it is recrystallized from water by slow cooling from 80°C.

The black, lustrous, needle-shaped crystals tend to decompose on prolonged storage. Because of its limited sclubility, this salt is less suitable as a raw material for other permanganates than $Ba(MnO_4)_2$.

SYNONYM:

Silver permanganate.

PROPERTIES:

Solubility (room temperature) 9 g./liter H_0O ; d 4.49, Crystal structure: type $H0_{\rm e}$.

REFERENCE:

W. Büssem and K. Herrmann, Z. Kristallogr, A 74, 459 (1930).

BaSO,-KMnO, Solid Solution

The solid solution (mixed crystals), described and examined in detail by Grimm and Wagner, is prepared simply by mixing together solutions of $Ba(NO_3)_2$ and K_3SO_4 , both containing a high percentage of KMnO₄. As an example, the following conditions were found to be suitable:

A solution of 1.31 g. (5 mmoles) of $Ba(NO_3)_2$ and 50 g. of KMnO₄ in 1 liter of water is prepared; similarly, 0.87 g. (5 mmoles) of K_3SO_4 and 50 g. of KMnO₄ are dissolved in 1 liter of water. Heating is required in both cases. The clear solutions—suction-filtered through glass, if necessary—are brought to 50°C, added together, and allowed to stand for a short time at 50°C. The crystals are then separated by suction filtration.

Washing the mixed crystals with acetone until the wash liquid turns a light rose results in a product with a KMnO, content of 25-30 mole %; treatment with water, however, readily decomposes

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the crystals. A more stable solid solution, containing 6-8 mole %KMnO₄, is obtained by washing with water at 50°C, rinsing with a SO₂ solution, and repeating the washing. It is possible to boil the rose to purple powder with solutions of SO₂ or other reducing agents without a change in composition. The surface of the compound is decomposed on prolonged exposure to sunlight (with precipitation of manganese oxides).

REFERENCES:

H. G. Grimm and G. Wagner, Z. phys. Chem. <u>132</u>, 135 (1928); see also A. Benrath and H. Schackmann, Z. anorg, allg. Chem. <u>218</u>, 139 (1934).

Potassium Manganese (III) Chloride

K₂MnCl₅

In the method of Weinland and Dinkelacker the compound is prepared as follows: 5 g. of KMnO₄ powder is added (constant shaking) to 50 ml. of approx. 40% HCl (d 1.19). The initial fine, brown precipitate is slowly dissolved on frequent shaking, while copious quantities of Cl₃ are being evolved. The solution is left standing for two hours, then decanted from any black K₃MnCl₆ that may have precipitated, and conc. aqueous KCl is added dropwise to the deep dark-red to brown solution (constant agitation) until the liquid becomes nearly colorless. The crystalline, brownish K₂MnCl₅ precipitate is filtered off by suction and dried over KOR.

REFERENCES:

R. F. Weinland and P. Dinkelacker, Z. anorg. allg. Chem. <u>60</u>, 173 (1998). For the hydrate K₂MnCl₅ • H₂O, see C. E. Rice. J. Chem. Soc, (London) <u>73</u>, 260 (1898).

Potassium Hexachloromonganate (IV)

K_tMaCl₄

 $\frac{\text{Ca}(\text{M}_{12}\text{O}_{4})_{2} + 16 \text{ HCl} + 4 \text{ KCl} = 2 \text{ K}_{2}\text{M}_{12}\text{Cl}_{4} + \text{Ca}\text{Cl}_{2} + 6 \text{ H}_{2}\text{O} + 3 \text{ Cl}_{2}}{277.9} \frac{583.5}{298.2} \frac{298.2}{691.7} \frac{691.7}{111.0}$

is the method of Weinland and Dinkelacker, 5.0 g. of $Ca(MnO_4)_3$ is added (constant agitation) to 50 ml. of 40% hydrochloric

25. MANGANESE

acid cooled with an ice-salt mixture. A solution of 2 g. of KCl in 8 ml. of water is added simultaneously in drops. The almost black, crystalline precipitate is rapidly separated by suction filtration and dried for a short time on a clay plate over conc. $H_{z}SO_{4}$.

PROPERTIES:

Formula weight 345.9. Small, translucent, deep dark-red crystals; liberates Cl₂ continuously even in dry air.

REFERENCE:

R. F. Weinland and P. Dinkelacker. Z. anorg. allg. Chem. <u>60</u>, 173 (1908).

Manganese (II) Sulfide

MnS

a-MaS, GREEN, CUBIC

This modification, which has been thoroughly studied by x-ray techniques, is obtained via the method of Classen.

A boiling solution of about 10 g. of $MnCl_2 \cdot 4H_2O$ in 500 ml, of water containing a small quantity of $K_3C_3O_4$ is reacted with an excess of a 50% NH_3 solution and saturated at its boiling point with H_2S . Upon further heating, the initial flesh-colored MnS precipitate is rapidly converted to the stable dark-green α modification. To remove any coprecipitated sulfur, the sulfide is boiled three times with a dil. solution of freshly prepared, coloriess $(NH_4)_2S$ and, after filtering, washed successively with H_2S -containing water, alcohol and ether. It is dried in an oil-pump vacuum at 120°C.

The dry preparation of α -MnS(alahandite) is described by H. Haraldsen and W. Klemm, Z. anorg. alig. Chem. <u>220</u>, 271 (1936); for the synthesis of MnS₂ (hauerite), see W. Biltz and F. Wiechmann, ibid. 228, 271 (1936).

PROPERTIES:

Formula weight 86.99. M. p. 1610°C; d 3.99. Crystal structure: B1 (rock salt) type.

1466

REFERENCES:

 H. Schnaase. Z. phys. Chem. (B) <u>20</u>, 89 (1933); F. Mehmed and H. Haraldsen. Z. anorg. allg. Chem. <u>235</u>, 194(1938); A. Classen, Z. analyt. Chem. <u>16</u>, 319 (1877).

SAMS, RED. CUBIC

In the method of Schnaase, the γ -modification is obtained by introducing H₂S into a cold solution of 50 g. of Mn(CH₃COO)₂. 4 H₂O in 300 ml. of water. After some time, most of the sulfide settles on the bottom as a reddish-brown precipitate, while another fraction adheres to the glass wall as a beautiful, miniumred scale. The precipitate is washed with H₂S-saturated water (the preferred washing method is decantation), filtered off with suction while H₂S is being passed over it, washed again with alcohol and ether, and dried in an oil-pump vacuum at 80°C.

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Crystal structure: B3 (sphalerite) type.

REFERENCES:

H. Schnaase, Z. phys. Chem. (B) <u>20</u>, 89 (1933); F. Mehmed and H. Haraldsen, Z. anorg, alig. Chem. <u>235</u>, 194(1938).

y-MnS, RED, BEXAGONAL

Schnaase prepares the γ -modification by first dissolving 20 g. of analytically pure MnCla · 4 H₂O and some NH₄Cl in 500 ml. of boiled water through which a stream of O2-free N2 is being bubbled. Then H₂S is introduced at the boiling temperature and Mn(OH)₂ is precipitated out with a slight excess of concentrated NH₃ solution. The precipitate is initially white, gradually turns a light pink upon further contact with H₂S, and finally assumes the color of red meat, while the sulfide forming the surface layer is first orange yellow and later turns vermilion red. After settling, the precipitate is washed twice by decanting with H₂S-saturated water and boiled for two days in a 10% NHa solution while HaS is bubbled through. Finally it is washed by decanting several times with HaS-saturated water, filtered off in the absence of air while under a N₂ stream, washed with alcohol and ether, and dried in an oil-pump vacuum at 80°C. Any coprecipitated sulfur is removed by extraction with bolling CS, under nitrogen,

Crystal structure: B4 (wurtzite) type.

The conversion of the two dry, metastable red MnS modifications to the stable form starts at 200°C. The rate is appreciable, and is higher at 300°C. The red modifications also differ from the α -form in their magnetic behavior. REFERENCES:

H. Schnaase. Z. phys. Chem. (B) <u>20</u>, 89 (1933); F. Mehmed and H. Haraldsen. Z. anorg. allg. Chem. <u>235</u>, 194 (1938).

Manganese (III) Sulfate

Mn₂(SO₄)₁

 $\frac{2 \text{ KMnO}_4 + 4 \text{ H}_2 \text{SO}_4}{316.1} = \frac{\text{Mn}_2(\text{SO}_4)_3}{392.3} + \frac{\text{K}_2 \text{SO}_4}{398.0} + \frac{4 \text{ H}_2 \text{O}_4}{174.3} + 2 \text{ O}_2$

In the method of Domange, the crystalline Mn_d(SO_d)_s is prepared by introducing 20 g. of KMnO4 powder into 100 ml. of H-SO4 (d 1.84) contained in a porcelain crucible (agitation); the mixture is carefully heated for 10 minutes at 60°C while stirring vigorously, whereby vapors of the explosive Mn₂O7 are removed. The solution is then heated to 70°C (or at most to 75°C) with continued very vigorous agitation and accurate temperature control (thermometer). Vigorous evolution of Og takes place while the liquid turns brown and becomes clouded, with a tendency for a spontaneous rise in temperature, so that the danger of an explosion persists. After about 15 minutes, with most of the reaction completed, the danger of an explosion passes. The mixture is now slowly (10 minutes) brought to 140°C with continued stirring and is finally raised to 200°C (in 15 minutes). Following slow cooling, the solution is washed twice by decantation with H₂SO₄ (d 1.84) to remove the K₂SO₄. The product is collected on a glass filter and placed on a clay plate. The latter is placed for three to four days in a desiccator containing P₂O₅. The H₂SO₄ may be completely removed by heating the preparation, together with a receiver cooled to -80 °C, for about three hours at 200°C and high vacuum: the salt itself does not begin to decompose until about 300°C.

PROPERTIES:

Extremely hygroscopic sait consisting of small, dark-green needles. Soluble in 75.25% wt. % or more H_2SO_4 without alteration; a brown salt of composition $Mn_2(SO_4)_3 \cdot H_2SO_4 \cdot 6H_3O$ crystallizes out from dilute (preferably 70%) sulfuric acid [A.R.J.P. Ubbelohde, J. Chem. Soc. (London) <u>1935</u>, 1605]. Sulfuric acid in concentrations lower than 52% produces hydrolysis.

REFERENCE:

L. Domange, Bull. Soc. Chim. France [5] 4, 594 (1937).

Cesium Manganese (III) Sulfate CsMn(SO4),+12H3O

 $\begin{array}{rcl} Cs_{s}SO_{4} & \leftarrow & 2 \operatorname{Mn}(CH_{s}COO)_{s} \cdot 2 \operatorname{H}_{2}O & + & 3 \operatorname{H}_{2}SO_{4} \\ c_{1} \circ c_{1} \circ c_{2} & & 53.6 \\ & & & & 2 \operatorname{Cs}Mn(SO_{4})_{2} \cdot 12 \operatorname{H}_{2}O & \leftarrow & 6 \operatorname{CH}_{3}COOH \\ & & & & & & \\ & & & & & 119.2 & & 36.0 \end{array}$

In Christensen's method, 5.3 g. (0.01 mole) of $Mn(CH_3COO)_3$. 2H₂O is dissolved in sulfuric acid (conc. H₃SO₄ diluted 1:3), starting at room temperature. Then, a solution of 3.6 g. (0.01 mole) of Cs₂SO₄ in 10 ml. of sulfuric acid of the same concentration is added; the solution is first cooled to -25°C in order to accelerate the precipitation and then left to stand for a long time at -5°C. The alum crystals are filtered off with suction and stored in a hermetically sealed bottle.

SYNONYM:

Cesium manganese alum.

PROPERTIES:

Coral-red crystalline powder. Melts at 40°C in the water of hydration; however, turns brownish black slightly above room temperature. The hydrated Mn_2O_3 is precipitated upon addition of water. The corresponding Rb alum melts at room temperature.

REFERENCES:

O. T. Christensen, Z. anorg. Chem. 27, 329 (1901); H. Bommer. Z. anorg, allg. Chem. 246, 281 (1941).

Manganese Nitride

 Mn_4N

The nitride is prepared from very reactive sublimed manganese. The metal is heated in an apparatus which permits the continuous measurement of the amount of N_2 used in the reaction. A completely O_2 -free nitrogen is used, under a pressure of ~100 mm. and a temperature of 690°C. The reaction is continued until a constant final pressure is obtained (12-24 hours).

The product corresponds quite exactly to the formula $Mn_{\bullet}N$ (6.0% N; ϵ -phase according to Hägg) and is strongly ferromagnetic. Below 400°C the homogeneous region of the phase extends from about 6.0 to 6.5% N.

2

REFERENCES:

[1] Zwicker. Z. Metallkunde <u>42</u>, 277 (1951); R. Schenk and A. Kortengräber. Z. anorg. allg. Chem. <u>210</u>, 273 (1933); G. Hägg. Z. phys. Chem. <u>B4</u>, 346 (1929); L. F. Bates, R. E. Gibbs and D. V. Reddi Pantulu, Proc. Phys. Soc. <u>48</u>, 665 (1936); see also H. Nowotny. Z. Elektrochem. <u>49</u>, 245 (1943).

For Mn₄P, Mn₂P, etc., see W. Blitz and F. Wiechmann, Z. anorg. ailg. Chem. <u>234</u>, 117 (1937).

Manganese (III) Acetate

Mn(CH₂COO)₂, Mn(CH₂COO)₂ · 2 H₂O

Mn(CH₂COO), 2 H₁O

 $4 \operatorname{Mn}(\operatorname{CH}_{3}\operatorname{COO})_{2} \cdot 4 \operatorname{H}_{2}\operatorname{O} + \operatorname{KMnO}_{4} + 8 \operatorname{CH}_{3}\operatorname{COOH}$ $\frac{3}{10^{2}} \quad 98.0 \quad 15.8 \quad 48.0$ $= 5 \operatorname{Mn}(\operatorname{CH}_{3}\operatorname{COO})_{3} \cdot 2 \operatorname{H}_{2}\operatorname{O} + \operatorname{CH}_{3}\operatorname{COOK} + 10 \operatorname{H}_{2}\operatorname{O}$ $134.0 \quad 9.8 \quad 16.0$

in the method of Christensen, the salt is obtained in the following manner: 19.6 g. (80 mmoles) of Mn(CH3COO)₂ · 2H₂O powder is added to 200 ml. of glacial acetic acid at the boiling temperature of the latter, and is stirred until completely dissolved. Then, KMnO, powder (3.1 g. = 20 mmoles) is gradually added and the mixture heated for a short time with constant agitation. After cooling, 3 ml. of water is added to the darkbrown solution; the mixture is allowed to stand overnight. If the quantity of precipitate is too small, another 3 ml. of water is added and the solution stirred. The formation of orystallization nuclei is promoted by frequent rubbing of the container walls with a glass rod. As a rule, copious crystallization occurs within about one hour. If necessary, the solution is allowed to stand for a few more days (frequent agitation) until the mother liquor is almost colorless. The salt is then filtered off with suction. washed with some glacial acetic acid and recrystallized. The last procedure consists in dissolving 30 g. of salt in 200 ml. of glacial acetic acid (heating), filtering off and working up further in the manner described above. Finally, the salt is dried over CaO,

PROPERTIES:

The cinnamon-brown crystals of a silky luster are immediately decomposed by cold water (hydration). s,

- 1 Cha

b activity the compound is likely to be a complex sait with three nuclei, of the following structure: $[Mn_3(CH_3COO)_8(H_2O)_2, (CH_3COO)_3 - 4 H_3O]$.

REFERENCES:

O. T. Christensen, Z. anorg. Chem. <u>27</u>, 325 (1901); R. F. Weinland and G. Fischer. Z. anorg. allg. Chem. <u>120</u>, 161 (1921).

Ma(CH₄COO)₁

$$\frac{2 \operatorname{Mn}(\operatorname{NO}_{3})_{x} \cdot 6 \operatorname{H}_{2} O}{57.4} + \frac{15 (\operatorname{CH}_{3} \operatorname{CO})_{z} O}{53.9}$$

$$= 2 \operatorname{Mn}(\operatorname{CH}_{3} \operatorname{COO})_{x} + 4 \operatorname{NO}_{3} + \frac{1}{2} \operatorname{O}_{3} + 24 \operatorname{CH}_{3} \operatorname{COOH}_{46.4}$$

$$= 46.4 \qquad 144.1$$

Chretien and Varga obtain the sait from $Mn(NO_3)_2$ and acetic anhydride. A mixture of 20 g, of $Mn(NO_3)_2 - 6 H_2O$ and 80 g, of acetic anhydride is heated slightly (shaking) until the vigorous, strongly exothermic reaction evolving large amounts of gas is well under way. When the reaction is completed, the homogeneous, oily liquid is cooled; the anhydrous acetate precipitates out as a brown, crystalline powder. The latter is collected on a glass filter, washed first with acetic anhydride and then with some ether to remove the odor of acetic acid, and stored in a closed container (anhydrous conditions). The yield, based on manganese, is 85%.

REFERENCE:

A. Chretien and G. Varga, Bull. Soc. Chim. France [5] <u>3</u>, 2387 (1936).

Potassium Trioxalatamanganate (III)

Ka[Mn(CrO4)2] · 3 H2O

 $\begin{array}{r} \text{KMnO}_{s} + 5 \text{H}_{s}\text{C}_{s}\text{O}_{4} \cdot 2 \text{H}_{2}\text{O} + \text{K}_{s}\text{CO}_{3} = \text{K}_{3}[\text{Mn}(\text{C}_{2}\text{O}_{4})_{3}] \cdot 3 \text{H}_{2}\text{O} + 12 \text{H}_{2}\text{O} \\ 159.0 & 630.4 & 138.2 & 490.3 \\ & + 5 \text{CO}_{2} \end{array}$

Cartiedge and Ericks prepare the ferric ion-free compound (which is very sensitive to light) from analytically pure KMnO₄ according to the equation presented above. A solution of 31.5 g. (0.25 moles) of $H_2C_2O_4 \cdot 2H_3O$ in 200 ml. of water is heated in

a,

25. MANGANESE

a 500-ml. beaker to 70-75°C; then, 6.32 g. (0.04 moles) of KMAG₄ powder is added little by little (constant agitation) and as soon as the solution turns colorless, 6.9 g. (0.05 moles) of K_2CO_3 is introduced in a similar manner. The mixture is cooled to 4-5°C (frequent stirring) and diluted with 150 ml. of 0-1°C water.

In all of the following operations light must be excluded as much as possible. The oxidation to Mn^{3+} is effected through the gradual addition of 1.58 g. (0.01 mole) of KMnO, powder; the solution is then stirred for about 10 minutes at 0 to 2°C. The intense cherry-red liquid is then suction-filtered through a glass filter precooled to 0°C, and is collected in a similarly cooled beaker. Next, the solution is reacted with half its volume of ice-cold alcohol and left to crystallize for two hours in an ice-sait mixture.

The precipitate is collected on a precooled glass filter, washed four times with 25 ml. of 50 vol. % alcohol, then with 95% alcohol, absolute alcohol and finally (three times) with ether; all of the wash liquids must be ice cold. After filtration with suction, the deep reddish-purple crystals are spread in a thin layer and exposed to air for a few hours; they are stored in brown bottles. The yield is ~50%.

PROPERTIES:

Very pure product can be stored for a long time at 20°C in the absence of air; stable for an almost unlimited time at -6°C. Readily soluble in water: concentrated solutions are deep reddishbrown; very dilute or acidified solutions are yellowish-brown. The color change is due to the shift of the instantly established equilibrium:

$$[\operatorname{Mn}(\operatorname{C}_{*}\operatorname{O}_{4})_{*}]^{-*} + 2\operatorname{H}_{*}\operatorname{O} \rightarrow [\operatorname{Mn}(\operatorname{C}_{*}\operatorname{O}_{4})_{*}(\operatorname{H}_{*}\operatorname{O})_{*}]^{-1} + \operatorname{C}_{2}\operatorname{O}_{4}^{-*}$$

The salt is a normal complex.

REFERENCE;

G. H. Cartledge and W. P. Ericks. J. Amer. Chem. Soc. <u>58</u>, 2061 (1936).

Potassium Dioxalatedihydroxomanganate (IV)

$K_{t}[Mn(C_{t}O_{t})_{t}(OH)_{t}] \cdot 2 H_{t}O$

 $\frac{\text{KMnO}_4 + 3 \text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O} + \frac{1}{2} \text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}}{158.0 378.2 92.1}$

 $= K_{s}[Mn(C_{s}O_{i})_{t}(OH)_{s}] \cdot 2H_{t}O + 3CO_{s} + 6\%_{s}H_{s}O.$

379.2

This compound, discovered by Cartledge, and Ericks, is press, pared in a manner quite similar to that of $K_3(Mn(C_3O_4)_2)$. Thus,

1474

17.64 g. (0.14 moles) of $H_2C_2O_4 \cdot 2H_2O$ is dissolved in 250 ml. of water and the solution is cooled to 0°C; then, 6.32 g. (0.04 moles) of KMnO₄ powder and 4.78 g. (0.026 moles) of $K_2C_2O_4 \cdot H_2O$ are added with constant agitation. The mixture is stirred vigorously for about 20 minutes; the temperature should rise gradually to 7°C during this time. As soon as CO_2 begins to evolve at this temperature, the dark-green solution is rapidly cooled to 0°C in an efficient cooling mixture (swirling necessary) and is quickly suction-filtered through a Büchner funnel (filter paper). The filtrate is immediately placed in a cooling mixture and reacted with 100 ml. of alcohol in small portions at 0°C; the complex salt is thus precipitated as a very fine, crystalline powder. The latter is rapidly filtered off, washed successively with ice-cold 50% alcohol, 95% alcohol, absolute alcohol and ether, and stored at 0°C.

The salt can be recrystallized at 0°C: the powder is dissolved in 25 times its volume of cold 0.1 M oxalic acid, filtered rapidly at 0°C, the solution diluted with 1/6 its volume of ice-cold 95% alcohol and placed in a cooling mixture for crystallization. It is best to prepare the salt in a cold room, otherwise proper cooling becomes cumbersome.

PROPERTIES:

Green, crystalline salt; not homogeneous; consists of green and orange rods (probably the cis and trans forms). Rapidly decomposed at room temperature, particularly when exposed to light; remains stable for a few weeks at -6° C if light is excluded. Solutions are initially green, but rapidly turn brown and become clouded; solutions containing some oxalic acid kept at 0°C remain clear for some time.

REFERENCE:

G. H. Cartledge and W. P. Ericks, J. Amer. Chem. Soc. <u>58</u>, 2061 (1936).

Potassium Hexacyanomanganate (I)

K₄Mn(CN)₄

 $3 \operatorname{Na_{4}Mn}(CN)_{6} + AI + 4 \operatorname{NaOH} = 3 \operatorname{Na_{5}Mn}(CN)_{6} + \operatorname{NaAI}(OH)_{4}$ $\sum_{i=1}^{3} 90.9 \qquad 2.7 \qquad 18.0 \qquad 97.8$ $3 \operatorname{Na_{6}Mn}(CN)_{6} + 15 \operatorname{K^{+}} = 3 \operatorname{K_{6}Mn}(CN)_{6} + 15 \operatorname{Na^{+}}$ $97.3 \qquad 121.9$

According to Manchot and Gail, the salt is best prepared by marting with $Na_4Mn(CN)_8 \cdot xH_2O$ (see p. 1473). Thus, 10 g, of the

25. MANGANESE

salt is dissolved in 150 ml. of 2% sodium hydroxide (Erlenmeyer flask), the air being kept out during this operation by a stream of Ha. Then, 8 g. of Al granules is added little by little, but rather rapidly (2 minutes); the sparingly soluble Na_Mn[Mn(CN)s] should not precipitate in the process. After about five minutes the solution becomes intensely yellow-brown; it is then rapidly suctionfiltered through a Pyrex filter of small pore size. The filtrate is allowed to flow into 150 ml. of a solution containing 15 g. of KOH and 30 g. of KCN and saturated with KCl. The desired compound is thereby precipitated as a white, crystalline powder, only soaringly soluble in water; any Mn⁺⁺present remains in solution. The salt is separated by rapid filtration through a Pyrex filter and thoroughly washed, first with 200 ml. of 10% potassium hydroxide, then with 100 ml. of 20% KCN solution, and finally with about 700 ml. of boiled, ice-cold water (until the filtrate is completely colorless).

PROPERTIES:

The potassium salt obtained in the above manner is slowly oxidized in moist air, turning brown. The sodium salt solution is rapidly discolored in air; H_2 is liberated on boiling but there is a slow evolution even at room temperature.

REFERENCES:

W. Manchot and H. Gall, Ber. dtsch. chem. Ges. <u>61</u>, 1135 (1928).
 Preparation by means of a sodium amalgam is described by
 W. D. Treadwell and W. E. Raths. Helv. Chim. Acta <u>35</u>, 22?7 (1952).

Potassium Hexacyanomanganate (II)

K₄Mn(CN)₁ · 3 H₂O

 $\begin{array}{rcl} M_{\rm III} {\rm CO}_{\rm S} &+ \ 6 \ {\rm KCN} \ + \ 3 \ {\rm H_{\rm g}O} \ = \ {\rm K_4Mn} ({\rm CN})_{\rm g} \cdot 3 \ {\rm H_{\rm g}O} \ + \ {\rm K_8 CO_{\rm g}}^{-1} \\ 114.9 & 390.6 & 54.1 & 421.4 & 138.2 \end{array}$

A paste of 20 g. of freshly precipitated $MnCO_3$ (see the next preparation) is placed in a flask from which the air has been displaced with N₂ and heated on a water bath to 70-80°C. A solution of 80 g. of KCN in 100 ml. of water is added slowly in droit, and the mixture is maintained at this temperature for an additional half hour (occasional swirling). The small residue of undissolved $MnCO_3$ is removed by rapid filtration of the bot solution, air being excluded as completely as possible. The bluespurple crystals which precipitate from the yellow solution on ecciing are separated by suction filtration, washed with alcohes, and dried in a N₂ stream at room temperature. Alternate method: Readily prepared from $Mn(CH_3CO)_2$ and KCN. The sodium compound $Na_4Mn(CN)_6$ is prepared in a completely similar manner; it is more soluble than the potassium salt.

SYNONYM:

Potassium manganese (II) cyanide.

PROPERTIES:

Soluble without being altered only in solutions which have a KCN concentration higher than 1.5 N; at lesser CN concentrations, the greenish $K_2Mn[Mn(CN)_6]$ is precipitated. The crystals effloresce in sir with partial oxidation.

REFERENCES:

G. Grube and W. Brause. Ber. dtsch. Chem. Ges. <u>60</u>, 2273 (1927);
 J. Meyer. Z. anorg. allg. Chem. <u>81</u>, 390 (1913); P. Straus,
 Z. anorg. Chem. <u>9</u>, 6 (1895).

Potassium Hexacyanomanganate (III)

K₁Mn(CN)₄

 $\begin{array}{rl} MnSO_t \cdot H_tO &+ 2\,NaHCO_3 &= MnCO_3 &+ Na_2SO_4 &+ CO_2 &+ 2\,H_tO \\ 189.0 & 168.0 & 114.9 \\ 2\,MnCO_3 &+ 12\,KCN &+ H_tO_T &= 2\,K_xMn(CN)_4 &+ 2\,K_xCO_5 &+ 2\,KOH \\ 229.9 & 781.2 & 34.02 & 656.5 & 276.4 & 112.2 \end{array}$

A fresh precipitate of MnCO₃ is prepared by slowly adding a solution of 50 g, of MnSO₄ \cdot H₂O in 120 ml. water to a solution of 75 g, of NaHCO₃ in 950 ml. of water (20°C, good stirring; caution: the mixture tends to foam). The product is filtered off with suction, washed with a large amount of water, and, while still wet, thoroughly mixed with a solution of 135 g, of KCN in 270 ml. of water, producing a dark-blue solution of K₄Mn(CN)₈. Following cooling to ~15°C, 150 ml. of 3% H₂O₂ is added slowly and with sitrring. The solution is allowed to stand for a few minutes until its color turns deep dark brown. With sufficient cooling no appreciable amount of O₂ is evolved.

The solution is now passed without delay through a suction filter (to remove any small residues of MnO_2 and similar compounds) and allowed to crystallize overnight in a refrigerator. The precipitated crystals (60-70 g., 63-74% yield based on MnSO4)

25. MANGANESE

are filtered off with suction, washed with alcohol and dried the desiccator. An additional crop can be recovered from the mattice liquor by covering it carefully with a layer (roughly the same volume) of alcohol and allowing to stand for several days.

If it is necessary to recrystallize the salt, it is covered with 8-10 times its volume of 10% KCN, rapidly heated on a water with to 45°C (stirring), immediately suction-filtered, cooled with ice and covered with alcohol as described above.

SYNONYM:

Potassium manganese (III) cyanide.

PROPERTIES:

Dark red-brown needles; stable in air; decomposed by water, forming hydrated Mn₂O₃.

REFERENCES:

This procedure was developed in (unpublished) experiments a cooperation with E. Brodkorb; G. Grube and W. Brause. Ber dtsch. chem. Ges. 60, 2273 (1927); J. Meyer. Z. anorg. all Chem. 81, 390 (1913).

4.45

SECTION 26

Rhenium

O. GLEMSER

Rhenium Metal

Prepared by reduction of NH4ReO4 or KReO4 with H2.

I. Fine NH_4ReO_4 powder is slowly heated to 200-250°C in very pure H_2 and held at that temperature for three hours. The temperature is then raised to 500°C and the reduction completed at 1050°C (six hours). The boats and reactor tubes should be porcelain.

If heating rates are too high, part of the product evaporates as the oxide and deposits to form a mirror on the cooler parts of the tube.

II. KReO₄. In a silver boat, is reduced in very pure H_3 at 500°C. The product is extracted with H_3O containing a small amount of HCl, dried and again reduced with H_3 in a porcelain boat at 1000°C.

PROPERTIES:

Atomic weight 186.22. Gray metal powder; the solid has a platinum-like luster. M.p. 3170°C; d 20.35; Brinell hardness 250. Readily soluble in nitric acid and slowly in sulfuric acid. Crystal structure: A 3 type.

REFERENCES:

I. W. Biltz and G. A. Lehrer. Nachr. Gött. Ges. 1931, 193.

II. W. Biltz. Z. Elektrochem. <u>37</u>, 498 (1931); W. Geilmann, Private communication.

Rhenium (III) Chloride

ReCi,

 $Re + 3/_2 Cl_2 = ReCl_3$ 188.2 33.0 f. 292.6

Elass tabe joined to a receiver manifold with seven bulbs

RHENIUM

sealed on. The air is displaced with oxygen-free H_2 and the Rethen heated in a stream of Cl_2 . The raw sublimate is collected in the first bulb; it is resublimed into the second bulb under oxygen-free, dry N_2 (the less volatile ReCl₃ remains in the first bulb). The operation is repeated using the next set of bulbs, etc... The ReCl₃ fractions are then collected from all the bulbs and resublimed at 2-3 mm. and 500~550°C.

ANALYSIS:

Oxidation to ReO_4^- with sodium hydroxide + H_2O_2 ; the ReO_4^- ion is precipitated as nitron hydrogen perrhenate.

18

PROPERTIES:

Dark purple-red crystals. Bimolecular under normal conditions (Re_3Cl_6). Converted in moist air to $\text{ReCl} \cdot 2\text{H}_3\text{O}$ (2-3 hours); the water of hydration is readily removed by heating to 100°C in vacuum over P_3O_5 . Soluble in water with a deep dark-red color; the solution turns cloudy after several hours because of hydrolysis, and black $\text{Re}_3O_5 \cdot \text{H}_3O$ is precipitated. Complete hydrolysis of boiling. Soluble in glacial acetic acid and dioxane (reddish-purple color), alcohol and liquid ammonia; slightly soluble in ether. A AgNO_3 solution produces a precipitate only after lengthy heating with nitric acid. Forms well-crystallized compounds with RbCl_{*} CsCl and organic bases. Hexagonal crystal structure.

REFERENCES:

 W. Geilmann, F. W. Wrigge and W. Biltz. Nachr. Gött. Ges. <u>1932</u>, 582; W. Geilmann and F. W. Wrigge. Z. anorg. alig. Chem. <u>214</u>, 249 (1933); O. W. Kolling. Trans. Kansas Acad. Sci. <u>56</u>, 378 (1953).

Rhenium (V) Chloride

ReCl₆

 $Re + \frac{5}{3}Cl_2 = ReCl_5$ 188.2 55.0 l. 363.5

Rhenium metal is placed in a boat which is inserted into the hard glass apparatus of Fig. 328. The air is displaced by O_2 -free nitrogen and the Re chlorinated at 500°C in a stream of Cl_2 . The evolving black-brown vapors are condensed at a.as a black solution. The apparatus is scaled off at 1, connected at 5.46 a bigh vacuulo.

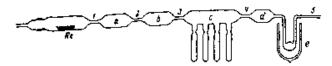


Fig. 328. Preparation of rhenium (V) chloride

evacuated and heated from 20 to 50° C; small fractions of the very volatile ReOCl₄ (b.p. 223°C) are then condensed in d and e. The bulk of the ReCl₅ is driven into b at 150 to 250°C, the tube meltsealed at 2, and the substance sublimed at 200°C from b to c, leaving only a slight residue in b. Finally, the tube is melt-sealed at 3 and 4 and the preparation distributed (by shaking) into the small tubes attached at c; the latter are then melt-sealed.

PROPERTIES:

A deep, black-brown powder; dark brown vapor. Sensitive to air, sublimation at atmospheric pressure results in decomposition. Hydrolyzed by water, forming various products. Soluble in hydrochloric acid (green solution) with liberation of Cl_2 .

REFERENCES:

W. Geilmann, F. W. Wrigge and W. Blitz. Angew. Chem. <u>46</u>, 223 (1933); Z. anorg. alig. Chem. <u>212</u>, 244 (1933).

Potassium Rhenium (IV) Chloride

K_rReCl_t

 $\frac{\text{Re} + 2 \text{Cl}_2 + 2 \text{KCl}}{186.2} = \frac{\text{K}_2 \text{Re} \text{Cl}_4}{44.9 l} = \frac{149.1}{477.1}$

Fine Re powder is intimately ground with KCl (10% excess) and slowly heated to about 300°C in a porcetain boat, first under N₂ and then in a slow Cl₂ stream. The $K_2 \text{ReCl}_6$ is formed immediately and only a slight quantity of rhenium chlorides is volatilized. Following cooling in a stream of N₂, the substance is dissolved in some hot 5% HCl and recrystallized; the remainder is obtained by concentration and crystallization during cooling.

Alternate method: Reaction of KReO, with KI and hydrochloric acid. The procedure is involved and it is difficult to obtain a pure product [H. Schmidt, Z. anorg, allg. Chem. 212, 188 (1933); O. W. Kolling, Trans. Kansas Acad. Sci. 56, 379 (1953)]. SHEN(UM

PROPERTIES:

Yellowish-green powder or regular green crystals. Meits with decomposition. Addition of conc. H_2SO_4 at moderate temperatures produces HCl. Fair solubility in water. Solubility in 12% HCl: 21.4 (0°C); 30.3 (18°C) g./liter; in 37% HCl: 3.3 (0°C); 3.7 (18°C) g./liter. d_4^{15} 3.34. Crystal structure; type J 1₁,

REFERENCE:

W. Geilmann. Private communication.

Rhonium (VI) Oxychlarido

ReOCL

Prepared via reaction of Re₂O₇ with ReCl_s.

Rhenium metal is chlorinated at 500°C in a stream of Cl_3 in the apparatus described for the preparation of ReO_3Cl . Following cooling, the Cl_3 is displaced with O_3 and the sections of the tube in which brown-black crystals of $ReCl_5$ have appeared are heated with a small flame to 50-70°C. The $ReCl_5$ melts (often with appearance of a flame) and the crystals turn into a brown liquid, which is then distilled in a stream of N_3 into a well-cooled U tube receiver. The excess Cl_3 is evaporated, the apparatus filled with O_3 , and the liquid brought to a gentle boil. Heating at 200°C in an N_3 stream is continued for an hour in order to completely remove all traces of ReO_3Cl . Then about one third of the remaining liquid is distilled off. The receiver is now replaced by a fresh one and, except for a small residue, the remaining liquid is distilled over.

Alternate method: From ReČl₃ and dry O₂ at 110 to 130°C [O. W. Kolling, Trans. Kansas Acad. Sci. <u>56</u>, 378 (1953)].

PROPERTIES:

Formula weight 344.05. Fibrous needles; dark orange in thin, brownish-red in thick layers. M. p. 29.3 °C, b. p. 223 °C (slight decomposition). Decomposes at 300 °C. Immediately forms ReO_3 Cf on heating in a stream of O₂. Hydrolyzed by water to rhenium (IV) hydroxide and HReO₄.

REFERENCE:

A. Brukl and K. Ziegler. Ber. dtsch. chem. Ges. 65, 916 (1932).

Rhenium (VII) Oxychloride

ReO,Cl

Prepared by reaction of Re₂O₇ (excess) with ReCl₅.

Two hoats, one containing five and the other two parts of Re. are placed in a high-melting glass reactor tube in a manner such that heating of one will not raise the temperature of the other. A U-shaped tube and two condensation traps are connected to the reactor by means of ground-glass joints (the traps are cooled to -65 °C with alcohol-Dry Ice). The air in the apparatus is displaced with O₂ and the first boat (the one containing five parts of Re) is heated in a slow stream of O₂ in such a way that the Ready formed is deposited in the tube (the U tube must be cooled to a low temperature during this operation). The oxygen is then displaced with Cl₂ and the second boat heated in a stream of Cl₂. The rhenium chlorides formed in this manner react with the ReaO, and the products of this reaction are condensed in the U tube. Any cocondensed Cl₂ is evaporated; then, the ReO₃Cl is distilled over as the first fraction boiling above 100°C (it is usually very light blue or green). On repeated fractionation in a stream of Na the product becomes colorless.

Alternale method: From ReO₃ and dry Cl₃ at 160-190°C. Yields exceed 70% [C. J. Wolf, A. F. Clifford and W. H. Johnston, J. Amer. Chem. Soc. <u>79</u>, 4257 (1957)].

PROPERTIES:

Formula weight 269.68. Colorless liquid: strongly light refracting. M.p. 4.5°C, b.p. 131°C (corr.). Reacts instantaneously with Hg, Ag, stopcock grease and numerous other organic compounds. Soluble in CCl_4 . Hydrolyzes to HReO₄ and HCL.

REFERENCE:

A. Brukl and K. Ziegler, Ber. dtsch. chem. Ges. 65, 916 (1932).

Rhenium (IV) Oxide

ReO.

1,

$$2 \operatorname{Re}_2 O_7 + 3 \operatorname{Re} = 7 \operatorname{Re}O_7$$

 $\frac{1}{10}$: 96.9 55.9 152.8

A stoichiometric mixture of Re and Re_3O_7 is heated to 300°C for one day in a small, evacuated, thick-wall quartz tube, which is

RHENLUM

sealed by melting; the reactants are then heated to 600-650°C to an additional day. The product is orthorhombic ReO₂.

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II. Heating of NH_4ReO_4 in vacuum at 500°C yields monoclinic ReO₂ of the MoO₂ type; above 500°C, orthorhombic oxides are formed.

PROPERTIES:

Formula weight 218.22. Gray-black powder; dissociates in a high vacuum at 1000°C to Re and Re₃O₇. Readily oxidized by O₂. Insoluble in weak acids, but dissolved by conc. halogen acids. Converted to HReO₄ by H₃O₂ and HNO₃. d_4^{25} 11.4. Heat of formation: -70 kcal.

REFERÊNCES:

- I. W. Biltz. Z. anorg. allg. Chem. 214, 227 (1933).
- II. W. H. Zachariasen. Amer. Crystallographic Assoc. Program and Abstracts of Winter Meeting, F4 (1951); A. Magnéli, Acta Crystallogr. (Copenhagen) 9, 1038 (1956).

Rhenium (VI) Oxide

ReO₁

I. REDUCTION OF Re207 BY CARBON MONOXIDE

 $Re_2O_7 + CO = 2 ReO_3 + CO_2$ 484.4 22.4 i. 468.4 22.4 i.

The apparatus is a glass tube sealed at one end; about 1 g. of Re_2O_2 is sublimed into it in a stream of O_2 . When the reaction is completed, the apparatus is evacuated and filled with CO to a pressure of 760 mm. The glass tube is then slowly heated to 175°C in a glycerol bath and held at that temperature until the preparation turns blue. The temperature is then slowly raised to 225°C and later, when red ReO₃ is formed, to 280°C. The run requires two to three hours. The yield is quantitative.

II. Reaction of Re_3O_7 with dioxane to form a complex compound which dissociates at 125-145°C to ReO_3 and some volatile products.

The apparatus consists of a reaction flask protected against moisture; 4 ml. of dioxane is rapidly added to i g. of Ready under anhydrous conditions (the dioxane should be predistilled over Na metal). The mixture is gently heated on a water bath until a clear, coloriess solution is obtained. Local overheating must be avoided, since it produces cloudy solutions and, ultimately, contaminated products. The flask is then placed in an ice bath to freeze the solution. After the freezing, the frozen substance is allowed to melt. The Re₃O₇-dioxane complex crystallizes in the form of a dense, pearly-gray precipitate; the excess dioxane becomes liquid. The freezing-melting operation is then repeated, the excess of dioxane decanted, and the compound dried in a vacuum desiccator at room temperature over conc. H_2SO_4 . The dry complex is rapidly placed in a crucible and carefully heated on a hot plate (125 to 145°C). The substance is melted, forming a colorless to bluish-green liquid, which later dissociates to red ReO₃ and some volatile, Re-free products. The ReO₃ thus formed is pure. The yield is about 95%.

PROPERTIES:

Formula weight 234.22. Red powder. During reduction of $\text{Re}_{2}O_{7}$, the preparation passes through intermediate stages with hues ranging from green to dark blue (rhenium blue) until the final red color is obtained. Decomposed in high vacuum at 400°C to $\text{Re}_{3}O_{7}$ and $\text{Re}O_{4}$. Not attacked by hot hydrochloric acid, but converted to $\text{HRe}O_{4}$ by strong HNO_{3} . Disproportionates in warm NaOH to ReO_{3} and NaReO_{4} ; NaOH + H₂O₂ instantaneously produce NaReO₄. d_{4}^{25} 6.9; heat of formation: -146.0 kcal. Crystal structure: DO_{9} type.

REFERENCES:

- I. A. D. Melaven, J. N. Fowle, W. Brickel and C. F. Hiskey in: L. F. Audrieth, Inorg. Syntheses, Vol. III, New York-Toronto-London, 1950, p. 187.
- II. H. Nechamkin and C. F. Hiskey. Ibid., p. 186; H. Nechamkin, A. N. Kurtz, and C. F. Hiskey. J. Amer. Chem. Soc. <u>73</u>, 2828 (1951).

Rhenium (VII) Oxide

Re₁O7

 $2 \operatorname{Re} + \frac{1}{2} \operatorname{O}_{2} = \operatorname{Re}_{1} \operatorname{O}_{3}$ $372.4 \quad 78.4 L \quad 484.4$

The compound is prepared in a combustion tube to which a = 1U tube is sealed on; the latter is attached to a condensation trape

RHENIUM

Both ends of the tube are protected against humidity by vessels containing $CaCl_2$ and conc. H_2SO_4 . The rhenium metal is placed in a porcelain boat situated in the front section of the tube, which is heated to 150°C while a very fast stream of oxygen is passed over the metal. Crystals of Re_2O_7 deposit in the front section of the tube and in the condenser tube (there is virtually no vapor mist); if the starting Re is not entirely alkali-free, some KReO2 will remain in the boat. The Re_2O_7 should be resublimed in a stream of O_2 .

The compound is used in the preparation of HReO $_{*}$ of the lower oxides and of very pure Re (reduction with H_{2}).

PROPERTIES:

Bright-yellow crystalline powder. M. p. 301.5 °C, b.p. 362.4 °C; d_4^{25} 6.103; heat of formation: --295.9 kcal. Extremely hygroscopic. Readily soluble in H₈O, forming HReO₄; soluble in alcohol; sparingly soluble in ether. Stored in melt-sealed glass tubes. Rhombic crystals.

REFERENCES:

W. Geilmann, Private communication; W. A. Roth and C. Becker, Z. phys. Chem. <u>159</u>, 29 (1932); K. Wilhelmi, Acta Chem. Scand. <u>8</u>, 693 (1954).

Sodium Rhenate (IV)

Na,ReO,

 $ReO_{2} + 2 NaOH = Na_{2}ReO_{3} + H_{2}O$ 218.2 80.0 280.2

The apparatus is shown in Fig. 329. A gold crucible c is introduced into the quartz apparatus through opening s and placed in

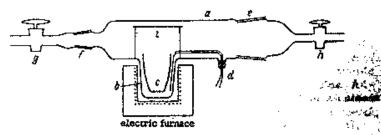


Fig. 329. Preparation of sodium rhenate (IV). & quartz tibe; ** orucible-shaped attachment; c gold orucible; & thermocouple; ** movable gold shield (splash shield) the attachment b; a stream of oxygen-free N_2 is passed from h to c. After thorough flushing with N_2 , 10 g, of very pure and dry NNON is introduced (through f) into c. The apparatus is then beated to 500°C and 4 g, of dry ReO₂ added by shaking to the melt. The ReO₂ dissolves, the melt turns reddish-brown, and water vapor escapes through f. After the reaction is completed, the beater is removed and attachment b cooled with ice water; this spalls the solidified melt off the crucible walls. The fused material contains (clearly separated) an upper layer of NaOH and a lower stratum of the brown rhenate. The fused cake is gently crushed, leached with descrated ice water, decanted, filtered in the absence of air, washed with alcohol and dried, again in the absence of air. The filtering and drying device shown in Fig. 52, p. 74, is handy in this operation.

Alternate method: Fusion of ReO3 with NaOH [W. Geilmann, F. W. Wrigge and W. Biltz, Z. anorg. allg. Chem. 214, 233 (1933)].

SYNONYM:

Sodium rhenite.

PROPERTIES:

Brown powder. On heating in air, converts to the yellow perrhenate. Insoluble in H_2O and in bases; soluble in conc. hydrochloric acid, converting to the green H_2ReCl_6 .

REFERENCE:

I. and W. Noddack. Z. anorg. alig. Chem. 215, 134 (1933).

Ammonium Perrhangte

NH,ReO,

 $\frac{\text{Re}_{2}\text{O}_{1} + 2\text{NH}_{3} + \text{H}_{2}\text{O}_{2} = 2\text{NH}_{4}\text{ReO}_{1}}{484.4}$ $\frac{1}{538.6}$

A solution of Re_2O_7 in some water is prepared, excess ammonia is added and the solution evaporated in a platinum crucible placed on a water bath.

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Alternale method: Rhenium sulfides, oxides or rhenium metal are dissolved in HNO₃. The solution is evaporated and diluted with ammonia. Recrystallization is required ! May be used to prepare pure rhenium (see p. 1476).

RHENSUM

PROPERTIES:

Thick, white, bexagonal crystals. Dissociates in air above 200°C to form NH₃, H₂O and Re₂O₇. Solubility: 2.9 (0°C); 6.2 (20°C); 32 (80°C) g. of salt/100 g. H₂O; d 3.63. Crystal structure: H0₄ type.

REFERENCE:

I. and W. Noddack, Z. anorg. allg. Chem. 181, 23 (1929).

Barium Perchenote

Ba(ReO₄),

An aqueous solution of $\text{Re}_{3}O_{7}$ (= HReO_{4}) is neutralized exactly with baryta water, using neutral red as the indicator. The residue is dried, and the water-containing salt is converted to anhydrous Ba(ReO_4)₂ in vacuum or by heating to 120°C.

PROPERTIES:

Formula weight 637.80, Colorless columns or rhombolds. Solubility: 1.8 (0°C); 5.3 (20°C); 47 (70°C) g. of salt/100 g. $H_{2}O$. Solubility in alcohol; 2.4 g/liter of solution at 18.5°C.

REFERENCES;

I. and W. Noddack. Z. anorg. allg. Chem. <u>181</u>, 25 (1929); W. Lewino. Thesis, Univ. of Hamburg, 1932.

Barium Rhenate (VI)

BaRcO₄

Prepared by reducing $Ba(ReO_4)_2$ with ReO_2 and NaOH in a melt: The apparatus is the same as that used in the preparation of Na_2ReO_3 (Fig. 329). Sodium hydroxide (20 g.) is fused in oruciple. c under a stream of N_2 ; then, 8.00 g. of $Ba(ReO_4)_2$ is added, for lowed by 2.00 g. of ReO_2 . The melt is heated to 500°C and held at that temperature for one hour. It is then cooled to 300°C and held at that temperature for one hour. The heater is then removed and attachment b cooled with ice water. The melt cake is broken up and treated with 96% alcohol at 0°C; this loosens the NaOH and NaReO₄ in the melt: the former reacts with any unconverted $Ba(ReO_4)_2$ to form NaReO₄ and $Ba(OH)_2$; the latter remains in the

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residue. The product is filtered, using the device shown in Fig. 52, p. 74, and washed with some alcohol. It contains some NaOH and $Ba(OH)_{2^{-1}}$

ANALYSIS:

The compound is disproportionated in acetic acid. The leachedout Re (VII) fraction is filtered off and precipitated with nitron; the Re (IV) fraction is oxidized to Re (VII) and also precipitated with aitron.

PROPERTIES:

Formula weight 387.58. Foliage-green powder; readily dissociated. Slowly turns black in vacuum and white in air (formation of ReO_{+}). Instantaneously dissociated by water, acids and bases. The presence of a slight amount of free NaOH is required for stability.

REFERENCE:

1. and W. Noddack. Z. anorg. alig. Chem. 215, 143 (1933).

Rhenium (IV) Sulfide

RcS_z

I.

 $Re + 2S = ReS_{e}$ 188.2 64.1 250.3

Rhenium and sulfur are mixed in stoichiometric proportions and heated for 18 hours in an evacuated, sealed small quartz tube at 980-1000°C.

II. Hydrogen sulfide is used to precipitate Re_2S_7 from a hydrochloric acid solution; the precipitate is filtered off with suction and washed with water and briefly with acetone. It is dried in a quartz or hard glass tube sealed at one end. It is then heated in high vacuum to 600°C until no further S sublimes out. The result is ReS₂ only slightly contaminated with sulfur.

Alternate method: Heating of Re in a stream of H₂S to red heat [H. V. A. Briscoe, P. C. Robinson and E. M. Stoddart, J. Chem. Soc. (London) <u>1931</u>, 1441].

PROPERTIES:

Black solid (platelets are seldom recognizable); somewhat voistile at 1000°C. Strongly attacks quartz at 1000°C. No appreciable solubility in bases, alkaline sulfides, hydrochloric and sulfurio

RHENIUM

acids. Converted by oxidizing agents to HReOs. d²⁰ 7.506; heat of formation: -70.5 keal. Crystal structure: C7 type.

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REFERENCES:

- 1. R. Juza and W. Biltz. Z. Elektrochem. 37, 499 (1931).
- II. W. Geilmann and G. Lange. Z. analyt. Chem. 126, 321 (1953).

Rhenium (VII) Sulfide

Re₅S₇

 $2 \text{ KReO}_4 + 7 \text{ H}_2 \text{S} + 2 \text{ HCl} = \text{Re}_2 \text{S}_7 + 2 \text{ KCl} + 8 \text{ H}_4 \text{O}$ 578.6 155.01. 72.9 596.9 149.1

A solution of KReO₄, containing 30 ml. of hydrochloric acid per 100 ml. of solution, is saturated for four hours with H_2S . The precipitated sulfide is washed with H_2S -saturated, 3% HCl water. The product is filtered in the absence of air, washed and then dried, first in a high vacuum for two hours at 140°C and then in high vacuum over freshly prepared P_2O_8 (60 hours at 165-170°C).

Alternate method: Precipitation with compressed H_2S from a solution of KReO₄ in hydrochloric acid; there is no need for the high HCl concentration in this case. The workup is similar to that described above [W. Geilmann, Z. analyt. Chem. <u>126</u>, 321 (1943)].

PROPERTIES:

Black, readily exidized powder. Dissociation to ReS_2 and S begins at 250°C. Insoluble in hydrochloric and sulfuric acids in the absence of air; exidized by nitric acid or H_3O_2 plus a base to $H\text{ReO}_4$, d_4^{25} 4,866.

REFERENCE:

W. Biltz and F. Weibke. Z. anorg. allg. Chem. 203, 4 (1931).

Barium Mesoperrhenate

Bas(ReOs);

Prepared by fusion of Ba(ReO) with NaOH. The apparents is the same as used in the preparation of Na₂ReO₃ (Fig. 329).

26. G. GLEMSER

Crucible c is used to fuse 3 g. of Ba(ReO₄)₃ with 5 g. of carboaste-free NaOH under a stream of CO_3 -free air. The hot melt is red and cloudy. After cooling, it is crushed, leached with 90% alcohol to remove the excess NaOH and the NaReO₄ formed in the process, then filtered, again washed with alcohol and dried with suction.

ANALYSIS:

The salt is decomposed with CO_2 -free water; the Ba is precipitated as BaSO₄ and the ReO₄⁻ as nitron hydrogen perrhenate.

PROPERTIES:

Formula weight 944.52. Small, lemon-yellow hexagonal tablets and columns. Turns red upon heating to 800° C, returns to yellow on cooling. Stable in dry air. The wet salt is decomposed by CO₂ into BaCO₃ and Ba(ReO₄)₂.

REFERENCE:

I. and W. Noddack, Z. anorg. Chem. 215, 146 (1933).

Workup of Rhenium Residues

Precipitates of nitron hydrogen perrhenate from analyses of rhenium are collected and stored separately from rhenium solutions.

Workup of nitron precipitates: The material is carefully decomposed in a stream of H_2 , the products washed and oxidized to Re_3O_7 , and the latter dissolved in H_3O and concentrated in the presence of KOH or ammonia. The KReO₄ or NH₄ReO₄ obtained in this manner can be used without further purification.

Workno of various solutions. To avoid unnecessary contamination of the air with Re, the solution is neutralized and concentrated (if necessary, by boiling). It is then cooled and acidified with hydrochloric acid and the Re precipitated under pressure as Re $_{2}S_{7}$. The Re $_{2}S_{7}$ is washed and dissolved in KOH + H $_{2}O_{3}$, and the KReO₄ is allowed to crystallize out. If the KReO₄ is still not sufficiently pure, it is reduced with H $_{2}$ and oxidized with O $_{3}$ to Re $_{2}O_{7}$, and the latter is used to obtain Re or the perchenate.

If traces of Mo must be removed, the procedure is as follows: the Re is precipitated with H_2S (under pressure) as Re_2S_7 . the precipitate is dissolved in KOH + H_2O_3 , and the traces of MO.

RHENIUM

are removed by extraction of the neutral solution with 8-hydroxy quinoline or chloroform. Following repeated precipitation under pressure as Re_2S_7 , the product is dissolved in KOH + H_2O_2 and crystallized as KReO4. The KReO4 is recrystallized from hot water.

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SECTION 27

Iron

H. LUX

Metallic from

ELECTROLYTIC IRON

The following conditions are suitable for the preparation of very pure electrolytic iron; each liter of electrolyte contains about 800 g. of very pure FeCl₂ · 4H₂O (Fe³⁺ content less than 0.05%; sulfate-free) and 1.5-2.0 g. of AlCl3 · 6 H2O or 0.1 g. of CrCl₃ · 6H₂O. The concentration of free HCl is 0.01-0.02 N, and the temperature is 90°C or higher. The anode is made of the purest iron possible, and is wrapped in an asbestos bag. A sheet of vanadjum steel serves as the cathode. The nature of cathode pretreatment is important if the deposit of electrolytic iron is to be easily stripped off. The steel sheet is first polished to a high luster, degreased by being used as a cathode in an alkaline KCN bath, rinsed with water, and after being connected to the electrical circuit, placed in a FeCl2 bath. The cathodic density is 0.65-1.0 amp./in?; if the operation is of long duration or proceeds at still higher current densities (up to 2 amp./ in?), the electrolyte must be continuously taken out of the bath, filtered, retreated, the HCl content adjusted to the one indicated above, and recycled to the bath.

The relatively soft α -iron deposited contains H_2 but no Al or Cr. The H_2 may be completely removed by baking in vacuum at 950°C. Electrolytic iron is free of C or Si, and of other metals if the electrolyte itself is pure.

PROPERTIES:

M.p. 1535°C, b.p. 2730°C; d 7.86. Crystal structure of α -Fe: A2 type.

REFERENCES:

G. A. Moore. J. Metals <u>5</u>, 1443 (1953); F. Müller. Z. Elektrochem. <u>47</u>, 135 (1941); F. Halla. Korrosion und Metallschutz <u>15</u>, 380. (1939). REDUCED IRON

$$2 \operatorname{Fe}(OH)_{s} \div 3 \operatorname{H}_{t} = 2 \operatorname{Fe} + 6 \operatorname{H}_{t}O$$

213.7 67.2 *i*. 111.7 108.1

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It is best to start from very pure $Fe(OH)_{s}$; this is prepared by adding a $Fe(NO_{3})_{3}$ solution to aqueous NH_{3} and drying the precipitate at 65°C. The product, finely ground, is placed in an aluminum or Pt boat (with Pt foil insert) and reduced in a stream of H_{2} as the temperature is slowly raised. If the reduction temperature is lower than 550°C, the iron product is pyrophoric. As a rule, the temperature is raised slowly from 400 to 700°C (with 20 g. of $Fe_{3}O_{3}$, this requires about 40 min.) and then held constant (about 20 min.) until further $H_{3}O$ is produced. If less reactive starting materials (e.g., $Fe_{3}O_{3}$ prepared from the nitrate) are used, it may be necessary to heat to higher temperatures (1050-1100°C) and for much longer times (60 hours or more) to insure complete reduction. The preparations are cooled in H_{2} ; their hydrogen content is minimal.

REFERENCES:

R. Fricke and L. Klenk. Z. Elektrochem. <u>41</u>, 617 (1935); R. Fricke,
O. Lohrmann and W. Wolf, Z. phys. Chem. (B) <u>37</u>, 60 (1937);
P. M. Savelevich. Trudy Insi. Chist. Khim. Reaktivov, No. 15, 51 (1937); abstract in Chem. Zentr. <u>1939</u>, I, 4563; G. P. Baxter and C. R. Hoover. Z. anorg, allg. Chem. <u>80</u>, 211 (1913).

VERY PURE IRON :

O. Hönigschmid, L. Birckenbach and R. Zeiss. Ber. dtsch. chem. Ges. <u>56</u>, 1473 (1923); T. W. Richards and G. P. Baxter. Z. anorg. Chem. <u>23</u>, 247 (1900); also A. Gatterer. Commentationes Pontific. Acad. Sci. <u>1</u>, 77 (1937); abstract in Chem. Zentr. <u>1938</u>, I, 1745; A. Gatterer and J. Junkes. Specola astronom. Vaticana Comun. No. 6 (1938); abstract in Chem. Zentr. <u>1938</u>, H, 2243; J. Talbot, P. Albert, M. Caron and G. Chaudroa, Rev. Met. <u>50</u>, 817 (1953).

tron (II) Chloride

FeCl₂

 $Fe + \frac{3}{2}Cl_{2} = FeCl_{3}$; $FeCl_{3} + \frac{3}{2}H_{3} = FeCl_{2} + HCl_{55.8}$ 55.8 33.6 i. 162.2 162.2 11.2 i. 126.8 38.5

The starting anhydrous FeCl₃ is prepared from Fe and Cl₃. The Cl₃ is then displaced by means of a stream of very dry Navard H, LUX

completely dry, pure H_2 is immediately introduced. The reduction proceeds rapidly at 300-350°C. It is advisable to spread the solid in a tube placed in a long electric furnace and to heat slowly, section by section, in the H_2 stream. Partly unconverted FeCl₃ sublimes in the H_2 below 300°C, while above 350°C the FeCl₃ tends to be reduced too far (to Fe).

The preparation of FeCl₂ from Fe and HCl is less satisfactory because of the higher temperatures required.

SYNONYMS:

Ferrous chioride, iron dichloride.

PROPERTIES:

White hygroscopic powder; can be resublimed in a stream of HCl at about 700°C. M.p. 674°C, b.p. 1023°C; d (25°) 3.162. Vapor pressure at 700°C: 12 mm. Readily soluble in water and alcobol. Crystal structure: C 19 type.

REFERENCES:

H. Wolfram. Thesis, Techn. Hochschule Dresden, 1913; W. Kangro and E. Petersen, Z. anorg. allg. Chem. <u>261</u>, 157 (1950).

Iron (III) Chloride

FeCl,

 $2 \text{ Fe} + 3 \text{ Cl}_2 = 2 \text{ FeCl}_3$ 111.7 67.24, 324.4

A stream of Cl_2 is very thoroughly dried over conc. H_2SO_4 and P_2O_5 , and is then liquefied by passage through a U tube cooled with Dry Ice-acetone mixture to about $-40^{\circ}C$. The bath temperature is then raised to $-34.1^{\circ}C$; pure Cl_2 volatilizes out. It passes into a very dry Pyrex tube containing the purest possible iron wire (about 0.2 mm. in diameter). The reaction takes place at 250-400°C; an excess of Cl_2 should always be present and should always bubble out from the H_2SO_4 -containing safety valve which terminates the reactor train. To avoid plugging the tube, the electric furnace (or the aluminum heating block) is occasionally shifted, so that a fresh condensation zone may be created.

At the end of the reaction, the preparation should be resublimed in a stream of Cl_2 at about 220°C (the temperature should

not exceed 300°C). All of the Cl_2 is then displaced from the apparatus with very dry N_2 (or air), and the product is transferred (under N_3) to storage vessels, which are then tightly sealed.

SYNONYMS:

Ferric chloride; iron trichloride.

PROPERTIES:

Formula weight 162.2. Leaflets with a somewhat greenish metallic luster. Extremely hygroscopic. M. p. (in Cl₂) 308°C, b. p. (calcd.) 316°C; d (25°) 2.898. Decomposes partially on sublimation in high vacuum. In the range of 160-210°C the decomposition pressure of Cl₂ over solid FeCl₃ and FeCl₂ obeys the equation: log P = 11.33-5.67 \cdot 10³/T. Very readily soluble in water, ethyl alcohoi, ethyl ether and acetone. FeCl₃ and FeCl₂ form a eutectic, m. p. 297.5°C, containing 13.4 mole % of FeCl₂.

REFERENCES:

G. G. Maier. Techn. Pap. Bur. Mines Washington No. 360, 40 (1925);
O. Hönigschmid, L. Birckenbach and R. Zeiss. Ber. dtsch. chem. Ges. <u>56</u>, 1476 (1923);
H. Schäfer. Angew. Chem. <u>64</u>, 111 (1952); for the preparation of larger amounts, see B. R. Tarr in; L. F. Audrieth, Inorg. Syntheses, Vol. III, New York, 1950, p. 191.

iron (II) Bromide

FeBr.

FeBr₂, ANHYDROUS

I.

 $Fe + 2 HBr = FeBr_{t} + H_{t}$ 55.9 161.8 213.7 22.41.

Very pure Fe (reduced with H_2) is placed in an unglazed procelain boat situated in a porcelain tube and heated to about 800%. in a completely dry stream of HBr-saturated nitrogen, so that the nascent FeBr₂ distills out at once. The preparation is transferred (in dry N_2) to well-sealed vessels. This last operation is facilitated by attaching a singly fitting tube onto the axit and of the reactor; the FeBr₂ can then sublime into this second tube.

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B. Careful dehydration of $FeBr_2 \cdot 4H_2O$ in a stream of N₂ and HBr.

SYNONYM:

Ferrous bromide.

PROPERTIES:

Light-yellow to dark-brown crystals; bygroscopic. M. p. 684°; d (25°) 4,624. Crystal structure: C 6 type.

REFERENCES:

I. G. P. Baxter. Z. anorg. Chem. 38, 236 (1904).

II. G. P. Baxter, Th. Thorvaldson and V. Gobb. Z. anorg. Chem. 70, 333 (1911).

FeBra. HYDRATE

 $F_e + 2 HB_T - 6 H_eO = FeBr_z \cdot 6 H_eO + H_e$ 55.9 181.8 323.8

To prepare the hexahydrate, pure iron is dissolved in aqueous HBr and the solution evaporated below 49° C. Above this temperature one can obtain the tetrahydrate, and above 83° C the dihydrate.

Alternate method: Shaking Bra and water with an excess of iron powder.

PROPERTIES:

Pale-green rhombic tablets; not deliquescent.

REFERENCE:

F. Schimmel. Ber. dtsch. chem, Ges. 62, 963 (1929).

lron (III) Bromide FeBrs

 $2 \text{ Fe} \Rightarrow 3 \text{ Br}_{s} = 2 \text{ FeB}_{Ts}$ 111.7 479.5 591.2

A Pyrex tube, sealed at the left end and provided with a 45° bend in the middle, is connected at the right to a high-vacuum pump and a supply of Br₂. Reduced iron powder is introduced into the left leg with the aid of a long-stem funnel, and the right end of the tube is then drawn out to a capillary. The Fe is thoroughly degeneral by evacuation and heating. Bromine is then condensed on

the iron (liquid nitrogen bath); the Br_2 excess is such that after completion of the reaction the pressure in the tube will still be at least 5 atm.

After the pump end of the reactor tube is sealed off, the Br_{2} is condensed in the right leg by cooling the latter in ice water. The left leg is then heated to 175-200°C (maximum) and then the right leg to 120°C; this produces a Br_{2} pressure of about 5 atm. The heating is done with two mating aluminum heating blocks. The butting ends are cut at an angle of 22.5° and separated only by a thin disk of asbestos (Fig. 320).

The reaction begins, although slowly, even at room temperature, but cannot be completed at this temperature even in several months. However, under the conditions given above, pure FeBr₃ condenses outside the 200°C zone. If the temperature of the Fe is too high or the Br_3 pressure too low, some yellow FeBr₂ is also deposited at the left end of the tube.

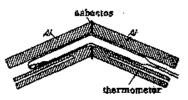


Fig. 330. Preparation of iron (III) bromide.

SYNONYM:

Ferric bromide.

PROPERTIES:

Lustrous black plates; very hygroscopic. The decomposition pressure of Br₂ at 90°C is 55 mm. and at 139°C is 760 mm.; below 139°C, it obeys the equation: log p (mm.) = -3478.6/T +11.327. The vapor pressure of FeBr₃ becomes detectable above 139°C. Crystal structure: D0₅ type (same as FeCl₃).

REFERENCES:

N. W. Gregory and B. A. Thackrey. J. Amer. Chem. Soc. <u>72</u>, 3176 (1950); N. W. Gregory. Ibid. <u>73</u>, 472 (1951).

> from (1) lodide FeI, Fe + $I_{t} = FeI_{t}$

55.6 258.8

I,

A high-melting glass tube is sealed at one end and provided with a side arm terminating in a break-seal capillary d (see Fig. 331). Very pure iron wire is placed at location a of the tube, and a small plug of freshly ignited asbestos wool b is inserted slope.

\$09.7

to the iron. Pure, dry I_2 (less than stoichiometric quantity), in the form of a coarse powder, is then placed on top of the asbestos wool plug. The reactor tube is then drawn out to smaller size at a, the I_2 is moved forward to c, and a good vacuum is applied by means of I_3 is moved forward to c, and a good vacuum is applied by means of a mercury diffusion pump. At the same time, the other sections of the tube (a, b) are heated in an electric furnace to 500 °C to degas the T_6 and the asbestos. The tube is then sealed off at f, and section ccontaining the I_3 is heated to 180 °C with a suitable Ai block or in an air bath (the section containing the Fe is maintained at 500 °C). The tube is slightly inclined forward to prevent the liquid iodine from flowing into the hot section. If the above temperatures are adhered to, the internal pressure does not exceed one atmosphere.

The nascent FeI₂ sublimes slowly toward the cooler zone, where it deposits as black leaflets which appear brownish red when viewed by transmitted light. As soon as the iodine vapor disappears completely, the tube is allowed to cool and a vacuum hose is carefully slipped over side arm d. The hose is connected via a three-way stopcock to a canned-rotor pump and a nitrogen supply. Vacuum is applied, the sealed capillary on the side arm is broken off, and pure, dry N₂ is slowly admitted. Care should be taken during this step to avoid entraining any glass fragments in the tube. As soon as a slight gage pressure is established, the reactor tube is broken off at e and the product is transferred in nitrogen to a storage vessel.

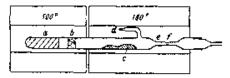


Fig. 331. Preparation of iron (II) iodide. *a* iron wire; *b* asbestos wool; *c* iodine; *f* seal location (after sealing, the section to the right of *f* is removed).

Alternate methods: II. Heating reduced Fe in a stream of I_2 -saturated hydrogen, followed by distillation in a steel tube.

III. Thermal decomposition of Fe(CO) 12. The product is an extremely fine powder.

SYNONYM:

Ferrous iodide.

PROPERTIES:

M.p. 587°. Hygroscopic; becomes whitish in air. Aqueous solutions are colorless. Crystal structure: C 6 type. REFERENCES:

- I. M. Guichard, Comptes Rendus Hebd, Seances Acad. Sci. 145. 807 (1907).
- 11. C. L. Jackson and I. H. Derby, Amer. Chem. J. 24, 16 (1900); Bull. Soc. Chim. France [3] 24, 863 (1900); see also W. Fischer and R. Gewehr. Z. anorg. allg. Chem. 222, 303 (1935).
- 1II. W. Hieber and H. Lagally. Ibid. 245, 300, 313 (1940).

iron (II) Oxide

FeO

I.

 $FeC_{2}O_{4} = FeO + CO + CO_{2}$ 143.8 71.8 28.044.0

Thermal decomposition of FeC₂O₄ yields pure FeO only under specific conditions. The decomposition is carried out in a quartz vessel (Fig. 332) whose lower section is kept at 850°C by means of an electric furnace. The joint is surrounded by a water-cooled lead coil or a rubber hose. The nascent gases should be removed as quickly as possible; for this reason, the reactor is connected to two parallel mercury pumps and a good forepump; the gas is carried into two liquid-nitrogen-cooled traps containing activated charcoal.

The starting FeC_aO_4 (0.5-0.8 g.) is placed in the small bulb above the quartz vessel, and the water of crystallization is completely vaporized by heating in vacuum for 12 hours at 200°C. The bulb is turned in the joint, and the FeC₂O₄ drops into the heated lower section of the reactor where it is rapidly decomposed to FeO, CO and CO₂ (the decomposition is complete in about 20 seconds). The product FeO is retained by a quartz wool plug, which must be loose enough to prevent a buildup of pressure during the decomposition.

The furnace is now removed and the hot quartz tube is chilled as rapidly as possible in cold water, since FeO is unstable in the range of 300-560°C and decomposes according to:

$$4 \operatorname{FeO} = \operatorname{Fe_3O_4} + \operatorname{Fe}$$

(this decomposition proceeds most rapidly at about 480°C, but ceases below 300°C). The above procedure yields a jet-black

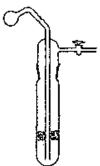


Fig. 332. Preparation of iron (II) Oxide." ' - <u>1</u>

192 - **16**3

7: .

product, readily soluble in dilute acids; it is rapidly oxidized in air, but does not ignite.

II. The preparation from stoichiometric quantities of commercial $Fe_{a}O_{3}$ and reduced iron can also be recommended. The mixture and a few drops of water are sealed into a preevacuated quartz tube, heated for about three days at 900°C, and quenched in cold water.

SYNONYM:

Ferrous oxide.

PROPERTIES:

M.p. 1360°; d 5.7. Crystal structure: B1 (rock salt) type.

REFERENCES:

- P. L. Günther and H. Rehaag. Z. aborg, allg. Chem. <u>243</u>, 60 (1939).
- U. R. W. Blue and H. H. Claassen, J. Amer. Chem. Soc. <u>71</u>, 3839 (1949); J. P. Coughlin, E. G. King and K. R. Bonnickson, Ibid. <u>73</u>, 3891 (1951); see also L. Wöhler and R. Günther, Z. Elektrochem. <u>29</u>, 281 (1923).

Iron (II) Hydroxide

Fc(OH)_z

The preparation of pure $Fe(OH)_3$ has been described in detail by Rihl and Fricke as an example of operation under an inert atmosphere. The general experimental arrangement is further described in Part I, p. 72 ff. It consists essentially of a bulb, one side of which can be connected to a high-vacuum pump as well as a source of N₂ or a drying vessel, while the other side is attached to devices for filtration, washing and transfer of products. All operations must be carried out with the most rigorous exclusion of O₂ in an atmosphere of pure, dry N₂.

The apparatus is first evacuated (high vacuum); then a continuous stream of N_2 is introduced. A centrifuged solution of $Fe(OH)_2$ (prepared from very pure $FeCi_2$) in conc. aqueous NH_3 is admitted through the filter and diluted with a large quantity of water, causing precipitation of the $Fe(OH)_2$. To obtain a denser precipitate (which settles more rapidly), the mixture is heated for about three hours at 80°C and allowed to settle. The mother liquor is filtered off, and the precipitate is washed 10 to 12 times in similar fashion until a positive test for chloride is no longer obtained.

To remove the remaining water, the residue is solidified by immersion of the flask in an ice-salt mixture, full vacuum is spplied, and the water is distilled off overnight as the solid slowly melts. The water is condensed in a large trap chilled in Dry Iceacetone. Complete drying of the product is achieved by keeping it for several additional hours under high vacuum together with a vessel containing P_{aO_5} .

PROPERTIES:

Nearly white, slight greenish tinge. When sprayed into air, burns with sparks. Crystal structure: C 6 type.

REFERENCE:

S. Rihl and R. Fricke, Z. anorg. allg. Chem. 251, 406 (1943).

Iron (II, III) Oxide

Fe₂O₄

 $3 Fe_iO_i + H_i = 2 Fe_iO_i + H_iO_i$ 479.0 22.41. 463.0 18.0

Fine Fe_2O_3 powder is heated to 400°C in a large boat placed in a stream of N_3 ; then the N_2 is replaced with H_3 saturated with water vapor at 50°C. The connecting tubing between the saturating vessel and the reactor tube must be as short as possible and well insulated against thermal losses. When the reduction is complete, as shown by the disappearance of all of the red Fe_2O_3 , the product is cooled in a stream of N_3 . Conversion of 10 g. of Fe_2O_3 requires about five hours.

PROPERTIES:

Black, ferromagnetic powder. M.p. 1590°; d 5.11. Mohs hardness 6. Crystal structure: H11 type.

REFERENCE:

S. Hilpert and J. Beyer. Ber. dtsch. chem. Ges. 44, 1608 (1911).

iron (III) Hydroxide FeO(OH)

4-FeO(OH)

 $\begin{array}{rl} Fe(NO_{2})_{3} \cdot 9 H_{2}O &+ 3 NH_{3} = FeO(OH) &+ 3 NH_{4}NO_{3} &+ 7 H_{2}O \\ \hline 404.0 & 51.1 & 85.9 & 940.2 \end{array}$

A cold solution of 810 g. of $Fe(NO_3)_3 \cdot 9H_2O$ in two liters of water is poured slowly, with vigorous stirring, into an annuonia

solution prepared by dissolving 120 g. of gaseous NH_3 in two liters of water (cooling necessary). The hydroxide which precipitates is amorphous to x-ray analysis. It is washed by stirring at least five times with eight-liter portions of cold water, each portion being decanted as completely as possible. The residual slurry is then stirred with sufficient conc. KOH solution to give a mixture approximately 2N and allowed to stand for 3-4 hours. Finally 100°C steam is bubbled through for two hours. The precipitate is thereby transformed completely into bright-yellow α -FeO(OH), which shows a crystalline x-ray diffraction pattern. Since removal of the potassium hydroxide by washing is difficult.

Since removal of the potassimility divides by watching in divident, it is converted to KCl by treatment with somewhat more than the calculated amount of NH₄Cl. The precipitate is then washed thoroughly with hot water until no further Cl⁻ can be detected. The K content is then usually below 0.04%. Drying in a vacuum desiccator affords a product whose water content still exceeds the theoretical (10.14%) by about 2%. Heating in vacuum or in a stream of dry air yields pure α -Fe₂O₃.

The naturally occurring form of α -FeO(OH), "needle iron ore" or goethite, has an E0₂ type structure.

REFERENCES:

R. Fricke and P. Ackermann, Z. Elektrochem. <u>40</u>, 630 (1934); O. Glemser, Ber. dtsch. chem. Ges. <u>70</u>, 2117 (1937); R. Fricke and G. F. Hüttig, Hydroxyde und Oxydhydrate [Hydroxides and Hydrated Oxides], Leipzig, 1937, p. 316; W. Hoppe, Z. Kristallogr. (A) <u>103</u>, 73 (1940).

7-FeO(OH)

| 2 FeCls · 4 H ₂ C | O + (CH₂)₄N | $_{s} \pm 2 \mathrm{H_{I}O}$ | $= 2 \operatorname{Fe}(OH)_{1}$ | + 4 NH₄CÌ | $+ 6 H_{I}O$ |
|------------------------------|-----------------------|-------------------------------|---------------------------------|-----------|--------------|
| 397.6 | 140.1 | 36.0 | 179.7 | 214.0 | 108.1 |
| Fe(OH): | + NaNO _z + | HCl = Fe | O(OH) + NO | + NaCl + | H,O |
| 89.9 | 69.0 | 36.5 | 88.9 30.0 | 58.5 | 18.0 |

A solution of 120 g. of FeCl₂ - 4 H₃O in three liters of water is filtered, and the filtrate is added to a filtered solution of 168 g. of hexamethylenetetramine (Urotropin) in 600 ml. of water. Bluegreen Fe(OH)₂ is precipitated. Then a solution of 42 g. of NaNO₂ in 600 ml. of water is added with constant stirring; the mixture is heated to about 60°C and allowed to stand three hours (not longer) with occasional agitation. The oxidation, which produces γ -FeO(OH), proceeds with the evolution of considerable quantities of nitrogen oxides. The supernatant liquid is drained off; the precipitate is washed thoroughly with warm water until free of chloride and dried at 60°C in a drying oven. PROPERTIES:

Very friable deep-orange powder comprised of extremely fine needles. Can be converted to pure γ -Fe₂O₃ by heating in vacuum or in a dry air stream at about 250-400°C. On heating at higher temperatures, or in a scaled tube at 110°C, or even on very intensive grinding, the metastable preparations of the γ series are converted to the stable α modification.

Occurs in nature as lepidocrocite. Crystal structure: E04 type. For metastable 8-FeO(OH), see O. Kratky and H. Nowołny, Z. Kristallogr. (A) 100, 356 (1938).

REFERENCES:

O. Giemser. Ber. dtsch. chem. Ges. <u>71</u>, 158 (1938); R. Fricke and
 W. Zerrweck. Z. Elektrochem. <u>43</u>, 52 (1937); R. Fricke and
 G. Weitbrecht. Z. anorg. alig. Chem. <u>251</u>, 427 (1943); F.
 Wagenknecht. Kolloid-Z. <u>112</u>, 35 (1949).

Iron (III) Oxychloride

FeOCI

 $FeCl_3 \cdot 6H_7O + 5FeCl_3 = 6FeOCl + 12HCl_270.3$ 811.1 643.8 37.6

A mixture of 10 g. of $FeCl_3 \cdot 6H_2O$ and 35 g. of sublimed FeCl₃ is placed in a round, short-neck Pyrex reaction flask, fused on a steam bath, and allowed to solidify; then 15 additional g. of $FeCl_3$ is added. The reaction indicated above takes place when the mass is heated to 250-300°C (maximum). It is best to immerse the open flask rather deeply in an oil bath held at 250°C, so that no moisture condenses at the neck. The reaction is complete after 60-80 minutes, when no further evolution of HCl is observed.

The reaction mass, which converts to a solid red cake, is cooled and pulverized, washed briefly with a large amount of cold water and then with acctone (to remove excess $FeCl_3$), and dried in vacuum.

PROPERTIES:

Rust-colored powder consisting of small red needles. Free of Fe_3O_3 if made from sublimed FeCl₃ and if reaction temperatures no higher than 300°C are used. Disproportionates above 300°C into the oxide and chloride. Crystal structure: EO_3 type.

REFERENCE:

H. Schäfer, Z. anorg. Chem. 260, 279 (1949).

5.7

iron (II) Sulfide FcS

Fe + S = FeS55.8 32.1 87.9

Pure FeS of stoichiometric composition is obtained from pure reduced Fe and distilled S. Exactly weighed quantities of the two substances are sealed in a quartz tube evacuated in high vacuum, and are heated for about 24 hours at 1000°C; at higher temperatures, the quartz tube bursts. One then tests for completeness of the conversion: the reaction is complete if S no longer collects at that end of the hot tube which is cooled for test purposes. The lustrous gray product obtained is somewhat sintered and readily pulverized.

SYNONYM:

Ferrous sulfide.

PROPERTIES:

M. p. 1195°; d 4.84. Crystal structure: B 8 type.

REFERENCES:

H. Haraldsen, Z. anorg. allg. Chem. <u>231</u>, 81 (1937); G. Hägg and J. Sucksdorff, Z. phys. Chem. (B) 22, 444 (1933).

tron Nitrides

Fe₁N, Fe₁N

I.

 $4 \,\mathrm{Fe} \ \div \ 2 \,\mathrm{NH}_{3} \ = \ 2 \,\mathrm{Fe}_{2} \mathrm{N} \ \div \ 3 \,\mathrm{H}_{2}$ $223.4 \qquad 44.8 \,\mathrm{I}. \qquad 251.4 \qquad 67 \,\mathrm{I}.$

Fine $\operatorname{Fe}_{3}O_{3}$ powder is placed in a porcelain boat at 500°C and reduced as completely as possible with H₂; then, without allowing any air to penetrate, NH₂ is introduced at 350-550°C until the H₂ content of the exit gas decreases to a low, constant level. The product is then allowed to cool in the stream of NH₃. It corresponds in composition to the formula Fe₂N (theoretically 11.1% N), has the structure of Hägg's ζ phase, and exhibits a very narrow region of homogeneity. Often, however, the same composition yields a mixed crystal (solid solution) phase ϵ . On heating in vacuum at about 500°C the product is converted (with loss of N₂) 5.9% N).

27. IRON

H. Another method for preparing Fe_4N consists in heating reduced iron in the presence of an appropriate mixture of H_2 and NH_3 .

PROPERTIES:

Fe₂N: Formula weight 125.7; d 5.02.

Fe4N: Formula weight 237.4; d 6.57 (?). Crystal structure; L 10 type.

REFERENCES:

- G. Hägg, Z. phys. Chem. (B) 8, 455 (1930); also E. Lehrer. Z. Elektrochem. <u>36</u>, 388, 460 (1930); O. Eisenhut and E. Kaupp. Ibid. <u>36</u>, 394 (1930); S. Satoh. Bull. Chem. Soc. Japan 7, 315 (1932); abstract in Chem. Zentr. <u>1933</u>, 1, 752.
- St. Brunauer, M. E. Jefferson, P. H. Emmett and S. B. Hendricks. J. Amer. Chem. Soc. <u>53</u>, 1778 (1931); Ch. Guillaud and H. Creveaux. Comptes Rendus Hebd. Seances Acad. Sci. <u>222</u>, 1170 (1946); H. W. Kohlschütter and M. Pavel. Z. anorg. allg. Chem. <u>255</u>, 65, 73 (1947).

Iron Carbide

FeaC

It is best to start with electrolytic iron sheet; this is held over benzene vapor to deposit a layer of carbon, then baked for a long time in vacuum at 700°C and slowly cooled. To isolate Fe_3C the sheet is placed in a neutral $FeCl_2$ bath and used as an anode at the lowest possible current density. The bath is the same as used in the preparation of electrolytic iron. In this way very pure Fe_3C is left behind as a coarsely crystalline gray powder. It is washed with dilute acetic acid, water, alcohol and ether, and dried in vacuum.

Alternate methods: a) Iron carbide may also be isolated quantitatively while measuring the anode potential; see E. Houdremont, P. Klinger and G. Blaschczyk, Techn. Mitt. Krupp, Forschungsber. <u>4</u>, 311; Arch. Elsenbüttenw. <u>15</u>, 257 (1941).

b) Solution of white, low-Si pig iron in 1 N acetic acid; see O. Ruff and E. Gersten, Ber. dtsch. chem. Ges. 45, 64 (1912).

c) For the preparation of almost pure fused Fe₃C, see F, Wever, Mitt. KWI Eisenforschung <u>4</u>, 67 (1923).

SYNONYM:

Cementite.

PROPERTIES:

Formula weight 179.52. Hardness 3.2-3.3; d (15°) 7.66. Crystal structure: D011 type.

Sec.

H, LUX

The decomposition of Fe_3C to Fe and C proceeds at a high rate only above 1050°C. Below 500°C a carbide having the formula Fe_3C may also be obtained in various modifications [L. J. E. Hofer, S. M. Cohn and W. C. Peebles, J. Amer. Chem. Soc. 71, 189 (1949); H. H. Podgurski, J. T. Kummer, T. W. de Witt and P. H. Emmett, ibid. 72, 5382 (1950)].

REFERENCE:

G. Naeser, Mitt. KWI für Eisenforschung 16, 211 (1934).

Lithium Ferrate (III)

LiFeO₂

Obtained by heating to high temperature or fusion of an intimate mixture of Li_2CO_3 with fine Fe₂O₃ powder derived from FeC₂O₄. At temperatures above about 670°C, the stable modification is of the B1 type, with random distribution of the metal atoms; annealing at 570°C converts it to a nearly cubic tetragonal modification with ordered distribution.

Alternate method: Heating conc. LiOH solution with Fe_3O_3 at 600°C under pressure [E. Posniak and T. F. W. Barth, Phys. Rev. <u>38</u>, 2234 (1931)].

REFERENCE:

F. Barblan, E. Brandenberger and P. Niggli. Helv. Chim. Acta 27, 68 (1944).

Potassium Ferrate (VI)

K-FeO₄

I. BY OXIDATION WITH NEOCL:

 $2 \operatorname{NaOH} + \operatorname{Cl}_2 = \operatorname{NaOI} + \operatorname{NaOCI} + \operatorname{H_2O}$ ····· 80.0 70.9 58.5 74.5 $3 N_{a}OCl + 2 Fe(NO_{a})_{s} \cdot 9 H_{s}O + 10 N_{3}OH =$ 223.5 808.0 400.0 $2 \text{ Na}_{3}\text{FeO}_{1} + 6 \text{ NaNO}_{3} + 3 \text{ NaC}_{1} + 23 \text{ H}_{2}\text{O}_{2}$ 331.7 510.0 175.5 $Na_{4}FeO_{4} + 2KOH = K_{4}FeO_{4} + 2NaOH$ 165.9 112.2 198.0 80.0

A solution of 30 g. of NaOH in 75 ml. of water is cooled, and Ci_2 is admitted with vigorous stirring until a weight increase of

27. 180N

20 g. is recorded. The cooling rate should be such that the mixture temperature does not rise above 20°C. Then 70 g. of solid NaOH is added slowly and with constant stirring; the temperature is allowed to rise to 25-30°C to speed the dissolution. As soon as this is complete, the solution is cooled once again to 20°C and passed through a glass filter to remove the precipitated NaCl.

With the NaOCl solution held at 25-30°C, 25 g. of solid Fe(NO₃)₃. 9 H₂O is slowly added (stirring), the mixture is saturated with solid NaOH at 30°C, and the ferrate (VI) solution is either filtered through a coarse glass filter or, better, centrifuged.

The precipitation of K_aFeO_4 is carried out in a 250-ml, beaker by addition of 100 ml. of saturated KOH while stirring and cooling to 20°C. After precipitation, stirring is continued for five minutes; the compound is collected on a medium-porosity glass filter and redissolved by treatment with four or five 10-ml. portions of 3 M KOH. The solutions are combined in a 250-ml, beaker and 50 additional ml. of saturated KOH is added; after five minutes of stirring at 20°C the solution, which is now about 11 M in KOH, is filtered through a medium-porosity glass filter.

For further purification, the K_2 FeO₄ collected on the filter is treated with 10 ml. of benzene, then three to five times with 20-ml. portions of 95% ethanol (aldehyde-free), and finally stirred for 20 min. (in a large beaker) with 1000 ml. of 95% ethanol. This last treatment is repeated three additional times. The product is collected on a glass filter, washed in the absence of atmospheric moisture with 50 ml. of ether, and dried in a vacuum desiccator.

The yield is 45-75% of theoretical, the purity 92-96%. One further reprecipitation from 6 M KOH raises the purity to 98.5-99%.

II. ELECTROLYTIC METHOD:

 $F_e + 8 KOH = K_s F_e O_t + 8 K^+ + 4 H_s O + 8 e^{-1}$ 55.85 448.8 198.0

The electrolysis is conducted in a cylindrical vessel (95 mm. I. D. and 100 mm. high) in which a porous clay cell (50 mm. J. D. and 80 mm. high) is set. The cell is held in place by a parafilmsoaked cork ring in such a way that it touches the bottom of the cylinder. The anode is a strip of transformer iron sheet (0.3% Mn; 27 \times 3.7 cm. = 100 cm.² of surface on each side) which adheres closely to the outer wall. The cathode consists of a screen of iron wire rolled into a cylinder and placed inside the cell. The anode is welded to a thick, acetylene-flame-sleaned iron wire, which passes through the cork ring and is scaled by

with picein wax. The cork ring also carries a thermometer, a two-bulb pressure release tube containing 30% KOH, and a short tube (7 mm. I. D.) for removing samples.

Both cathode and anode are etched with 1:1 HCl shortly before the start of the experiment, and are then rinsed with water. The cylinder is now filled with 200 ml. and the cell with 60 ml. of freshly prepared 40% NaOH precooled to 25-28°C. The apparatus is assembled and cooled externally with ice water. To start with, the electrode intended as the anode is connected as the cathode and the electrolysis conducted for 3-5 min. at 3.5 amp. and 110 v. d.c. The resistance in the circuit should be about 30 ohms. The polarity is then reversed; the actual electrolysis takes four hours at 4.5 amp. (approximately 5.8 v.); the temperature in the anode space must never exceed 35°C.

The current is shut off and the anode electrolyte freed of traces of Fe(OH)₃ by centrifuging or filtering rapidly through a mediumporosity glass filter. The filtrate is cooled to 10°C, and 75 g. of KOH pellets is added with continued cooling and vigorous shaking. An additional hour at 0°C is allowed for completion of the reaction. The K_3FeO_4 precipitate is rapidly collected on a medium-porosity glass funnel, washed at once with ice-cold absolute methanol, and dried in vacuum over P_3O_5 . The anode electrolyte, which after four hours is about 0.15 M in ferrate (VI), affords about 5 g. of K_3FeO_4 with a purity of 95%. The main impurity is carbonate; in addition there is 0.1% Mn, as well as compounds passing into the solution from the earthenware cell. These could probably be avoided by using a cell made of polytetrafluoroethylene or a similar insterial. The current efficiency is about 25%.

PROPERTIES:

Small iustrous crystals, very dark violet to black; stable only when completely dry. Readily soluble in water; concentrated solutions decompose rapidly; very dilute solutions are much more stable. Chloride ions and FeO(OH) markedly accelerate the decomposition. The instability of solutions as a function of pH is described by J. M. Schreyer and L. T. Ockerman, Anal. Chem. 23, 1312 (1951).

i

i

REFERENCES:

 G. W. Thompson, L. T. Ockerman and J. M. Schreyer, J. Amer. Chem. Soc. <u>73</u>, 1379 (1951); H. J. Hrostowski and A. B. Scott. J. Chem. Phys. <u>18</u>, 105 (1950); B. Helferich and K. Lang. Z. anorg. Chem. <u>263</u>, 171 (1950); R. Scholder, H. von Bunsen, F. Kindervater and W. Zeiss, Z. anorg. allg. Chem. <u>282</u>, 268 (1955); L. Moeser, J. prakt. Chem. [2] <u>56</u>, 431 (1897). II. G. Grube and H. Gmelin. Z. Elektrochem. <u>26</u>, 160 (1920); modified directions based on unpublished experiments made together with H. Noeth.

Potassium tron (III) Sulfide

KFeS,

 $6 \text{ Fe} + 4 \text{ K}_{2} \text{CO}_{3} + 13 \text{ S} = 6 \text{ KFeS}_{2} + \text{K}_{4} \text{SO}_{4} + 4 \text{ CO}_{2}$ 335.0 525.8 416.5 954.4 174.3

An intimate mixture of 5 g. of Fe powder (obtained by reduction with H_2). 25 g. of K_3CO_3 , 5 g. of Na_4CO_3 , and 30 g. of S is slowly heated in a half-filled covered poroelain crucible until the mass flows smoothly; it is then held at bright-red heat for about one hour. A better method consists in heating the mixture (which is placed in a boat inserted in a porcelain tube) under nitrogen at 900-1000°C. In either case the crucible is cooled slowly and broken. The fragments of the melt are soaked in warm water, the solution being frequently decanted, until the only substance remaining in the flask is the reddish violet needles of KFeS₂ (semimetallic luster). If a considerable quantity of colloidal, amorphous product is obtained, the reaction temperature was not sufficiently high. The crystals are washed with water and alcohol and dried as rapidly as possible at 100°C. The yield is 12-14 g.; the theoretical yield, based on Fe, is 14.25 g.

PROPERTIES:

Formula weight 159.1. Insoluble in water; indefinitely stable in dry air.

REFERENCES:

K. Preis. J. prakt. Chem. <u>107</u>, 12 (1869); R. Schneider. Ibid. 108, 16 (1869).

Basic Iron (III) Sulfate

 $Fe_3(SO_4)_3(OH)_4 \cdot 2H_3O$ or $3Fe_3O_3 \cdot 4SO_5 \cdot 9H_8O$

 $3 \operatorname{Fe}_{t}(SO_{4})_{1} + 14 \operatorname{H}_{2}O = 2 \operatorname{Fe}_{3}(SO_{4})_{2}(OH)_{5} \cdot 2 \operatorname{H}_{2}O + 5 \operatorname{H}_{3}SO_{4}$ $Y_{1+2}: 120.0 25.2 96.1 42.0$

The basic sulfate, which is stable over a large temperature range (up to 170°C), is readily obtained in crystalline form by

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beating a scaled tube containing an approximately 20% solution of FegSO $_{3}$ at 150°C. The product is a fine, orange-yellow powder consisting of small, transparent, cubelike rhombohedra.

REFERENCES:

 E. Posniak and H. E. Merwin, J. Amer. Chem. Soc. <u>44</u>, 1965 (1922);
 N. V. Shishkin, Zh. Obsheh, Khim. <u>21</u>, 456(1951); Athanasesco. Comptes Rendus Hebd. Seances Acad. Sci. <u>103</u>, 271 (1886).

Basic Iron (III) Acetate

[Fe₄(CH₁COO)₄(OH)₇]CH₂COO · H₂O

 $Fe(OH)_{a} - 7 CH_{a}COOH = [Fe_{a}(CH_{a}COO)_{d}(OH)_{d}]CH_{b}COO \cdot H_{a}O + 6 H_{a}O$ 320.6 420.2 632.7

The monoacetate of the complex base, which occurs predominantly in the monoacidic form, crystallizes readily from dilute acetic acid (about 10% or 1.6 N). The triacetate is formed only from solutions containing at least 65% acetic acid by weight (11.4 N); these are allowed to stand in a vacuum desiccator over conc. H_2SO_4 .

To prepare the monoacetate, a very dilute FeCl₃ solution is treated at room temperature with aqueous NH_3 ; the precipitate is washed for several days with cold water, which is frequently decanted, and washed thoroughly again on a filter. The slurry of hydrated iron oxide thus obtained is dissolved (heating) in about an equal amount of acetic acid. Crystallization takes place if the solution is allowed to stand in an open dish for several days in a well-ventilated spot. After filtration, the salt is kept for some time over soda lime to absorb the acetic acid.

STNONYM:

Triiroa (III) hexaacetatodihydroxomonoacetate.

PROPERTIES:

Transparent, brick-red rhombic leaflets. Dissolves slowly in cold water, rapidly in hot water. Only sparingly soluble in acetic acid.

REFERENCES:

 A. Krause. Z. anorg. alig. Chem. <u>169</u>, 286 (1928); R. Weinland and E. Gussmann. Ber. dtsch. chem. Ges. <u>42</u>, 3888 (1909); Z. anorg. Chem. <u>66</u>, 157 (1910). 27. IRON

Hexacyanoferric (II) Acid

H₄Fe(CN)₅

$\begin{array}{rrrr} K_{4}Fe(CN)_{6} \cdot 3 H_{7}O &+ 4 HCl &+ 2 (C_{2}H_{3})_{8}O &= \\ & 422.4 & 145.9 & 146.2 \\ H_{4}Fe(CN)_{6} \cdot 2 (C_{2}H_{3})_{7}O &+ 4 KCl &+ 3 H_{2}O \\ & 364.1 & 298.2 \end{array}$

A solution of 42 g. of K_4 Fe(CN)₆ · $3H_2O$ in 350 ml. of water is mixed with 100 ml. of conc. HCl (d 1.19); any KCl which separates is redissolved by addition of some water. After thorough chilling, about 50 ml. of ether is added. The etherate separates in several hours as colorless tablets. These are filtered off, washed with a small quantity of dilute HCl containing some ether, and redissolved in 50 g. of alcohol. After residual undissolved KCl is removed by filtration, the compound is reprecipitated by addition of 50 g. of ether, filtered off, and washed with ether. It is finally transferred to a round flask and converted to H_4 Fe(CN)₆ by heating at 40-50°C in aspirator vacuum.

SYNONYMS:

Hydrogen hexacyanoferrate (II), ferrocyanic acid.

PROPERTIES:

Snow-white when pure. $d(25^{\circ})$ 1.536. Indefinitely stable if dry; gradually becomes blue in moist air. Elimination of HCN begins at about 100°. Readily soluble in water or alcohol; insoluble in ether or acetone. The bright lemon-yellow aqueous solution docomposes on heating or in light. Solubility (14°) 13 g./100 g, of aqueous solution.

REFERENCES:

W. Biltz, Z. anorg. allg. Chem. <u>170</u>, 161 (1928); A. Mittasch and E. Kuss. Z. Elektrochem. <u>34</u>, 159 (1928).

Ammonium Hexacyanoferrate {||}

(NH4)4Fe(CN)4

 $H_4Fe(CN)_8 + 4NH_5 = (NH_4)_4Fe(CN)_4$ 216.0 68.1 284.1

To prepare a completely potassium-free salt, a conc. aqueous solution of pure hexacyanoferric (II) acid is neutralized with pure 10% aqueous NH_3 ; the salt which precipitates is collected, washed several times with alcohol and then with ether.

PROPERTIES:

Readily soluble in water, insoluble in alcohol. In vacuum, decomposition begins above 100°C.

REFERENCE:

A. Mittasch and E. Kuss. Z. Elektrochem. 34, 59 (1928).

Hexacyanoferric (III) Acid

H₂Fe(CN)₁

$K_3F_2(CN)_5 + 3 HCl = H_3F_2(CN)_4 + 3 KCl$ 329.3 109.4 214.9 223.7

Cold saturated $K_3Fe(CN)_6$ solution (40 ml.) is treated slowly and in the cold with 40 ml. of fuming HCl; the mixture is allowed to stand in an ice bath with frequent agitation for about half an hour. The KCl precipitate is removed by filtration and the filtrate is shaken with 70 ml. of ether. Three layers are formed; aqueous, oily and ethereal. After draining the aqueous layer, the middle, oily layer is allowed to clarify. It is then separated from the ether layer and the oil is completely freed of ether under vacuum. This results in crystallization of a yellow etherate of $H_3Fe(CN)_6$; finally, however, pure $H_3Fe(CN)_6$ remains as a brown mass. The acid may be recrystallized by solution in absolute ethanol and evaporation of the solvent. The compound must not be allowed to contact metal or rubber and should be kept as dry as possible.

SYNONYM:

Hydrogen hexacyanoferrate (iii), ferricyanic acid.

PROPERTIES:

Rather readily soluble in water and alcohol; unlike $H_4Fe(CN)_5$, it is also soluble in ether-alcohol mixtures. The aqueous solution is yellow to brown.

REFERENCE:

W. M. Cumming and D. G. Brown, J. Soc. Chem. Ind. Trans. <u>44</u>, 110 (1925). Charles Street

27. IRON

Sodium Hexathiocyanoferrate (HI)

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Na,Fe(SCN), · 12 H₂O

| Fe(OH)_ + | 3 HSCN | + 3 NaSCN | + 9H,O | = Na ₄ Fe(SCN) ₄ · 12 H ₄ O |
|-----------|--------|-----------|--------|--|
| 106.9 | 177.2 | 243.3 | | 689.4 |

Aqueous HSCN solution is added in the cold to a known amount of freshly precipitated and well washed hydrated iron (III) oxide until the solid is barely dissolved. Then NaSCN is added until about nine moles of NaSCN are present for each mole of $Fe(SCN)_3$. The solution is allowed to stand in a desiccator over conc. H_2SO_4 for several weeks; very dark-red crystals, which exhibit an intense green color when viewed by reflected light, separate out. On further evaporation of the mother liquor, precipitation of NaSCN also begins; on heating, the Fe^3 ⁺ is partly reduced.

SYNONYM:

Sodium iron (III) thiocyanate.

PROPERTIES:

Deliquescent in air; converted to the trihydrate by storage over conc. H_2SO_4 . Soluble in alcohol, giving a permanganatelike violet color; may be recrystallized from such solutions without decomposition.

REFERENCES:

G. Krüßs and H. Moraht. Liebigs Ann. 260, 209 (1890); A. Rosenheim and R. Cohn. Z. anorg. Chem. 27, 295 (1901); H. I. Schlesinger and H. B. van Valkenburgh. J. Amer. Chem. Soc. 53, 1215 (1931).

Sodium Pentacyanoamminoferrate (II)

Nar[Fe(CN),NH.] · 3 H.O

 $Na_{2}[Fe(CN)_{5}NO] \cdot 2 H_{2}O + 2 NH_{3} + NaOH$ 998.0 34.1 40.0

 $= Na_9 [Fe(CN)_5 NH_3] \cdot 3 H_4 O + N_2 + H_4 O$

A mixture of 30 g. of $Na_{s}[Fe(CN)_{5}NO] \cdot 2 H_{2}O$ with 120 ml, of water is prepared and cooled in an ice-salt mixture. Ammonia is then introduced at +10°C until saturation; the temperature during

this operation must not exceed 20°C. The solution is allowed to remain under a loose cover for several hours (not longer) at 0°C, and the crystals which separate from the deep brownishyellow solution are collected by filtration. The remainder of the compound can be precipitated from the solution by addition of CH₃OH. The product may be purified by solution in some cold water, from which it is precipitated as fine, bright-yellow needles by careful addition of 90% alcohol.

The hexabydrate is hygroscopic and readily loses NH_3 . It is dried to constant weight by storing for several days in a vacuum desiccator over CaCl₂. It then contains three (or, according to Hölzl, 2.5) moles of H₂O. Yield: 24 g. (73%). The yellow aqueous solution decomposes on heating, precipitating the hydroxide.

REFERENCES:

K. A. Hofmann, Z. anorg. Chem. <u>10</u>, 264 (1895); W. Manchot, E. Merry and P. Woringer. Ber. dtsch. chem. Ges <u>45</u>, 2876 (1912);
 F. Hölzl and K. Rokitansky. Monatsh. Chem. <u>56</u>, 82 (1930).

Sodium Pentacyanoamminoferrate (I)!)

Na₂[Fe(CN)₂NH₁] · H₁O

$$\begin{split} & Na_{3}[Fe(CN)_{4}NH_{3}] \cdot 3 H_{2}O + NaNO_{2} + CH_{2}COOH = \\ & 328.0 & 69.0 & 60.0 \\ & Na_{2}[Fe(CN)_{4}NH_{3}] \cdot H_{2}O + NO + NaOH + CH_{3}COON_{2} + 2 H_{2}O \\ & 268.9 & 30.0 & 40.0 & 82.0 \\ \end{split}$$

A solution of 20 g. of NaNO₃ in 50 ml. of water is treated at 0°C with 20 ml. of 30% acetic acid and then with 30 g. of Na₃[Fe-(CN)₅NH₃] · 3H₂O. After two hours, 1:1 alcohol-ether is added; this first precipitates a violet aquo complex salt (formed in a side reaction); further addition of the alcohol-ether mixture precipitates the desired salt. This is purified by repeated solution in cold water and reprecipitation with alcohol. The dark-yellow powder is dried to constant weight in vacuum over conc. H₂SO₄; it then contains one or two moles of water.

The salt dissolves readily in water, giving a brownish-red color.

REFERENCES:

K. A. Hofmann. Liebigs Ann. <u>312</u>, 24 (1900); F. Hölzl and K. Rokitansky. Monatsh. Chem. <u>56</u>, 82 (1930).

SECTION 28

Cobalt, Nickel

O. GLEMSER

Metallic Cobalt

I. Prepared by reduction of precipitated cobalt oxalate with hydrogen.

Cobalt oxalate, precipitated in the cold, is dried at 120°C and ground to a fine powder. It is then reduced with H_2 (six hours at 500°C), with the temperature being raised rapidly at the beginning of the run. The product is cooled, ground and reduced once more; the fine metal powder is stored in a glass vessel under alcohol.

II. VERY PURE COBALT

Impurities, principally Fe, Cu and Ni, are removed by various precipitation reactions and by electrolysis. Finally, very pure Co is deposited electrolytically from a $CoSO_4$ solution. According to Kershner, Hoertel and Stahl, the pure metal still contains 0.001-0.002% Ni, 0.001-0.003% Fe, a maximum of 0.001% Cu, and 0.005% S.

A) REMOVAL OF IMPURITIES

A solution of the cobalt (II) salt is treated with Na₂CO₃ \cdot 10 H₂O, added in small portions and with stirring, until the pH reaches 3.5; then 1 N Na₃CO₃ solution is added until the cobalt carbonate just barely precipitates. The precipitated carbonates are removed by filtration. Following this, 8 ml. of a saturated aqueous solution of 1,2-cyclobexanedione dioxime is added for each 10 mg. of Ni, Cu and Fe present in the filtrate. The Ni precipitates out; the suspension is heated for one hour at 90-95°C with occasional stirring, and the precipitate is filtered off.

The solution, which should now contain about 10% Co, is adjusted to a pH of 5.5 with H_2SO_4 or Na_2CO_3 . Then, 0.2 moles of pyridine is added per liter of solution; the latter is electrolyzed

at 25°C (stirring), using a mercury cathode (206 cm.² of surface area) and a platinum sheet anode. The cathode potential stays constant at 0.78 volt. At a Ni content of 0.05-0.10 g./liter of solution, the electrolysis requires eight hours; at a level of 0.5 g. of Ni/liter, it takes 24-32 hours.

After the electrolysis, the solution is filtered and the $Co(OH)_{S}$ precipitated from the filtrate by addition of NaOH. The precipitate is washed by decantation with hot distilled water until the odor of pyridine is no longer apparent. The precipitate is then filtered off and dissolved in dilute H_2SO_4 in such a way as to give a solution containing 90-100 g. of Co. This solution then constitutes the starting material for the electrolytic separation of the metal (see the following).

B) SEPARATION OF THE METAL.

The electrolysis cell is a 4-liter beaker with a side arm through which the solution can overflow into a collecting vessel. To avoid contamination from external sources, the cell and collecting vessel are placed in a glass cabinet. The solution is passed through the cell at 1-2 liters per hour, the pH being maintained at 1.2-1.6 by addition of the pyridine-free $CoSO_4$ solution. The electrolysis conditions are: 50-55 °C, three platinum anodes and two titanium cathodes (the latter having about the same surface area as the anodes), cathode current density 40 amp./in.² The deposit of highly purified cobalt can be removed from the titanium cathodes.

To avoid accumulation of impurities in the electrolyte, the latter is periodically (as the need arises) reprocessed according to the procedure given in subsection A on removal of impurities (filtration, precipitation, washing and redissolution in H_3SO_4).

Alternate method: Reduction of CoO or Co_3O_4 with H₂ for five hours at 500°C (Gmelin, 8th ed., volume on cobalt).

PROPERTIES:

Atomic weight 58.94. Black metallic powder. M. p. 1492°C, b.p. 3183°C. Ferromagnetic. Readily soluble in dil. HNO₃; passivated by conc. HNO₃.

REFERENCES:

 W. Biltz. Z. anorg. allg. Chem. <u>134</u>, 25 (1924); G. F. Hültig and R. Kassler. Z. anorg. allg. Chem. <u>187</u>, 24 (1930). II. K. K. Kershner, F. W. Hoertel and J. C. Stahl. U. S. Dept. Interior, Bur. Mines Rep. invest. 1956, I (Chem. Zentr. 1957, 255). 28. COBALT, NICKEL

Cobalt (II) Chloride

CoCl,

 $CoCl_{z} + 8 SOCl_{z} = CoCl_{z} + 12 HCl + 6 SO_{s}$ (6H_zO) 238.0 713.9 129.9 437.6 384.4

Fine $CoCl_2 \cdot 6H_2O$ powder is placed in a flask provided with a ground joint and is covered with $SOCl_2$. The mixture is refluxed for several hours. The excess $SOCl_2$ is then evaporated on a steam bath. The $SOCl_2$ which clings to the product is removed by repeated evacuation of the flask.

H. $C_0(CH_3COO)_2 \cdot 4H_2O + 6CH_3COCI =$ 249.1 471.0 $C_0Cl_2 + 2(CH_3CO)_2O + 4CH_3COOH + 4HCI$ 129.9 204.2 240.2 145.9

A Pyrex tube 18×200 mm. is charged with 4.0 g. of fine $Co(CH_3COO)_a \cdot 4H_2O$ powder. It is then closed off with a rubber stopper; the latter carries a dropping funnel and a fritted-glass filtering finger. Then, 15 ml. of benzene is added with agitation (magnetic stirrer), followed by CH_3COCI (slow addition until about 10% excess). The mixture is stirred for 30 minutes, the $CoCl_a$ precipitate allowed to settle, and the mother liquor siphoned off through the filtering finger. The residue is treated with benzene and CH_3COCI to complete the reaction. The supernatant liquid is removed by filtration and the CoCl_a is washed three or four times with anhydrous benzene; it is then dried for two hours at 150°C under nitrogen.

Alternate methods: a) Heating of $CoCl_2 \cdot 6H_2O$ with $COCl_2$ in a sealed tube at 200°C (H. Hecht (1947)).

b) Heating of CoCl₂ · 6 H₂O in a stream of dry HCl at 160-170°C
 [G. L. Clark, A. J. Quick and W. D. Harkins, J. Amer. Chem. Soc.
 42, 2483 (1920)]. Simple heating at 140°C yields a somewhat basic salt.

PROPERTIES:

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Leaflets, coloriess in very thin layers, pale blue in layers over 1 mm. thick. M. p. 735°C, b. p. 1049°C; d_2^{15} 3.367. Heat of formation (25°C): -77.8 kcal./mole. Decomposes on long heating in air at 400°C. Sublimes at 500°C in HCl gas, forming loose crystalline fragments. Hygroscopic. Solubility in H₄O (g. of CoCl₂/100 g. of solution): 29.5 (0°C); 34.86 (20°C); 51.93 (98°C). Soluble inf methanol, ethanol, acetone, pyridine and other. Crystal structure: C19 type.

REFERENCES:

- 1. H. Hecht. Z. anorg. Chem. 254, 51 (1947).
- E. G. W. Watt, P. S. Gentile and E. P. Helvenston, J. Amer. Chem. Soc. 77, 2752 (1955).

Hexaamminecobalt (II) Chloride

[Co(NH₁)₁]Cl₂

 $C_0Cl_s + 6 NH_s = [C_0(NH_s)_s]Cl_s$ (6H.O) 232.0102.2 235.0

A mixture of 15 g. of CoCl₂ · 6 H₂O and 14 ml. of H₂O is heated to boiling in the absence of air and treated hot with sufficient conc. NH₃ to produce complete solution; the solution is then filtered, Descrated alcohol (air boiled out under reflux) is added to the hot filtrate until a permanent clouding is just barely obtained. The solution is cooled in running water and the solid thus precipitated is filtered off. It is washed with 1:1 conc. NH₃: alcohol, then with the same mixture in 1:2 ratio, and lastly with deaerated, NH3saturated alcohol. The product is dried over KOH in a high vacuum, Yield: 7g.

The precipitation, washing, filtration and drying must be carried out in an O₂-free atmosphere (for technique see Part I).

Alternate method: Passage of NHa over CoCla at room temperature [W. Biltz and B. Fetkenheuer (1914)].

FROPERTIES-

Fiesh-colored powder or rose-red crystals. In high vacuum over H2SO4 (65-67°C), converts to blue trans-[CoCl2(NH4)2]. Relatively stable to O2 when dry; gradually oxidized in air when moist. Readily soluble in dil. ammonia, sparingly soluble in conc. ammonia, insoluble in alcohol. d25 1.479. Crystal structure: J11 (K₂PtCl_s) type.

RETERENCE:

W. Blitz and B. Fetkenheuer, Z. anorg. alig. Chem. 89, 97 (1914).

28. COBALT, NICKEL

Cobalt (II) Bromide

CoBra, CoBra 6 HaO

ANHYDROUS CoBr,

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 $CoBr_{s} \cdot 6 H_{s}O = CoBr_{s} + 6 H_{s}O$ S28.9 = 218.8 = 108.1

Prepared by careful heating of $CoBr_3 + 6H_3O$ to 130-150°C, followed by sublimation in high vacuum at 500°C.

II. Treatment of $Co(CH_3COO)_2 \cdot 4H_2O$ with CH_3COBr in benzene in a manner analogous to the preparation of $CoCl_2$.

Alternate methods: a) Heating of CoBr₂ · 6H₃O in a stream of HBr at 500°C [G. Crut. Bull. Soc. Chim. France [4] <u>35</u>, 550 (1924)].

b) Allowing $CoBr_2 + 6H_2O$ to stand for one week over conc. H_2SO_4 [G. L. Clark and H. K. Bruckner (1922)].

PROPERTIES:

Green solid or lustrous green crystalline leaflets. M. p. 678° (under HBr and N_2); d_1^{25} 4.909. Heat of formation: -63.8 koal./mole. Hygroscopic; in air, transforms to CoBr₂ · 6 H₂O. Readily soluble in H₂O (red color). Saturated aqueous solution contains 66.7 g. of CoBr₂ at 59°C, 68.1 g. at 97°C (per 100 g. solution). Readily soluble in methanol, ethanol, acctone and methyl acctate; sparingly soluble in tetranitromethane. Crystal structure: C6 type.

REFERENCES:

G. L. Clark and H. K. Bruckner, J. Amer. Chem. Soc. 44, 230 (1922); W. Biltz and E. Birk, Z. anorg. allg. Chem. 127, 34 (1923); G. W. Watt, P. S. Gentile and E. P. Helveston, J. Amer. Chem. Soc. 77, 2752 (1955).

CoBrs · 6 H,O

Precipitated cobalt carbonate is dissolved in aqueous HBr (d 1.49). The solution is heated on the steam bath until a deep blue color appears; it is then concentrated by evaporation on the steam bath. Cooling in ice water precipitates crystals of the hexahydrate; these are filtered off and washed with ice water

PROPERTIES;

Formula weight 326.88. Red crystals. M.p. 47-48°C; d_4^{36} 2:46: Deliquescent in air. All water is removed by standing over const H₂SO₄ or by heating to 130-140°C. REFERENCE:

G. L. Clark and H. K. Bruckner, J. Amer. Chem. Soc. 44, 230 (1922).

Cobalt (II) Iodide

a-Col₂, β-Col₂, Col₂ · 6 H₂O

u-Col,

 $C_0 + 2 HI = Col_2 + H_2$ 58.9 255.8 312.8 22.41.

Fine Co powder obtained from cobalt oxalate is heated to 400-500°C in a stream of HI (4-5 hours). The product iodide is melted by heating to 550°C and allowed to cool in high vacuum.

PROPERTIES:

Black, graphitelike solid. M.p. 515-520 °C (in high vacuum); d²⁶ 5.584. Heat of formation: -39.13 kcal./mole. Solubility in H₃O: 58.7% (-2°C); 66.4% (25°C); 80.9% (111°C). Dilute solutions are red; concentrated solutions are red at low temperatures, while at higher temperatures all shades from brown to olive green are present. Very hygroscopic, becomes blackish green in air. Soluble in SOCl₂, POCl₃. Crystal structure: C 6 type.

REFERENCE:

W. Biltz and E. Birk. Z. anorg. allg. Chem. 127, 34 (1923).

β-CoI₂

Sublimation of α -CoI₂ in high vacuum yields β -CoI₂.

The starting α -Col₂ is placed at location a of the tube shown in Fig. 333 and heated slowly in a high vacuum to 570-575°C. Cobalt metal remains as a residue at a, and a black sublimate of α -Col₂ is deposited at b. Ochre-yeilow β -Col₂ appears at c, as do the l₂ crystals present in the tube. The tube is placed in a horizontal furnace in such a way that the section from a to d is at 100°C. The section projecting from the furnace is fanned with a flame until all l₂ collects at c. The loosely adhering β -Col₂ is shaken from c into f. The apparetus is filled with N₂, and f with its contents is sealed off. About 0.8 g. of β -Col₂ is obtained from 10 g. of α -Col₂.

Fig. 383. Sublimation of cobalt(II) iodide,

28. COBALT, NICKEL

PROPERTIES:

Ochre-yellow powder. d_{2}^{25} 5.45. Very hygroscopic; deliquescent in moist air, forming green droplets. Solution in H₂O is colorless, becoming rose-colored on heating. Blackens at 400 °C and converts to α -Col₂.

REFERENCE:

E. Birk and W. Biltz. Z. anorg. allg. Chem. 128, 46 (1923).

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Colt 6 HrO

Precipitated cobalt carbonate or $Co(OH)_3$ is dissolved in aqueous HI. The solution is concentrated on a steam bath to a sirupy consistency and is then allowed to cool. The product is filtered off and washed with some water.

Alternate method: A solution of Coi_2 in water is cooled to a low temperature [G. L. Clark and H. K. Bruckner, J. Amer. Chem. Soc. <u>44</u>, 230 (1922)].

PROPERTIES:

Formula weight 420.86. d 2.90. Long, dark-red crystals, which begin to lose water of crystallization above 27°C and become anhydrous at 130°C.

REFERENCES:

O. Erdmann, J. prakt, Chem [1] 7, 254 (1836); A. Étard. Ann. Chim. Phys. [7] 2, 503 (1894).

Cobalt (II) Oxide

CoO

Prepared by thermal decomposition of cobalt salts containing a volatile acid moiety.

Cobalt carbonate, precipitated from $Co(NO_3)_2 \cdot 6H_2O$ with aqueous Na_2CO_3 in the absence of air, is heated for several hours in high vacuum at 350°C.

Analysis for active oxygen is necessary (treatment with hydrochlorio acid and determination by the Bunsen method).

Alternate method: (The product is less certain to have the composition CoO): heating of $Co(NO_3)_3 = 5H_2O$ or Co.C. 10, 1000°C and cooling in a stream of N₂.

PROPERTIES:

Formula weight 74.94, d_1^{16} 6.47. Heat of formation: -57.5 kcal./mole. Olive-green powder; takes up O₂ from air at room temperature. Becomes brown, and finally black, as the oxygen content increases. Stable in air when calcined at a high temperature. Converts to Co₃O₄ on heating in air at 390-900°C. Readily soluble in HCl, H₂SO₄ and HNO₃. Fine CoO powder is also soluble in conc. alkali. Crystal structure: B1 (NaCl) type.

REFERENCE:

M. Le Blanc and E. Moebius, Z. phys. Chem. (A) 142, 151 (1929).

Cobalt (II,III) Oxide

Co₁O₆

Precipitated cobalt carbonate is heated for one hour at 700°C, Analysis for active oxygen is required (treatment with hydrochloric acid and determination by the Bansen method).

Alternate methods: a) Heating of $Co(NO_3)_2 + 6 H_2O$ at 700°C (crucible, one hour) (J. A. Hedvall and T. Nilson).

b) Heating of CoO in air at 700°C [L. Wöhler and O. Balz, Z. Elektrochem. 27, 406 (1921)].

FROPERTIES:

Formula weight 240.82, d 6.073. Heat of formation: -206.1 kcal./mole. Blackish-gray powder. Converts in air to CoO (905-925°C). Coarse crystalline Co₃O₄ is attacked only by conc. H₂SO₄; fine powder dissolves slowly in acids. Crystal structure: H 11 (spinel) type.

SEFERENCE:

J. A. Hedvall and T. Nilson, Z. anorg. allg. Chem. 205, 425 (1932).

Cobalt (III) Hydroxide

CoO(OH)

 $\begin{array}{rcl} \textbf{Co(NO_{4})_{6}} &+ 3 \text{ KOH } + \frac{1}{2} \text{ Br}_{8} &= \text{CoO(QH)} + 2 \text{ KNO}_{8} + \text{ KBr} + \text{H}_{9}\text{O} \\ \hline \textbf{SH_{0}} \\ \textbf{SH_{0}} \\ \textbf{SH_{1}} & 168.3 & 79.8 & 91.9 & 202.2 & 119.0 \end{array}$

A DESCRIPTION OF A DESC

A solution of 56 g. of KOH in 300 ml. of H_2O is added dropwise (stirring) to a solution of 90 g. of $Co(NO_3)_2 + 6H_2O$ and 12 ml. of

Br₂ in 1300 ml. of H₂O. The resulting precipitate settles in alimit three hours. It is washed by decantation with four 5-liter portents of CO₂-free water. Should the precipitate undergo peptization on repeated addition of wash water, it is filtered on a Zsigmondy membrane filter, suction-dried and slurried in five liters of CO₂-free water. The slurry is filtered as above and the solid dried in a vacuum desiccator over conc. H₂SO 4.

All operations (precipitation, decantation and filtration) must be conducted in a CO_2 -free atmosphere. After drying in the vacuum desiccator, this precaution is no longer necessary.

Alternate methods: a) Air oxidation of a solution of $CoCl_{a} \cdot 6H_{a}O$ in aqueous NaOH [W. Feitknecht and W. Bédert, Helv. Chim. Acta 24, 683 (1941)].

b) Precipitation of $[Co(NH_3)_6]Cl_3$ with aqueous KOH [G. F. Huitig and R. Kassler (1929)].

ANALYSES RÉQUIRED:

Co (electrolytic), H_3O , CO_3 , and active oxygen (treatment with hydrochloric acid and determination by the Bunsen method). Used as an oxidation catalyst.

PROPERTIES:

Black powder. d 4.29-4.90. Converts to Co_3O_4 on heating in vacuum at 148-150°C. Dissolves in HCl, evolving Cl_3 . Soluble in HNO₃ and H₂SO₄. Not attacked by aqueous alkali or ammonia. Solution in organic acids such as oxalic or tartaric, accompanied by reduction.

REFERENCE:

G. F. Hüttig and R. Kassler. Z. anorg. allg. Chem. 184, 279 (1929).

Cobalt (II) Hydroxide

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Co(OH)

 $Co(NO_3)_2 + 2 KOH = Co(OH)_2 + 2 KNO_3$ (6 H₂O) 281.1 112.2 93.0 202.2

ROSE-COLORED Co(OH)2

A solution of 40 g. of $Co(NO_3)_2 \cdot 6H_2O$ in 1000 g. of H₂O, cooled to 0°C, is added dropwise and with vigorous shaking to a solution of 40 g. of KOH in 500 g. of H₂O maintained at 0°C. The initial blue color of the precipitate rapidly turns to rose. The precipitate is washed by decantation with CO_{2} - and O_{2} -free water with K^{+} and NO_{3}^{-} ions can no longer be detected. It is then filtered off and dried in a desiccator over 50% H₂SO₄.

Precipitation, washing, filtration and drying must be carried out in an atmosphere free of CO_2 and O_2 , since $Co(OH)_2$ oxidizes very readily (for technique, see Part 1).

ANALYSES REQUIRED:

Co (electrolytic) H₂O and CO₂.

PROPERTIES:

Rose-red powder. d_4^{18} 3.597. Heat of formation: - 63.4 kcal. per mole. Converts to CoO + H₂O when heated in vacuum at 168°. Oxidation leads to higher cobalt hydroxides. Readily soluble in acids, insoluble in dil. alkalies, appreciably soluble in ammonia. Crystal structure: C 6 type.

REFERENCE:

G. F. Hüttig and R. Kassler. Z. anorg. alig. Chem. 187, 16 (1930).

BLUE Co(OH)2

A small excess of NaOH solution is added to a 0.1 M cobalt sait solution containing about 1% glucose. The precipitate is thoroughly washed in the absence of air with aqueous alcohol, aqueous acetone and finally with pure acetone. It is then dried. The resulting blue hydroxide changes color very readily on drying (oxidation).

When only small quantities are needed, 5 ml. of the 0°C, 0.1 M cobalt salt solution is treated with 5.2 ml. of 0°C, carbonatefree 0.2 N NaOH in a small Erlenmeyer flask. The precipitate and the mother liquor are poured at once into a centrifuge tube chilled in ice-salt mixture and frozen. The tube, containing the frozen block of solution plus precipitate, is then removed from the ice-salt bath; as soon as the block detaches from the glass tube it is crushed in a porcelain mortar and melted in the centrifuge tube by addition of 25% alcohol. The precipitate is rapidly centrifuged and washed twice with chilled aqueous acetone and with pure acetone. The acetone clinging to the blue precipitate is evaporated in vacuum.

PROPERTIES:

Blue powder. Constitution: "double-layer lattice," related to C 6 type.

States Barnes

REFERENCE:

W. Feitknecht. Helv. Chim. Acta 21, 766 (1938) and private compmunication.

Cobalt Sulfides

CoS, CoS2, Co1S4, Co4S4

a-CoS

 $\begin{array}{rcl} Co(NO_4)_t &+ H_2S &= CoS + 2 HNO_8 \\ (6H_1O) \\ 291.1 & 22.1 \, l, & 91.0 & 128.0 \end{array}$

Precipitated in the same way as α -NiS. The product is dried for 90 hours, with the temperature raised slowly from 100 to 540°C. The sulfide dried at 300°C is pyrophoric.

Catalyst for pressure hydrogenation of organic compounds.

PROPERTIES:

Black powder, soluble in HCl. Forms Co(OH)S in air. Amorphous (by x-ray analysis). Heat of formation: -21.71 kcal./mole.

REFERENCE:

E. Dönges, Z. anorg, Chem. 253, 346 (1947).

β-CoS

 $C_0 + S = C_0S$ 58.9 82.1 91.0

Fine Co powder is mixed with the stolchiometric quantity of fine S powder and heated at 650°C for 2-3 days in an evacuated, sealed quartz tube. The tube is then quenched in cold water.

Analyses for Co and S are necessary. The compound is used as catalyst in the hydrogenation of organic compounds.

Alternate method: A 1 N solution of CoCl₃ is treated with accetic acid and precipitated with H₂S; workup is the same as in the case of α -CoS.

PROPERTIES:

Gray powder. M.p. 1135°C; d 5.45. Soluble in acids. Crystal structure: B8 type. Long heating at 200°C produces a modification with a complicated structure. Material with an overall formula $CoS_{1,0}$ is not homogeneous; the CoS phase has the composition $CoS_{1,0,4}$ - $CoS_{1,13}$. REFERENCES:

D. Lundquist and A. Westgren. Z. anorg. allg. Chem. 239, 85 (1938); E. Dönges. Z. anorg. Chem. 253, 346 (1947).

CoS,

L
$$C_0 + 2.5 - C_0 S_y$$

59.9 64.1 123.1

Stoichiometric quantities of Co and S powders are mixed and reacted in the same way as described in the case of β -CoS.

II. REACTION OF H₂S WITH COBALT (III) COMPLEXES

Dry, Ha-free HaS is allowed to react with [Co(NHa) 5C1]C12 or [Co(NH₃)elCl_a. The temperature is raised to 600-630 °C over a period of one hour, and maintained at this level for two hours. The product is allowed to cool to 200°C in the stream of H-S: then the H₂S is displaced with dry CO₂ and the product is cooled further. It is sensitive to air; it is heated with S in a sealed tube (one day at 750°C), and the excess S is extracted with CS2 after the reaction is complete.

Analyses for Co and S are required. Used as a catalyst in organic syntheses.

PROPERTIES:

Gray-black crystalline powder; d 4.269. Liberates S when beated in absence of air. Not attacked by nonoxidizing acids or alkalies. Crystal structure: C 2 type.

REFERENCES:

- I. D. Lundquist and A. Westgren. Z. anorg. allg, Chem. 239, 85 (1938).
- II. O. Hülsmann and W. Biltz. Ibid. 224, 73 (1935).

Co,S, (H11 type) and Co,S, (cubic crystalline) are prepared in the same way as β -CoS: heating stoichiometric quantities of Co and S powders in an evacuated, sealed quartz tube at 650°C. [D. Lundquist and A. Westgren (1938)].

Cobalt (III) Sulfate

Co:(SO:): · 18 H:O

A sulfuric acid solution of CoSO 4 · 7 H₂O (formula wt. 281.11 is anodically oxidized at 0°C.

A porous clay cell (about 120 ml. capacity) is changed with a solution of 24 g. of $CoSO_4 \cdot 7H_3O$ in 75 ml. of warm $8 NH_3SO_4$. A cylindrical Pt sheet (4 cm. high, 12 cm. wide), which serves as anode, is also inserted. A Pt wire welded to the sheet serves as the electrical lead. A Cu cylinder (8 cm. high) with a suitable electrical lead is placed around the clay cell and serves as the cathode. The cathode electrolyte is 8 NH_2SO_4. The electrolysis vessel is cooled in ice water. The electrolysis starts when the anode electrolyte has reached $30^{\circ}C$ and takes about 12 hours. The thick, deep-blue suspension is rapidly filtered through a fritted-glass funnel and is then pressed dry on a clay plate with a Pt spatula.

Alternate method: Gaseous fluorine is passed through an icecold solution of 24 g. of CoSO . 7 H₂O in 150 ml. of 8 N H₂SO . (F. Fichter and H. Wolfmann, Helv. Chim. Acta <u>9</u>, 1093 (1926)].

PROPERTIES:

Formula weight 730.37. Lustrons, blue-green leafiets. Decomposes rapidly in ice-cold water, liberating O_2 and yielding $CoSO_4$. Dilute H_2SO_4 gives a green solution which is stable for several days. Aqueous NaOH precipitates CoO(OH). Decomposes rapidly when heated in dry air, forming a brown (later reddish) powder. Powerful oxidizing agent.

REPERENCE:

E. Muller. Elektrochem. Praktikum (Laboratory Manual for Electrochemistry), 5th ed., Leipzig, 1940, p. 218.

Cobalt Aluminate

CoAl,O.

 $C_0O + Al_2O_3 = C_0Al_1O_4$ 74.9 102.0 178.9

A stoichiometric mixture of CoO and AI_2O_3 is prepared and then mixed with 1.5 times its weight of KCl. The mixture is heated to about 1100°C in a porcelain crucible. The melt is cooled, pulverized, and extracted with boiling water until no further Clreaction is obtained. The residue is dried at 60°C in a drying oven.

SYNONYM:

Thenard's blue.

1526

PROPERTIES:

M.p. 1700-1800°; d_4^{16} 4.37. Not attacked by Cl_a, mineral acida or aqueous alkalies. Decomposed by fusion with KHSO₄ and by beating with H₂SO₄ in a scaled tube at 200°C. Crystal structure: B11 (spinel) type.

REFERENCES:

J. A. Nedvall. Z. anorg. allg. Chem. 92, 305 (1915); 96, 72 (1916).

Hexaamminecobalt (III) Nitrate

$[C_0(NH_3)_1](NO_3)_1$

 $[C_0(NH_4)_6]Cl_5 + 3 HNO_5 = [C_0(NH_3)_6](NO_5)_5 + 3 HCl_{267.5} + 159.0 - 347.2 - 109.4$

A solution of $[Co(NH_3)_6]Cl_3$ in a minimum quantity of water is prepared and dil. HNO₃ is added; the resulting precipitate is washed with dil. HNO₃ until free of the chloride ion, then with 90% alcohol until free of acid.

PROPERTIES:

Yellow tetragonal prisms. d_4^{25} 1.804. Solubility in H₂O in moles/liter: 0.0202 (0°C); 0.052 (20°C); 0.0704 (30°C).

REFERENCE:

S. M. Jörgensen, Z. anorg. Chem. 17, 457 (1898).

Cobalt (III) Amide

Co(NH₂)₂

Fluffy $Co(NH_2)_3$ precipitates upon addition of KNH₂ to a solution of $[Co(NH_3)_3]$ (NO₃)₃ in liquid NH₃.

| [Co(NH ₃) ₄](NO ₃) ₅ 347.2 | + 3 KNH _e = | Co(NH _z) ₃ | + 6 NH ₃ - | + SKNO ₈ |
|--|------------------------|-----------------------------------|-----------------------|---------------------|
| | 165.4 | 107.0 | 102.2 | 303.5 |

The process requires a supply of N_2 entirely free of oxygen traces (see p. 458 ff.); this nitrogen is then passed through a wash bottle with conc. KOH, a drying tower with solid KOH, and two. U tubes with P_2O_5 . The stream of N_2 is then led to a manifold.

from which it may be directed through stopcocks to various reaction vessels and auxiliary apparatus such as transfer and storage tubes. A branch terminating in a mercury-filled beaker serves as a pressure-relief valve.

In addition, a stream of very pure NH_a is required; this may be taken from a storage cylinder which contains some Na metal. The NH, is passed through a drying tube containing NaNH_a and then a frittedglass disk (not too fine) to remove any entrained solid particles. The NH₃ line has two side branches, one terminating in a vent stopcock, the other in an Hg manometer. The NHa line must be capable of withstanding pressures to about 10 atm.; thus, it must contain no ground joints and only a few well-secured stopcocks. The NH₃ line itself terminates in the above-mentioned manifold.

The reaction takes place in the pressure-resistant vessel shown in Fig. 334. This vessel and accessory equipment are attached to the manifold via flexible couplings made of lead tubing or corrugated pinchbeck (copper-zinc alloy); thus, they may be connected to the N_2 or NH_3 streams, as desired, and also can be moved to some extent.

The pressure apparatus is first heated while the N2 stream passes through. Then, 1.5-2 g. of (Co(NH3)s(NO3)s is admitted through a from a charging funnel and placed on the fritted-glass disk. The tube is then sealed at c. Next, a few mg, of Pt black and the required quantity of metallic K (3 moles of K per mole of $[Co(NH_3)_6](NO_3)_3 + 5\%$ excess K) are placed in reactor b, and the tube is sealed at d. The stopcock on the Na line is closed and the valve on the NH3 cylinder is opened. When the manometer in the NH3 line shows about 4 atm., the valve is closed and the NH3 is vented to the atmosphere by opening the vent stopcock. This purging process is repeated three times to displace the Na from the apparatus. Then reactor b is immersed in ice-salt mitture. the valve on the NHa cylinder fully opened, and NHa allowed to condense in b until the latter is 3/4 full of liquid. Stopcock h is then closed and tube a is cooled so that NH3 distills from b inte a. The hydrogen evolved in the reaction of K with NH3 is vented

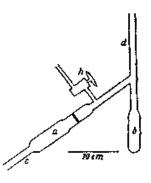


Fig. 334. Pressure vessel for preparation of cobalt (III) amide. Stopcock h and associated tubing are perpendicular to the plane of the diagram. The plug in his held in place by a clamp to prevent it from being blown out by pressure in the apparatus.

from time to time by carefully opening h and the vent stopcock in the NHs line. All of the potassium is allowed to react, whereby all the [Co(NRs)s](NOs)s dissolves. The apparatus is then tilted while tube a is cooled. The KNH2 solution is thereby filtered into a (at the same time, the apparatus is rocked to mix the contents). Reactor b is then recooled, thus recondensing the NH3 in it; this liquid NH, is again filtered into a. This procedure is repeated three times in order to react all of the KNH2. The reaction mixture is allowed to remain in a for six hours (ice cooling and frequent shaking). It is then filtered into b, the precipitate being retained on the fritted-glass disk. The ammonia is again evaporated from b and condensed in a, shaken there with the solid, and filtered into b once more. This is repeated ten times, after which the precipitate is completely free of KNO3. Finally, the NH3 is vented by opening h as well as the vent stopcock in the NH3 line. Nitrogen is then introduced into the apparatus, which is then inverted and opened by breaking the seal at c. The amide on the filter plate is crushed with the aid of a bent Ni spatula, and transferred (in a stream of Na) through the open end of a into a storage device (see Part I, Fig. 54b for the latter). This storage tube is also purged with very pure N2 and, after the amide has been introduced. is closed with a ground stopper. The storage tube is cooled in ice while N₂ is passed over the amide until no further NH₂ is given off.

ANALYSIS:

The product amide is placed in a small glass bulb (air must be excluded). The bulb is then sealed. The following may then be done:

Determination of NH_3 : Aqueous KOH is added to the amide and the liberated NH_3 is distilled into a known quantity of acid.

Determination of Co: The $Co(OH)_3$ which precipitates on addition of KOH is dissolved in sulfurous acid and the Co determined by analytical electrolysis.

The NO3 is determined with diphenylamine.

PROPERTIES:

Chocolate-brown powder; sometimes pyrophoric. Soluble in dil. acids with brown-red color, and in cold water with brown color; the slightly cloudy liquid gradually deposits brownish-black cobalt (III) hydroxide. Forms CoN in vacuum at 40-50°C. Heating in liquid NH₃ produces CoN, Co₂N and CoN_{0.26}.

REFERENCE:

O. Schmitz-Dumont, J. Plizecker and H. F. Piepenbrinck. Z. anorgalig. Chem. <u>248</u>, 175 (1941).

Dicobalt Nitride

Co₃N

 $2 \text{ Co} + \text{NH}_{2} = \text{Co}_{2}\text{N} + \frac{14}{2}\text{H}_{2}$ 117.9 22.11. 131.9 33.71.

Ten mg. of Co_3O_4 is reduced with pure H_2 by heating in a corundum boat for two hours at 350°C. The resulting Co powder is then heated for three hours at 380°C in a stream of NH₃ which passes through the tube at 22 cm./sec. The product is ground and treated once more under the same conditions.

The reduction and nitridation must be carried out in one continuous operation, since the Co powder obtained by reduction of Co_3O_4 is pyrophoric. The cobalt powder prepared from cobalt oxalate cannot be completely converted to nitride under these conditions.

Alternate method: Thermal degradation of Co(NH₂)₃ in vacuum at 160°C [O. Schmitz-Dumont, Angew. Chem. <u>67</u>, 231 (1955); J. Clarke and K. H. Jack, Chem. and Ind. <u>1951</u>, 1004].

PROPERTIES:

Grayish-black powder. d 6.4. In the cold, dil, acids and alkalies react slowly, conc. HCl rapidly, and conc. HNO₃ violently. Warm dil. acids also dissolve Co_2N rapidly. The slow attack by acids gives a quantitative yield of the NH₄ salts (this is an analytical method), while vigorous decomposition evolves part of the nitrogen as N₂. Forms a nitride with the approximate composition Co_3N on thermal decomposition. In vacuum, stable until formation of the compound $CoN_{0.41}$ at 200°C; at 250°C, hexagonal metallic Co containing small amounts of Ni is produced. Crystal structure: rhombically deformed hexagonal close packing of metal atoms.

REFERENCE:

R. Juza and W. Sachse, Z. anorg. Chem. 253, 45 (1945).

Cobalt Nitride

CoN

 $Co(NH_{e})_{3} = CoN + 2 NH_{3}$ 107.0 72.9 44.24.

Cobalt amide is placed in a vapor-pressure endiometer (see Part I, Fig. 85) and carefully decomposed at 50-70°C in the absence.

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of air. The NH₃ evolved is absorbed in conc. H_2SO_4 . The degradation is continued until all NH₃ has been eliminated. The CoN thus formed is transferred in the absence of air to a glass bulb, which is then sealed off. The exact stoichiometric composition is never attained, since a small amount of N₂ is evolved along with the NH₃. The degration products usually have the composition $CoN_{0.8^{\circ}}$ $CoN_{0.8^{\circ}}$

ANALYSE:

To determine the valence of Co, the sample is carefully heated with 2 N KOH until NH_3 can no longer be detected. The resulting blue liquid, which contains suspended cobalt (III) hydroxide, is treated with KI and NaHCO₃ in a flask closed off with a glass stopper, and is then carefully acidified. After standing for one day, the L₂ which separates is back-titrated with $Na_2S_2O_3$ solution.

PROPERTIES:

Black powder; pyrophoric. The nitrogen content of the degradation product drops off with increasing degradation temperature (the composition $CoN_{0.5}$, corresponding to the formula Co_2N , is obtained at 160°C). Heating in the presence of H₂O and aqueous alkali liberates NH₃. Dilute H₂SO₄ liberates part of the bound nitrogen as N₂. Crystal structure; Bi type.

REFERENCES:

O. Schmitz-Dumont, H Broja and H. F. Piepenbrink, Z. anorg. Chem. <u>253</u>, 118 (1947); O. Schmitz-Dumont. Angew. Chem. <u>67</u>, 231 (1955).

Cobalt Phosphides

CoP₄, CoP, Co₂P

Prepared by heating stoichiometric quantities of pure Co metal and red P for 20 hours at 650-700°C in sealed, evacuated quartz tubes. The starting Co powder is obtained by reduction of CoO or Co_3O_4 with H₂ at 700°C.

 $C_0 + 3P = C_0P_3$; $C_0 + P = C_0P$; $2C_0 + P = C_0P$ 53.9 92.9 151.9 58.9 31.0 89.9 117.9 31.0 148.9

PROPERTIES:

- CoPa: Grayish-black powder; das 4.26.
- CoP: Grayish-black powder; d2⁶ 6.24. Crystal structure: B21 type.

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Co₂P: Grayish-black powder; d³⁸ 7.4. Crystal structure: C 23 type.

REFERENCES:

- CoPs: W. Biltz and M. Heimbrecht. Z. anorg. allg. Chem. 241. 349 (1939).
 - CoP: K. E. Fylking, Ark. Kem. Mineral. Geol. 11 (B), No. 48 (1934).
- Co P: H. Nowotny, Z. anorg. Chem. 254, 31 (1947).

Dicobalt Carbide

Co₂C

 $2C_0 + 2C_0 = C_0C + C_0$ 117.9 44.81. 129.9 22.31.

Fine Co powder, obtained from CoO and H2 at 280-300°C, is heated at 220°C with dry, Og-free CO (flow rate 0.75 liter/hour) for 550 hours. Reduction of the oxide and preparation of the carbide must be carried out in one continuous operation, since the Co powder is pyrophoric. The temperature must be held exactly at 220°C since Co₂C decomposes above 225°C.

ANALYSIS:

Heating of Co₂C (9.24% C) with H₂ at 250°C gives a quantitative yield of CH₄ (free C gives no CH₄ under these conditions).

PROPERTIES:

Metailic-gray powder. Decomposes between 260 and 310°C. Hydrogen converts the orthorhombic carbide to a hexagonal form between 198 and 275°C, N2 between 297 and 369°C, and CO2 between 364 and 540°C. Space group of the rhombic carbide: daf.

REFERENCES:

H. A. Bahr and V. Jessen, Ber. dtsch. chem. Ges. 63, 2226 (1930); J. E. Hofer and W. C. Beebles, J. Amer. Chem. Soc. 69, 893 (1947). 144

Hexcamminecobalt (III) Chloride

[Co(NH,),]Cl,

| {CO((NHa)a)Cla | | | | | | |
|------------------------------|-----------------------|----------|--------------------|---|------------|--|
| 4 CoCl ₂ | + 4NH ₄ Cl | + 20 NH, | + 0 ₁ = | 4 [Co(NH ₃) ₄]Cl ₄ | + 8 H 0/0% | |
| (6H ₁ O) 951.8 | <u>814.0</u> | \$40.6 | 22,4 Î. | 1078.0 | 36.9 | |

A mixture of 240 g, of CoCla · 6 HaO, 160 g, of NH4Cl, and 200 ml. of H₂O is shaken until solution is almost complete. Then 4-5ig.

of activated charcoal and 500 ml. of conc. ammonia are added, and a fast stream of air is passed through the mixture until the red solution becomes yellow-brown. The air flow should not be so rapid as to reduce the ammonia content; should this occur, some additional conc, ammonia may be added.

The precipitated $[Co(NH_3)_8]Cl_3$ and the charcoal are filtered off, and the residue is dissolved in hot 1-2% HCi. The solution is filtered hot and the pure product is precipitated by adding 400 ml, of conc. HCi and chilling to 0°C. The precipitate is collected, washed first with 60% alcohol, then with 95% alcohol, and finally dried at 80-100°C. Yield: 85%.

Alternate method: From [Co(NH₃)₅Cl]Cl₂ and ammonia [S. M. Jörgensen, Z. anorg. Chem. <u>17</u>, 455 (1898)].

SYNONYM:

Luteocobalt chloride.

PROPERTIES:

Wine-red or brownish-red monoclinic crystals. d_4^{25} 1.710. Solubility in H₂O in moles/liter: 0.152 (0°C); 0.26 (20°C); 0.42 (46.6°C); Boiling in water yields Co(OH)₂.

REFERENCES:

J. Bjørrum. Metal Ammine Formation in Aqueous Solution, p. 241, Copenhagen, 1941; J. Bjørrum and J. P. McReynolds in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 217.

Chloropentaamminecobalt (III) Chloride

[Co(NH,),Cl]Cl,

Obtained by oxidation of an ammoniacal CoCl₂ solution, and purified via $[Co(NH_3)_5H_2O]_2(C_2O_4)_3 \cdot 4H_2O$.

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A) CRUDE PRODUCT, [Co(NH3)sCI]Cl2

A solution of 20 g. of precipitated cobalt carbonate in some 1:1 HCl is prepared, filtered and cooled; a mixture of 250 ml. of conc. ammonia and 50 g. of $(NH_4)_3CO_3$ dissolved in 250 ml. of H_2O is then added. The mixture is oxidized for three hours by bubbling in a stream of air. After addition of 150 g. of NH_4Cl the solution is evaporated to airup consistency on the steam bath. Dilute HCl is added to drive off the CO_2 and produce a weakly acid reaction.

28. COBALT, NICKEL

then ammonia is added to give a weakly basic solution, followed by 10 ml. of additional conc. ammonia. The liquid, whose volume at this point is 400-500 ml., is heated on the steam bath until all the tetraammine salt disappears; it is then treated with 300 ml. of conc. HCl and heated for 30-45 minutes on the steam bath. The $[Co(NH_3)_{s^-}$ Cl]Cl₂ precipitates on cooling. It is filtered off and washed with 1:1 HCl until free of NH₄Cl, then with alcohol until free of acid. The salt still contains some $[Co(NH_3)_5]Cl_2$. Yield: 34.5 g.

REFERENCE:

S. M. Jörgensen. Z. anorg. Chem. 5, 361 (1894).

B) AQUOPENTAAMMINECOBALT (III) OXALATE, $[C_0(NH_3)_5(H_2O)]_2 (C_2O_4)_3 + 4H_2O$

A mixture of 10 g. of finely powdered crude $[Co(NH_3)_5Cl]Cl_3$, 75 mi. of H₂O, and 50 ml. of 10% ammonia is heated on the steam bath in an Erlenmeyer flask covered with a watch glass (continuous agitation) until all of the basic aquopentaammine chloride dissolves and a deep-red solution forms. The solution is filtered, the filtrate is made very weakly acid with oxalic acid, and some additional $(NH_4)_2C_2O_4$ is added to complete the precipitation. The slurry is allowed to stand; the precipitate is then filtered off and washed with cold water. The yield of the dry salt is about 12 g.

SYNONYM:

Roseocobalt oxalate.

PROPERTIES:

Formula weight 660.36. Brick-red crystals. Solubility in water, at 17.5°C is 0.0019 moles/liter.

REFERENCE:

S. M. Jörgensen, Z. anorg. Chem. 19, 78 (1899).

C) PURE CHLOROPENTAAMMINECOBALT (III) CHLORIDE, {Co(NH₃)sCl}Cl₂

Twenty grams of $[Co(NH_3)_{g}(H_3O)]_{3}(C_2O_4)_3 \cdot 4H_3O$ is dissolved in 150 ml. of 2% ammonia in the cold, and the insoluble $[Co(NH_3)_{g}]_{3}^{-1}$ $(C_2O_4)_3 \cdot 4H_3O$ (intecoxalate) is filtered off. The filtrate is procipitated in the cold with dil. HCl. The $[Co(NH_3)_{g}Cl]Cl_3$ thus formed is filtered off, washed successively with alcohol, absolute alcohol and ether, and dried in air.

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The purification method given by Jörgensen does not yield $com_{pletely}$ pure [Co(NH₃)₅Cl]Cl₂.

ANALYSE:

ionizable C1 and total C1 are determined in order to determine whether impurities are present.

SYNONYM:

Chloropurpureocobalt chloride.

PROPERTIES:

Formula weight 250.47. Ruby-red crystals. d_4^{25} 1.783. Soluthility in H₂O: 0.0089 (0°C); 0.0225(25°C); 0.040(50°C) moles/liter. The presence of HCl lowers the solubility; at 25°, 10% HCl dissolves 0.00067 moles/liter. Neutral aqueous solutions decompose when boiled, and Co(OH)₂ is deposited. Heating to higher temperatures produces CoCl₂. Crystal type: orthorhombic-bipyramidal.

REFERENCE:

F. J. Garrick. Z. anorg. allg. Chem. 224, 27 (1935).

Nitropentoamminecobalt (III) Chloride

[Co(NH₃)₄NO₂]Cl₁

 $\begin{array}{rrrr} [Co(NH_3)_5Cl]Cl_1 + NaNO_2 \approx [Co(NH_3)_5NO_4]Cl_2 + NaCl \\ 250.5 & 69.0 & 261.0 & 58.4 \end{array}$

A mixture of 20 g. of $[Co(NH_3)_5Cl]Cl_3$, 200 ml. of H_2O , and 50 ml. of 10% ammonia is placed in an Erlenmeyer flask covered with a watch glass, and heated on the steam bath until the salt dissolves (frequent shaking is necessary). The solution is filtered, the filtrate cooled and made weakly acidic with dil. HCl, 25 g. of crystalline NaNO₂ is added, and heating on the steam bath is continued until the initial red precipitate dissolves completely. The cold, brownish-yellow solution contains a copious deposit of crystals. At this point, 250 ml. of conc. HCl is added (carefully at first). After chilling, the product is filtered off, washed with 1:1 HCl, then with alcohol until free of acid, and dried in air. Yield: 17 g.

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SYNONYM:

Xanthocobalt chloride.

PROPERTIES:

Brownish-yellow monoclinic crystals. d_s^{26} 1.804. Solubility in H_3O at 20°C: 0.11 moles/liter of solution; more soluble in hot H_3O . Decomposes on heating to 210°C.

REFERENCE:

S. M. Jörgensen. Z. anorg. Chem. 17, 463 (1898).

Nitritopentaamminecobalt (III) Chloride

[Co(NH₄)₄ONO]Cl₂

A solution of 10 g. of $[Co(NH_3)_5Cl]Cl_3$ in a mixture of 150 ml. of H₃O and 25 ml. of 10% ammonia is prepared with heating and agitation. The solution is filtered, cooled and exactly neutralized with dil. HCl. Then 25 g. of crystalline NaNo₂ is added and, when this has dissolved, 10 ml. of 1:1 HCl. The resulting precipitate is allowed to stand for several hours in the mother liquor while cooling in water; it is then filtered off and washed with cold water and alcohol.

PROPERTIES:

Chamois-colored crystalline powder, four times less soluble in water than nitropentaamminecobalt chloride. On standing for several weeks, converts to the isomeric form. The conversion is more rapid if a 10% aqueous solution of the compound is treated with an equal volume of conc. HCl.

REFERENCE:

S. M. Jörgensen, Z. anorg. Chem. 5, 168 (1894).

Carbonatotetraamminecobalt (III) Sulfate

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[Co(NH₄)₄CO₅]₅SO₄ · 3 H₇O

An aqueous solution of $CoSO_4$ is treated with $(NH_4)_3CO_3$ and NH_4OH , then oxidized in a stream of air.

Precipitated cobalt carbonate (20 g.) is dissolved in a minimum quantity of dil. H_3SO_4 . The clear solution (about 100 ml.) is pourse

into a solution of 100 g. of $(NH_4)_2CO_3$ in 500 ml. of H₂O and 250 ml. of conc. ammonia, and air is bubbled through for 2-3 hours. After complete exidation, the blood-red solution, containing several small pleces of $(NH_4)_2CO_3$, is evaporated on a steam bath until the volume is 300 ml. The solution is then filtered, concentrated to 200 ml. and chilled, whereupon $[Co(NH_3)_4CO_3]_2SO_4 \cdot 3H_2O$ crystallizes as red prisms. The mother liquor is decanted; the precipitate is filtered off and washed once with a saturated solution prepared from a small portion of the precipitate. More salt is obtained by further evaporation of the mother liquor [add some $(NH_4)_2CO_3]$. Yield: 32 g.

PROPERTIES:

Formula weight 524.27. Garnet-red prisms. d 1.882. The aqueous solution decomposes on standing in light. Forms $[Co(NH_3)_4-(H_3O)_2]SO_4$ (tetraammineroseocobalt sulfate) with dil. H_2SO_4 . Loses all water over conc. H_2SO_4 . Crystal form; orthorhomic-bipyramidal.

REFERENCE:

S. M. Jörgensen, Z. anorg. Chem. 2, 281 (1892).

Dichlorotetraamminecobalt (III) Chloride

[Co{NH₃},Cl₄]Ct

Two stable isomeric forms exist: these are the 1,2-dichloro-(cis-) and 1,6-dichloro- (trans-) compounds.

1,2-DICHLOROTETRAAMMINECOBALT (III) CHLORIDE (CIS), $[C_0(NH_3)_4CI_2]CI + 0.5H_2O$

Treatment of an ammoniacal solution of $Co(CH_3COO)_2 \cdot 4H_2O$ with NaNO₂, followed by air oxidation, affords $[Co(NH_3)_4(NO_3)_2]^-$ NO₂, which is converted to the dichloro compound with conc. HCl.

Air is bubbled for five hours through a solution of 20 g. of NaNO₂ and 20 g. of $Co(CH_3COO)_2 \cdot 4H_2O$ in 200 ml. of 20% NH₃. The violet solution is concentrated to a small volume with occasional addition of solid NaHCO₃, then chilled. A large excess of alcohol is added to cause precipitation. The precipitate is filtered off, washed with alcohol-ether, and dried in a vacuum desiccator. This is cis-dialitrotetraamminecobalt (III) nitrite, which is not contaminated with the trans compound. It is very easily hydrolyzed.

The cis-nitrite is added in small portions to conc. HCl main tained at -10° C, giving a quantitative yield of the chloride.

SYNONYM:

Formerly: Chlorovioleocobalt chloride.

PROPERTIES:

Formula weight 242.45. Violet needles. Water soluble; loses water of hydration at 60°C. Very unstable.

REFERENCE:

C. Duval. Comptes Rendus Hebd. Seances Acad. Soi. 182, 636 (1926).

DIAQUOTETRAAMMINECOBALT (III) SULFATE, $\{C_0(NH_3)_4(H_2O)_2\}_2(SO_4)_3 + 3|H_2O|$

This is formed by treatment of $[Co(NH_3)_4CO_3]_2(SO_4)_3 \cdot 3H_3O$ with dil. H_2SO_4 .

A solution of 5 g. of pure $[Co(NH_3)_4CO_3]_2SO_4 \cdot 3H_2O$ in 100 ml. of cold H_2O and 10 ml. of dil. H_2SO_4 is prepared; this results in evolution of CO_2 . The clear solution is treated with 50-60 ml. of alcohol, added in small portions. The precipitate is filtered off, washed with 50% alcohol until free of acid, and dried in air. Yield; 6.2 g. (theoretical: 6.37 g.).

PROPERTIES:

Formula weight 668.45. Red quadratic prisms, which lose water of crystallization over conc. H_2SO_{\bullet} . Solubility at 22°C: 0.175 moles/liter of water.

REFERENCE:

S. M. Jörgensen, Z. anorg. Chem. 2, 296 (1892).

1,6-DICHLOROTETRAAMMINECOBALT (III) CHLORIDE (TRANS), {Co(NH3)4Cl2}Cl + H2O

A solution of 10 g. of $[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3 \cdot 3H_2O$ in 50 ml. of cold cone. H_2SO_4 is prepared; the flask is allowed to stand for 24 hours, then placed in ice, and 50 ml. of cone. HCl is added. dropwise with frequent and vigorous shaking. The *trans* sales separates in 48 hours. The flask is tilted and the mother liquoper, decanted as thoroughly as possible. Dilute HCl is then added; the precipitate is filtered off and washed with dil. HCl until free of 2.5 H_2SO_4, then washed with alcohol until free of acid. Yield: 7.25 g. (theoretical: 7.53 g.).

SYNONYM:

Formerly: Chloropraseccobalt chloride.

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PROPERTIES:

Formula weight 251,46. Lustrous green crystals. d^{36} 1.860. Loses water of crystallization in 1-2 hours at 100°C. Solubility at 0°: 0.0141 moles/liter H₂O; hydration in solution, yielding [Co(NH₃) $\langle H_2O \rangle_2$]Cl₃. The trans compound is more stable than the cis form.

REFERENCE:

S. M. Jörgensen. 2. anorg. Chem. 14, 404 (1897).

Triethylenediaminecobalt (III) Bromide

[Co ens]Brs

The preparation from cobalt salt, ethylenediamine and NaBr yields the racemate of the optically active forms of $[Co en_3]Br_3$ as the first product. The racemate can be resolved with tartaric acid into the d- and l-tartrate, and further converted to the d- and l-tartrate.

A) RACEMIC TRIETHYLENEDIAMINECOBALT (III) BROMIDE, [Co eng]Br3 - 3H2O

A solution of 10 g. of $CoCl_2 \cdot 6 H_BO$ in 150 g. of 10% aqueous ethylenediamine is prepared and oxidized by bubbling air through it for several hours. The brown solution is then acidified with HCl and concentrated until crystallization. The crystal mass is dissolved in H₂O and treated with NH₄NO₃, which precipitates 1,6-[Co en₂Cl₂]NO₃. This precipitate is removed by filtration; then NaBr is added to the filtrate, whereupon completely pure [Co en₃]Br₃ · 3H₂O separates out.

PROPERTIES:

Formula weight 533.04. Small yellow needles. M. p. 271°; d_4^{25} 1.845. Solubility in H₂O at 16°C: 4.33 g. of anhydrous salt per 100 g. of solution.

B) RESOLUTION WITH TARTARIC ACID

A solution of 100 g. of $[Co en_3]Br_3$ in water is treated with the amount of silver tartrate (68.3 g.) needed for reaction with two atoms of bromine. After boiling, the AgBr precipitate is filtered off and then washed with boiling water until the water is no longer yellow. The filtrate and washings are combined and

26. COBALT, NICKEL

concentrated. On chilling, the *d*-tartrate separates and is removed by filtration. The mother liquor is further concentrated and the additional precipitate of *d*-tartrate is removed. Cooling gets the solution to a mass of *l*-tartrate, still somewhat contaminated with *d*-tartrate.

C) d-TRIETHYLENEDIAMINECOBALT (III) BROMIDE TARTRATE $[C_0 \ en_3]Br(d-C_4H_4O_6) - 5H_2O$

The d-tartrate crystals obtained in B are recrystallized from hot water. Rapid cooling yields needles with a silky luster; these disappear on standing for 1-2 hours in the mother liquor and are replaced by coarse platelike crystals.

PROPERTIES:

Formula weight 557.32. Small bright-yellow needles or darkyellow platelets. Optical rotation (1% solution) $[\alpha]_D$ +98°. [M]D +555°.

D) d-TRIETHYLENEDIAMINECOBALT (III) BROMIDE, d-[Co en 3]Br3 + 2H2O

The d-{Co en₃}Br(C₄H₄O₆) • 5 H₃O obtained above is triturated with warm conc. HBr and the solution is filtered. On standing, large hexagonal tablets (acid bromide?) separate out; these are recrystallized from water to yield columnar crystals of the dbromide.

PROPERTIES:

Formula weight 515.03. Yellow, columnar crystals. More readily soluble in H₂O than the racemic bromide. d_4^{35} 1.971. Optical rotation (1% solution): $[\alpha] D + 117^\circ$; $[M] D + 602^\circ$. Crystal-line form: ditetragonal-bipyramidal.

E) 1-TRIETHYLENEDIAMINECOBALT (III) BROMDE, I-{Co eng]Br3 + 2H2O

The gelatinous *l*-bromide tartrate is triturated with warm conc. HBr. The sparingly soluble racemic bromide tartrate which separates out is removed by filtration. On standing, the solution deposits crystals of *l*-bromide, which are recrystallized from hot water.

PROPERTIES:

Formula weight 515.03. Yellowish crystals. More readily solution ble in H_2O than the racemic bromide. Optical rotation (1% solution): $[\alpha]_D - 115^{\circ}; [M]_D - 592^{\circ}$. Can be converted (with AgCl or AgNCa) to the corresponding chioride or nitrate.

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REFERENCE:

A-E: A. Werner. Ber. dtsch. chem. Ges. <u>45</u>, 121 (1912).

Decaammine-µ-peroxocobalt (88) Cobalt (1V) Sulfate

1{NH₃}₃Co¹¹¹(O₂)Co¹¹⁷(NH₄)₃](SO₄)₂ · SO₄H · 3 H₂O

The preparation involves exidation of an ammoniacal solution of $CoSO_4 + (NH_4) \otimes SO_4$

A mixture of 0.5 liter of 1 M (NH₄)₂SO₄, 1 liter of conc. ammonia, 1 liter of H₂O, 0.5 liter of 1 M CoSO₄, 0.5 liter of 1 M H₂O₂ and 0.5 liter of 1 M (NH₄)₂S₂O₉ is prepared in the indicated sequence, the solutions being added at approximately 10-second intervals. The mixture is vigorously agitated after each addition. After all additions have been completed it is allowed to stand for 10-15 minutes. Most of the supernatant liquid is siphoned off; the precipitate is filtered off, washed first with dil, ammonia and then with alcohol and suction-dried. The crude product (50-70 g.) is dissolved as rapidly as possible in 1250-1750 g. of 2 N H₂SO₄ (heating to 80-85°C is necessary). The solution is filtered at once and allowed to stand one day. The yield is 30-50 g. of pure product.

ANALYSIS:

 $2 \left[Co_{2} (NH_{2})_{10} O_{2} \right]^{4} + 20 H^{4} + As^{4+} = 2 O_{2} + 4 Co^{2+} + 20 NH_{2} + As^{4+}.$

The product, in the sulfuric acid solution, is reduced with As^{3^+} ; the evolving O_2 is collected in an azotometer over strong KOH by means of CO_3 . An aliquot of the solution is used to backtitrate the excess As^{3^+} with $Ce(SO_4)_3$ and ferroin; another aliquot is used to determine Co by precipitation with 8-hydroxyquinoline and titration with KBrO₃.

PROPERTIES:

Formula weight 663.45. Grayish-black, lustrous prisms. Almost insoluble in cold dil. sulfuric acid; more soluble at 50-60°C.

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REFERENCE:

K. Gleu and K. Rehm. Z. aborg. allg. Chem. 237, 79 (1938).

28. COBALT, NICKEL

Sodium Hexanitritocobaltate (III) Nas Co(NOs),1

 $2 \operatorname{Co(NO_3)}_{\bullet} \cdot 6 \operatorname{H_2O} + 12 \operatorname{NaNO_5} + 2 \operatorname{CH_3COOH} + 4/_2 \operatorname{O_5}$ 582.1 828.0 120.1 1121. = $4 \operatorname{NaNO}_{3} + 2 \operatorname{CH}_{3} \operatorname{COONa}_{4} + 2 \operatorname{Na}_{3} \operatorname{Co}(\operatorname{NO}_{2})_{5} + 7 \operatorname{H}_{3} \operatorname{O}_{5}$ i. wite 340.0 164.1 807.9

A solution of 150 g, of NaNO2 in 150 ml. of H2O is cooled to 50-60°C; some of the NaNO, is thus reprecipitated. Then 50 g. of Co(NO3)2 · 6H2O is added, followed by 50 ml. of 50% CH3COOH in small portions (agitation). Then a fast stream of air is bubbled through for one half hour. After standing for two hours, the brown precipitate is filtered off. The filtrate must be clear at this point. The precipitate is stirred with 50 ml, of H₂O at 70-80°C. The solution is separated from undissolved Ka[Co(NOa)a] on a small filter and combined with the above-mentioned clear filtrate. The combined solution (about 300 ml.) is treated with 250 ml. of 96% alcohol. The resulting precipitate is allowed to settle for about two hours, then filtered, suction-dried, washed four times with 25 ml. of alcohol, then twice with ether, and dried in air. Yield: 50-53 g. (75%).

Reprecipitation with alcohol is desirable. The pure preparation must give a perfectly clear solution in H₂O. To precipitate the salt, the alcohol is added from a wash bottle; during the addition, the flask is vigorously shaken to insure that the particle size of the precipitate will not be too small.

SYNONYM:

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Sodium cobaltinitrite.

PROPERTIES:

Yellow crystalline powder. Very soluble in water, sparingly scluble in alcohol and ether. The aqueous solution is not stable and forms HNO2 and HNO3. Crystal structure: J2, type (oubic).

REFERENCE:

E. Bijlman. Z. analyt. Chem. 39, 284 (1900).

Potassium Hexacyanocobaltate (III)

K₄[Co(CN)₄]

The intermediate K (Co(CN)s) is prepared from Co(CN), and KCN. Boiling of its solution precipitates K3[Co(CN)6].

A clear, filtered solution of 48 g. of CoCl2 · 6 H2O in 500 ml. of H₂O is heated to boiling, and a clear solution of 30 g, of KON

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in 200 ml, of H₂O is added dropwise with vigorous stirring. Before adding the final portions of the KCN, a sample of the solution is filtered and the filtrate is treated with a drop of KCN solution, in order to establish whether any CoCl₂ is still present in the solution. The violet-red precipitate of Co(CN), is filtered off. washed with cold $H_{2}O$, and dissolved while still moist in a conc. solution of 60 g. of KCN. The deep red solution of K (Co(CN) 6] is heated to boiling for 10-15 min., whereupon it becomes yellow and evolves Ha. If a small quantity of yellow Ka[Co(CN) a] crystallizes at this time, some water is added to redissolve it. The boiling solution is filtered and cooled. The K₃[Co(CN)₆] precipitate is collected on a filter and washed with some cold water. Further quantities of the precipitate are obtained by concentrating the mother liquor to half its volume; this solid is worked up as above. The combined precipitates are recrystallized twice from hot water. some activated carbon being added to the solution. The pure. almost colorless crystals are filtered off and washed with some cold water. They must give a clear water solution.

The small excess of KCN called for in the directions for preparing the solution of $Co(CN)_2$ in KCN prevents the precipitation of green $K_3Co[Co(CN)_8]$, which is insoluble at room temperature.

Alternate method: Oxidation of $CoCl_2 \cdot 6H_2O + KCN$ in acetic acid solution with air, and several reprecipitations from acetic acid solution with alcohol [W. Biltz, W. Eschweiler and A. Bodensiek, Z. anorg. allg. Chem. <u>170</u>, 161 (1928)].

SYNONYM:

Potassium cobalt (III) hexacyanide.

PROPERTIES:

Formula weight 332.35. Small, almost colorless needles with a yellowish tinge. d_4^{25} 1.878. Readily soluble in water; solubility in 87-88% alcohol (20°C): 1:7500 parts. Decomposes on heating in absence of air. Crystalline form; monoclinic, isomorphic with K_3 Fe(CN)₈.

REFERENCE:

A. Benedetti-Pichler, Z. anal. Chem. <u>70</u>, 257 (1927).

Hexacyanocobaltic (III) Acid

H.Co(CN),

 $\frac{K_{s}C_{0}(CN)_{6}}{392.4} + \frac{3}{109.4} + \frac{3}{218.1} + \frac{3}{293.7} KCl$

A solution of 3 g. of $K_3Co(CN)_8$ in 9 ml. of H_2O is treated with 9 g. of conc. HCi. The KCl precipitate is removed by filtration.

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The solution is sensitive to light.

SYNONYM:

Hydrogen hexacyanocobaltate (III).

REFERENCE:

A. von Baeyer and V. Villiger, Ber. dtsch. chem. Ges. <u>34</u>, 2687 (1901).

H,Co(CN), · 5 H,O

A very small excess of H_2SO_4 (d 1.84) is added to a 25% aqueous solution of $K_3Co(CN)_6$, which is then heated for 15-20 minutes to 50-55°C and cooled. Absolute alcohol is added and the alcohol-insoluble K_2SO_4 is removed by filtration. The solution is carefully concentrated at 50-55°C and the $H_3Co(CN)_8 \cdot 5H_2O$ thus formed is recrystallized three times from alcohol.

PROPERTIES:

Colorless crystalline needles; hygroscopic. Heating at 100°C yields white $H_3 Co(CN)_6 \cdot 0.5 H_2O$. At higher temperatures, colored products are formed until finally a black cobait carbide remains. Not altered by brief boiling with HCl or HNO₃, but forms Co₃- $[Co(CN)_6]_3$ in hot H_3SO_4 (d 1.84).

REFERENCE:

O. K. Dobrolyubskiy. Zh. Prikl. Khimii 26, 1185, 1233 (1953),

Metallic Nickel

SABATIER METHOD

 $NiO + H_z = Ni + H_zO$ 74.7 22.41. 58.7

Very pure, O_2 -free H₂ dried over P_2O_3 is passed for 15 hours over NiO [obtained by thermal decomposition of Ni(NO₃)₂ • 6 H₂O] at 300-400°C. After cooling in the H₂ stream, the air-sensitive metal is transferred to small glass bulbs attached to the apparatus, and these are sealed off. The metal powder may also be stored in bottles under alcohol.

Used as hydrogenation catalyst.

PROPERTIES:

Atomic weight 58.71. Black metallic powder; pyrophoric. M.p. 1453°C, b.p. 3177°C. Ferromagnetic. Soluble in dil. HNO₃, passivated by conc. HNO₃.

REFERENCE:

P. Sabatier. Die Katalyse in der organischen Chemie [Catalysis in Organic Chemistry], translated into German and enlarged by B. Finkelstein and H. Häuber, Leipzig, 1927.

Nickel [II] Chloride

NiCl₂

J. NiCl₂ + 6 SOCl₂ = NiCl₂ + 12 HCl + 6 SO₂ $\begin{array}{c} (6 \text{ H}, 0) \\ 237,7 \\ 713,9 \\ 129,6 \\ 437.6 \\ 384.4 \end{array}$

Water is removed by refluxing with $SOCl_2$ as described for $CoCl_2$.

Π.

 $NiCl_{z} \cdot 6 H_{z}O = NiCl_{z} + 6 H_{z}O$ 237.7 129.6 108.1

The starting NiCl₂ \cdot 6H₂O is dried in a combustion tube at 150°C; the final heating to 400°C proceeds in a stream of Cl₂-containing HCl. After the yellow NiCl₂ has formed, the tube is sealed at one end and the product is sublimed (oil-pump vacuum) at the highest temperature that the tube can withstand. To remove HCl, the NiCl₂ is annealed in high vacuum over KOH at 160°C.

Alternate methods: a) Heating of NiCl₂ - $6 H_2O$ in a sealed tube with COCl₂ at 200°C (Hecht).

b) The frequently recommended thermal decomposition of $NiCl_2 \cdot 6 NH_3$ does not yield pure $NiCl_3$, since black by-products are formed.

c) Treatment of Ni(CH₃COO)₂ · 4 H₃O with CH₃COCl in benzene, analogous to the preparation of CoCl₂ [G. W. Watt, P. S. Gentile and E. P. Helvenston, J. Amer. Chem. Soc. <u>77</u>, 2752 (1955)].

PROPERTIES:

Bright-yellow powder or crystalline leaflets (like mosaic gold). Subl. 993°C (760 mm.); m.p. 1001°C (in sealed tube); d_4^{35} 3.521. Heat of formation: -73.0 kcal./mole (25°C). Sublimed NiCl₂ is States and states

relatively stable and takes up water slowly; fine NiCl₂ powder is hygroscopic and becomes green in air. Solubility in H_{3O} (g. NiCl₂/100 g. solution): 34.8 (0°C); 40.4 (26.3°C); 46.7 (100°C). Moderately soluble in methyl and ethyl alcohol. Crystal structure: C 19 type.

REFERENCES;

I. H. Hecht. Z. anorg. Chem. 254, 51 (1947).

II. W. Biltz and E. Birk. Z. anorg. allg. Chem. 127, 34 (1923).

Hexaamminenickel (III) Chloride

$[Ni(NH_{2})_{c}]Cl_{2}$ NiCl₂ + 6 NH₃ = $[Ni(NH_{3})_{c}]Cl_{2}$ (6 H₄O) 237.7 103.2 231.6

A conc. solution of cobalt-free NiCl₂ · 6 H₂O is treated with excess conc. NH₃, then cooled in running water. The separation of fine crystals of $[Ni(NH_3)_6]Cl_2$ is completed by addition of an ammoniacal NH₄Cl solution. The precipitate is filtered off and successively washed with conc. ammonia, alcohol and ether.

Alternate methods: Action of NH₃ on anhydrous NiCl₂ at room temperature [F. Ephraim, Z. phys. Chem. <u>81</u>, 513 (1913)].

PROPERTIES:

Blue-violet, fine crystalline powder. d_{28}^{28} 1.468. Heat of formation: -16.3 kcal./mole. The decomposition pressure at 176.5°C is 1 atm. Decomposes in H₂O, liberating NH₃. Soluble in aqueous ammonia; not soluble in conc. ammonia or alcohol. Crystal structure; J1₁ type.

REFERENCE:

S. P. L. Sörensen, Z. anorg. Chem. 5, 354 (1894).

Nickel (II) Bromide

NiBra

ANRYDROUS NiBr:

Ni + Br₂ = NiBr₂ 58.7 159.8 218.5

Nickel powder, produced by heating NiCl₂ in a hydrogen stream at 400°C, is covered with a layer of completely dry ether and then

يت در اويو treated with dry bromine. After 12 hours the ether is removed and the residue heated in vacuum at 130° C. In order to purify the preparation, which still contains some Ni, it is sublimed at 900°C (quartz or porcelain tube) in a CO₂-free stream of N₂ + HBr.

Alternate methods: a) Heating of NiCla in a stream of HBr at 500°C (G. Crut).

b) Heating of NiBr₂ · 6H₂O at 140°C in a drying oven [J. A.
 A. Ketelaar, Z. Kristallog. <u>88</u>, 26 (1934)].

c) Reaction of Ni(CH₃COO)₃ · 4 H₂O with CH₃COBr in benzene, analogous to the preparation of CoCl₂ [G. W. Watt, P. S. Gentile and E. P. Helvenston, J. Amer. Chem. Soc. <u>77</u>, 2752 (1955)].

PROPERTIES:

Yellow powder or bronze-yellow micalike particles. M. p. 963° (in sealed tube); d_{4}^{25} 5.018. Heat of formation: -51.8 kcal. per mole (25°). Solubility in H₃O (g. NiBr₃/100 g. solution): 56.6 (19°C); 61.0 (100°C). Soluble in methyl and ethyl alcohols, acetone and quinoline; insoluble in toluene. Crystal structure: sublimed product, C19 type; unsublimed product, variable between C6 and V19 types.

REFERENCES

G. Crut. Bull, Soc. Chim. France [4] 35, 550 (1924).

NiBra 6 HaO

 $NiBr_2 + 6H_2O = NiBr_2 \cdot 6H_2O$ 218.5 108.1 326.8

A solution of $NiBr_{\partial}$ in water is concentrated until crystallization begins and is then cooled. The crystals are filtered off and recrystallized from alcohol.

Alternate method: Precipitated nickel carbonate or $Ni(OH)_2$ is dissolved in aqueous HBr, concentrated on the steam bath, and the product recrystallized from alcohol [J. A. A. Ketelaar, Z. Kristallog. <u>88</u>, 26 (1934)].

PROPERTIES:

Green crystals; transform to NiBr₂ · 3H₂O at +28.5°C.

BEFERENCE:

See G. L. Clark and H. K. Bruckner, J. Amer. Chem. Soc. <u>44</u>, 230 (1922). Contraction of the second second

Nickel (II) lodide

Nil,

ANHYDROUS Nil2

 $Ni(OH)_1 + 2HI = NH_2 + 2H_2O$ 92.7 255.8 312.5 36.0

Either Ni(OH)₂ or precipitated nickel carbonate is dissolved in hydriodic acid and the solution evaporated to dryness. The solid is recrystallized from alcohol and dried at 140°C. A final sublimation in high vacuum at 500-600°C is recommended.

Alternate method: Dehydration of $Nil_2 \cdot 6 H_2O$ (Riedel, Thesis, Univ. of Halle, 1913).

PROPERTIES:

Black solid; forms small justrous crystals when sublimed. M.p. 797 °C (in sealed tube); $d_2^{\pm 5}$ 5.834. Heat of formation: -41.40 kcal./mole. Decomposes when heated to high temperatures in air., Hygroscopic; rapidly forms a green solution when exposed to air. Solubility in H₂O (g. Nil₂/100 g. solution); 57.8(11°C); 64.1 (43°C); 65.7 (90°C). Aqueous solutions of Nil₂ can dissolve up to two atoms of iodine, thereby acquiring a brown color. Dilute solutions are pure green, concentrated solutions dirty green or reddish, brown. Slowly soluble in cold absolute alcohol, rapidly in hot. Crystal structure; C19 type.

REFERENCE:

J. A. A. Ketelsar, Z. Kristallogr. 88, 26 (1934).

Nil: • 6 H.O

 $NiI_{1} + 6H_{2}O = NiI_{2} \cdot 6H_{2}O$ 312.5 106.1 420.6

A solution of Nil₂ in H₂O is evaporated to a sirup. The crys of Nil₂ · 6 H₂O are filtered off and suction-dried.

Alternate method: As in the case of Nila, but without the deby dration at 140°C [J. A. A. Ketelaar, Z. Kristallogr. 88, 26 (1934)]

PROPERTIES:

Blue-green crystals; rapidly deliquescent in air, becoming brown and giving off iodine. Exists up to 43°C; becomes anhydronic when heated on steam bath.

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REFERENCES:

O. Erdmann, J. prakt. Chem [1] <u>7</u>, 254(1936); A. Étard. Ann. Chim. Phys. [7] <u>2</u>, 503 (1894).

Nickel (II) Oxide

NiO

Prepared by thermal decomposition of nickel salts of volatile acids.

I. Precipitated nickel carbonate or $Ni(NO_3)_2 \cdot 6H_2O$ is heated in a Pt crucible for six hours at 1000-1100°C and allowed to cool in O₂-free nitrogen.

On cooling in air, a surface skin forms, which can be removed by postreduction with pure H_2 at 100°C.

Test for active oxygen is essential.

II. Precipitated nickel carbonate is placed in a pear-shaped decomposition vessel, the air is displaced several times with O_2 -free nitrogen, and the entire apparatus is degassed in high vacuum at 100°C. After high vacuum is established, the system is heated, over a period of 90 minutes, to 350°C. The product is transferred to previously prepared storage bulbs, which are then sealed.

The oxide blackens immediately in the presence of air. Test for active oxygen is essential.

Alternate method: Small chips of nickel are heated in air at 1000°C (for procedure, see method II, subsection on Cu_3O) [H. H. von Baumbach and C. Wagner, Z. phys. Chem. (B) <u>24</u>, 61 (1934)].

Used as oxidation catalyst.

PROPERTIES:

Formula weight 74.71. M.p. 1990°C; d 6.67. Heat of formation: -58.4 kcal./mole. Bright-yeliow powder, brown when heated. When the oxygen content is in slight excess, the color is dark olive green, becoming darker as the oxygen content increases. NiO prepared at high temperatures is almost insoluble in acids and alkalies; the lower the temperature of preparation, the more soluble it is, especially in hot nitric acid and ammonia. Crystal structure: B1 type.

REFERENCE:

M. Le Blanc and H. Sachse. Z. Elektrochem. 32, 58(1926).

Nickel (II) Hydroxide

Ni(OH)

 $Ni(NO_3)_z + 2 NaOH = Ni(OH)_z + 2 NaNO_3$ (6 H.O) 290.8 80.0 92.7 170.6

A solution of 25 g. of KOH in 250 ml. of carbonate-free H_2O is added dropwise and with vigorous stirring to a warm (about 35°C) solution of 60 g. of Ni(NO₃)₂ · 6 H₂O in 250 ml. of H₂O. The precipitate is washed by decantation with several five-liter portions of warm, CO₂-free H₂O (until the washings are no longer alkaline), then once with five liters of CO₂-free H₂O containing some ammonia, and finally with similar portions of warm, CO₂-free water until both precipitate and washings are free of K⁺ and NO₃⁻. The precipitate is filtered off and dried in a vacuum desiccator over conc. H₂SO₄.

The preparation still contains about one mole of adsorptively bound water, which can be removed by heating to 200°C.

Precipitation, decantation and filtration are carried out in the absence of CO_2 . Another suitable starting material is Ni(NO₃)₂ -6 NH₃; however, NiCl₂ · 6 H₃O and NiSO₄ · 7 H₂O are not recommended, since the precipitate then tenaciously retains Cl⁻ and SO².

PROPERTIES:

Apple-green crystalline powder; d 3.65. Decomposes at 230°C into NiO and $H_{3}O$. Soluble in ammonia, ethylenediamine and acids. Crystal structure: C 6 type. Heat of formation: -62.68 kcal./mole.

REFERENCE:

G. F. Hüttig and A. Peter. Z. anorg. allg. Chem. 189, 183 (1930).

B-Nickel (III) Hydroxide

NiO(OH)

| Ni(NO ₃) ₂ + | 3 KOH | + 1/8Fz | = NiO(OH) | + 2 KNO ₁ | + KBr - | H H O |
|-------------------------------------|-------|---------|-----------|----------------------|---------|-------|
| (6 H ₁ O) 290.8 | 168.9 | 79.9 | 91.7 | 202.2 | 119.0 | 18.0 |

A solution of 100 g. of Ni(NO₃)₂ \cdot 6H₂O in 1500 ml. of H₃O is added dropwise and with vigorous stirring to a solution of 55 g. of KOH and 12 ml. of Br₂ in 300 ml. of H₂O. The precipitation temperature should not exceed 25°C. The precipitate is washed five times (decantation) with CO_2 -free H_2O , then several times (decantation) using a centrifuge, until NO_3^- and K^+ can no longer be detected in either the precipitate or the wash water. The wet product is dried for three days over conc. H_2SO_4 , then two weeks over 1:1 H_2SO_4 .

Precipitation, decantation and filtration must be carried out in a CO_2 -free atmosphere.

Tests for active oxygen, Ni, H_2O and CO_2 are necessary. The oxygen and H_2O contents vary. In view of the rapid conversion to Ni $_3O_2(OH)_4$, it is advisable to work up the precipitate as quickly as possible.

To determine active oxygen, a 100-mg. sample is covered with 100 ml. of H_2O , and 1 g. of KI and 25 ml. of 2 N H_3SO_4 are added. The liberated I_2 is titrated with Na₂S₂O₃.

Alternate method: A solution of $Ni(NO_3)_2 \cdot 6 H_2O$ is treated with sodium acetate and electrolyzed at room temperature. The low yield is a disadvantage of this method [O. Glemser and J. Einerhand (1950)].

PROPERTIES:

Black powder, d_4^{20} 4.15. Readily soluble in acids. Rapidly converted to Nl₃O₂(OH)₄ by H₂O and bases. Loses water when heated in vacuum and is converted to Nl₃O₂(OH)₄. Crystal structure: C 6 type.

REFERENCES;

G. F. Hüttig and A. Peter. Z. anorg. allg. Chem. <u>189</u>, 190 (1930);
 O. Glemser and J. Einerhand. Z. anorg. Chem. <u>261</u>, 26 (1950).

7-Nickel (III) Hydroxide

NIO(OH)

Metallic Ni is fused with Na_2O_3 + NaOH and the melt is extracted with H_2O_3 .

A crucible of pure nickel is filled to one third of its volume with a mixture of one part of Na_2O_2 and three parts of NaOH, and heated for four hours at 600°C. The melt is cooled, then carefully extracted with ice water, avoiding any rise in temperature. Washing by decantation with H_2O is carried out until there no longer is an alkaline reaction. The tiny crystals settle very easily; the floccalent precipitate is removed by slurrying.

Tests for active oxygen [see under β -NiO(OB)], Ni, and H₃O are necessary.

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Used as an oxidation catalyst.

PROPERTIES;

Small, lustrous, black hexagons or needles. d_4^{30} 3.85. Soluble in dil. H₂SO₄ with evolution of O₂. Decomposes on heating to 138-140°C. Crystal structure: resembles C19 type.

REFERENCE:

O. Glemser and J. Einerhand, Z. anorg. Chem. 261, 26 (1950).

Nickel (II,III) Hydroxide

Ni₁O₂(OH)₄

The precipitation of Ni₃O₂(OH)₄ is carried out by dropwise addition of a solution of Ni(NO₃)₂ \cdot 6H₂O to aqueous KOH + Br₂ at 50°C (as described under β -NiO(OH)). The product is washed by decantation with warm, CO₂-free H₂O. All operations are conducted in a CO₂-free atmosphere.

Tests for active oxygen; see under β -NiO(OH). Analysis for Ni and H₂O is recommended. Water and oxygen contents vary. Used as an oxidation catalyst.

Alternate method: Electrolysis $(50-60^{\circ}C)$ of a solution of Ni(NO₃)₂ treated with sodium acetate. The low yield is a disadvantage of this method (O. Glemser and J. Einerhand, see reference below).

PROPERTIES:

Formula weight 276.16. Black powder. d_4^{20} 3.33. Readily soluble in acids. On heating to 140°C, converts to NiO, H_aO and O_a, Crystalline form: hexagonal.

REFERENCES:

O. Glemser and J. Einerhand, Z. anorg. Chem. 261, 26 (1950).

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Nickel (II) Suffide

NIS

a-NiS

 $N_iCl_i + H_iS = NiS + 2 HCl$ (6 H₄O) 237.7 22.1 *i*. 90.8 72.9

The apparatus used for precipitation of pickel sulfides, in the absence of air is shown in Fig. 335. The α -NiS is prepared

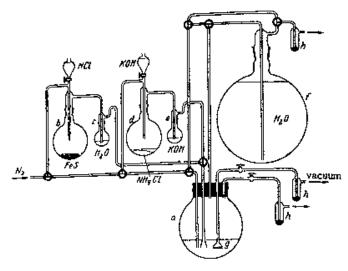


Fig. 335. Preparation of nickel sulfides in the absence of air.

as follows. The air is displaced from the apparatus by a stream of CO_3 -free, O_3 -free nitrogen. At the same time, all liquids in the apparatus are boiled and allowed to cool in the N₉ stream. These liquids comprise the solution in *a*, which is 0.4 N in NiCl₃ and 0.8 N in NH₄Cl; the water in *b*, which covers the chunks of FeS; the water in wash bottle *c*; the saturated NH₄Cl, with excess of solid NH₄Cl, in *d*; the conc. KOH in the bubble-counting tube *e*; and the wash water in *f*. The mercury trap *h* serves to prevent the entrance of air into the reactor. Now CO₂-free H₂S is generated in *b*, and the sulfide precipitates in *a*. The wash water is transferred into *a* (N₂ pressure), shaken with the precipitate, and (after the latter has settled) drawn off through fritted disc *g*. using a vacuum pump. The washing procedure is repeated 15-20 times.

The NiS should not be completely precipitated from the solution, otherwise it does not settle well during washing.

PROPERTIES:

Black powder, scluble in HCl. Converts to Ni(OH)S in air. Amorphous on x-ray analysis. Heat of formation: -- 19.37 kcal./mole.

REFERENCE:

E. Dönges. Z. anorg. Chem. 253, 345 (1947).

β-NiS

Ni + S = NiS58.7 32.1 90.8

A stoichiometric mixture of Ni and S is heated for six hours, at 900°C in a sealed, evacuated quartz tube.

Alternate methods: a) Precipitation with H_2S from a 1 N NiCl₂ solution containing acetic acid, workup as for α -NiS [A. Thiel and H. Gessner, Z. anorg. Chem. <u>86</u>, 1 (1914)].

b) The alpha form of NiS is digested with 0.2 N acetic acid for several days in the absence of air (A. Thiel and H. Gessner, see above).

PROPERTIES:

Black powder. M.p. 810°; d 5.0-5.6. Dissolves rapidly on boiling in 2 N HCl. Crystal structure: B8 type.

REFERENCE:

W. Klemm and W. Schüth. Z. anorg. allg. Chem. 210, 39 (1933).

;-NiS

 $NiSO_4 + H_2S = NiS + H_2SO_4$ (7 H₁O) 280.9 22.11. 90.8 98.1

The apparatus shown for α -NiS is used and H₂S is bubbled through 1 N NiSO₄ solution weakly acidified with dil. H₂SO₄. Air must be rigorously excluded during the reaction. The precipitate is worked up in the same way as α -NiS.

PROPERTIES:

Black powder. d_4^{30} 5.34. Converts to β -NiS at 396°C. Crystal structure: B13 type.

REFERENCE:

R. G. Levi and A. Baroni. Z. Kristallogr. 92, 210 (1935).

DRYING OF PRECIPITATED NIS

The slurry of the sulfide is dried in a drying pistol for eight hours (aspirator vacuum); the temperature is slowly raised to 150°C. Then NaOH is placed in the drying pistol and the material is dehydrated for four additional hours at 180°C in an oil-pump vacuum.

159

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O. GLEMSER

The sulfide is then transferred to another small flask and dried for 5-12 hours at 300-400°C (high vacuum). The latter operation must be carried out with care, to avoid dusting of the product.

REFERENCES:

W. Biltz. Z. anorg. alig. Chem. 228, 275 (1936); 239, 82, 126 (1938).

Nickel (IV) Sulfide

NiS,

 $NiS + S = NiS_{2}$ 90.8 32.1 122.8

Completely dry NiS is heated in a sealed tube with triple distilled S (five hours at 450° C). Four to five times the stoichiometric amount of S is used. After the reaction is complete, the excess S is removed by extraction with CS₂ in a Soxhlet apparatus.

Test for S: The sulfide is dissolved in HNO₃, and BaCl₂ is added to cause precipitation.

PROPERTIES:

Black to gray powder. d 4,39. Sensitive to air even when dry, evolving SO₂, which remains partly adsorbed. Can incorporate S into the crystal lattice. Soluble in nitric acid. Crystal structure: C2 type.

REFERENCES:

W. F. deJong and H. W. V. Willems. Z. anorg. allg. Chem. <u>160</u>, 185 (1927); W. Biltz. Ibid. <u>228</u>, 278 (1936).

Nickel (II) Amide

Ni(NH₂)₁

 $Ni(SCN)_2 + 2 KNH_2 + Ni(NH_2)_2 + 2 KSCN$ 174.9 110.2 30.8 194.4

The apparatus shown in Fig. 334 [see subsection on $Co(NH_2)s$] is charged with an excess of dry $Ni(SCN)_2$. Then a solution of KNH₂ in liquid NH₃ is added. A flocculent red precipitate forms; this is washed with liquid NH₃ until peptization just starts. The product is transferred to an auxiliary apparatus (as in the procedure on p. 1527) and dried in high vacuum at 40°C.

Used for the preparation of Ni3Na.

PROPERTIES:

Red powder. Reacts mildly with H₃O to form Ni(OH)₂ and NH₃. Decomposes when heated in vacuum to 120°C.

REFERENCE:

G. S. Bohart. J. Phys. Chem. 19, 537 (1915).

Trinickel Dinitride

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Ni₂N₇

 $\frac{3 \operatorname{Ni}(\operatorname{NH}_2)_2}{272.3} = \frac{\operatorname{Ni}_3 \operatorname{Ni}_2}{204.1} + \frac{4 \operatorname{NH}_2}{88.31}$

Nickel (II) amide (see preceding preparation) is heated in vacuum at 120 °C; NH₃ is slowly evolved and Ni₃N₂ is formed. Some N₂ is also produced in a side reaction.

Alternate method: A mixture of 10 parts of NiO and 7.4 parts of completely anhydrous Ni(CN)₂ is fused in an electric arc surrounded by pure N₂ [A. C. Vournasos. Comptes Rendus Hebd. Séances Acad. Sci. <u>163</u>, 889 (1919)].

PROPERTIES:

Black powder. Reacts very slowly with water. Decomposes to Ni and N_a above 120°C. Alkalies liberate NH_a.

REFERENCE:

G. S. Bohart, J. Phys. Chem. 19, 537 (1915).

Trinickel Nitride

Ni N

 $3 N_i + NH_3 = Ni_3 N + 1\frac{1}{2} H_1$ 176.1 22.1 *l*. 190.1 53.6 *l*.

An alumina boat is charged with 20 mg. of nickel obtained from Ni(CO). The boat is heated for three hours at 445°C in a reaction tube through which flows a stream of NH₃ (22 cm./sec.). The preparation is cooled in the NH₃ stream, ground carefully in an agate mortar, and allowed to react with NH₃ once more under the same conditions.

The test for N in the product may be made by the micro-Kjeldahl method.

PROPERTIES:

Black-gray powder. d_4^{25} 7.66. Unaffected by moisture and O_2 . Dissolved slowly by dil. mineral acids in the cold, rapidly by conc. HCl and conc. HNO₃. Dissolved rapidly by all hot acids. Not attacked by aqueous NaOH. Crystal structure: hexagonal close packing of Ni atoms, oriented incorporation of N.

REFERENCE:

R. Juza and W. Sachse. Z. anorg. allg. Chem. 251, 201 (1943).

Nickel Carbide

Ni_{*}C

 $3 N_i + 2 CO = N_{i_3}C + CO_t$ 176.1 44.8 l, 188.1 22.3 l.

Pure NiO is reduced with pure H_2 at 275-285°C until constant weight. The fine Ni powder is heated at once with pure CO (completely free of O₂) for 260 hours at 270°C. The Ni₃C thus produced is pyrophoric. This may be remedied by heating for a long time in O₂-free nitrogen at 250°C and cooling in the N₂ stream.

Test for bound C: Heating with pure H₂ at 250-270°C evolves C as CH₄.

PROPERTIES:

Gray-black powder. d_4^{10} 7.97. Heat of formation: -9.2 kcal. per mole. Decomposed at room temperature by conc. and dil. HCl: precipitation of C does not occur (see Fe₃C). Soluble in dil. HNO₃; dil. H₂SO₄ causes separation of C. Stable at temperatures up to 380-400°C. Crystal structure: bexagonal close packing of Ni atoms.

REFERENCE:

H. A. Bahr and Th. Bahr. Ber. dtsch. chem. Ges. 61, 2177 (1928).

Nickel (II) Carbonate

NiCO, 6 H₂O

Prepared by electrolysis of CO_{a} -saturated $H_{a}O$ with nickel electrodes.

28. COBALT, NICKEL

An electrolysis cell $(20 \times 15 \times 20 \text{ cm.})$ is covered with a woodsm lid from which three pieces of nickel sheet electrodes $(20 \times 12.7 \times 0.05 \text{ cm.})$ are suspended. Two of the electrodes are placed at the sides of the vessel and are interconnected; the third is in the center and serves as the anode. The cell is filled with conductivity water to 2.5 cm. below the top, pure CO₃ is bubbled through, and the current is turned on and controlled at 2-2.2 amp. The cell is cooled externally with running water. The NiCO₃ · 6 H₂O drops to the bottom. It is filtered off and dried at 100°C. The yield is about 30 g./day.

PROPERTIES:

Formula weight 226.82. Pale-green rhombohedra or monoclinic prisms. Readily soluble in acids. The product prepared in the above manner is free of alkali, but contains some black hydroxide.

REFERENCE:

E. C. C. Baly and N. R. Hood. Proc. Roy. Soc. London 122, 313 (1929).

NiCO,

Anhydrous NiCO₃ exists in two forms, one green (I) and one yellow (II).

GREEN FORM (I):

A solution of 0.12 moles of NiCl₂ in 100 ml. of water is acidified with HCl and charged into an autoclave. At 250°C and a CO₂ pressure of 1700 p.s.i., a solution of 0.18 moles of NaHCO₃ in 100 ml. of water is added dropwise. Green, crystalline NiCO₃ precipitates. Yield: 25-30%.

YELLOW FORM (II) :

The yellow NiCO₃ forms under the same conditions as the green, but at a temperature of 180° C and from very conc. solutions (0.22 moles of NiCl₃ in 25 ml. of water and 0.38 moles of NaHCO₃ in 100 ml. of water). The yield is poor. At lower temperatures only colloidal products are obtained; at temperatures between 180° and 250°C a mixture of I and II is produced.

PROPERTIES:

The green form consists of microscopically small, transparent, doubly refracting green rhombohedra; it is not attacked by warm

conc. acids or by boiling water. The habit and physical and chemical properties of II are the same as those of I. On heating to approximately 400°C, both carbonates decompose to CO_2 and green NiO. Both crystallize as rhombohedra.

REFERENCE:

R. de St. Léon Langlés. Ann. Chimie 7, 568 (1953).

Nickel (II) Thiocyanate

Ni(SCN):

Prepared by dissolving Ni(OH)₃ in a dilute HNCS solution and evaporating the resulting solution of Ni(SCN)₃.

A dilute HNCS solution is saturated with Ni(OH)₂ or nickel carbonate and the deep-green solution is evaporated at about 15°C. Large green crystals of Ni(SCN)₂ · 4 H₂O are deposited. Above 15°C and on drying of Ni(SCN)₂ · 4 H₂O, a yellow powder of Ni(SCN)₂ · 0.5 H₂O is obtained. It can be rendered anhydrous by heating to 150°C.

PROPERTIES:

Formula weight 174.88. Dark chocolate-colored powder. On addition of water, becomes first yellow and then dissolves with a green color.

REFERENCES:

A. Rosenheim and R. Cohn. Z. anorg. Chem. 27, 280 (1901); Ber. dtsch. chem. Ges. <u>33</u>, 1111 (1901); A. de Sweemer. Natuurwetensch. Tijdschr. <u>14</u>, 231 (1932).

Di-µ-sulfido-tetrakis(dithiobenzoato)dinickel (IV)

 $(C_tH_s \cdot CSS)_2NiS_tNi(SSC \cdot C_tH_s)_2$

This nickel (IV) complex compound is obtained by oxidation of the corresponding nickel (II) complex compound with O_2 .

An alcoholic solution of 1 mmole (0.13 g.) of NiCl₃ is treated with an alcoholic solution of 12 mmoles (0.15 g.) of monothiobenzoic acid and 6 mmoles (0.24 g.) of NaOH. The clear yellowbrown solution (in which the Ni is present as $[Ni(SCOC_{0}H_{5})_{4}]^{2^{-}}$) is refluxed at 50°C, and at the same time a gentle stream of O₃ is introduced. The oxidation is shown by a change in color, first to red and then to violet. The reaction is complete in about four hours. The dark-violet compound is filtered off, washed with alcohol and water, and recrystallized from benzene.

PROPERTIES:

Formula weight 794.65. Tuft-shaped aggregates of dark-violet crystals. May be recrystallized from benzene, alcohol, ether and CS_2 . Very stable to acids and bases; decomposed only by oxidizing acids.

REFERENCE:

W. Hieber and R. Brück, Z. anorg. alig. Chem. 269, 26 (1952).

Potassium Tetracyanonickelate (II)

K₁[Ni(CN)₄] · H₂O

 $NiSO_4 + 2 KCN = Ni(CN)_8 + K_7SO_4$ (6 H₂O) 262.9 130.2 110.7 174.3 NI(CN)_2 + 2 KCN + H_3O = K_7[Ni(CN)_4] \cdot H_3O
110.7 130.2 18.0 259.0

A solution of 60 g, of NiSO₄. $6 H_2O$ in 200 ml, of water is prepared, and a solution of 29.7 g, of KCN in 70 ml, of water is added slowly, with constant stirring. The gray-green precipitate of Ni(CN)₂ is washed until free of sulfate and then filtered off.

The solid Ni(CN)₂ is placed in a solution of 29.2 g. of KCN in about 30 ml. of water. The solution, which is now red, is heated on a hot plate until small crystals appear. These are redissolved and the solution is allowed to cool. The compound precipitates as beautiful crystals. The yield is 57.4 g. (97%).

SYNONYM:

Potassium nickel (II) cyanide hydrate.

PROPERTIES:

Orange-red crystals. The water of hydration is completely, removed by heating to 100°C. Very soluble, even in cold water decomposed to Ni(CN)₃ by mineral acids. Forms black precipitates of higher nickel hydroxides on addition of hypobromites.

REFERENCE:

W. C. Fernelius and J. J. Burbage in: W. C. Fernelius, Incres. Syntheses, Vol. II, New York-London, 1946, p. 227.

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SECTION 29

The Platinum Metals

H. L. GRUBE

Pure Platinum

Pt

Platinum obtained from Russian or Colombian platinum ores or by industrial recovery processes contains the other platinum metals as impurities, as well as gold, iron and copper.

The following methods are recommended for its purification: the lead fusion process, based on the analytical procedures of Saint-Claire-Deville and Stas, and the caustic soda precipitation of Schneider [1] and Seubert [2], in which all the platinum metals except Pt pass into their lower oxidation states, which are not precipitated by NH_4CL . There is also the Finkener process, based on recrystallization of Na_3PtCl_6 from dilute soda solutions; this has been described by Mylius and Förster [3]. However, this method leads to poor yields because of the low solubility of Na_3PtCl_6 . A process by Reerink [4] makes use of platinum's ability to form a volatile carbonyl chloride with Cl_3 and CO.

The hypochlorite method developed by Mylius and Mazzucchelli [5] for the preparative purification of the platinum metals can be recommended as a laboratory procedure. Platinum (in the form of small foil clippings or sponge) is dissolved in the purest aqua regia available (glass or porcelain vessels); the solution is withdrawn (or decanted) and carefully evaporated in a porcelain dish over a small flame; the concentrate is dissolved in hydrochloric acid and hot H2O. The chloride solution is diluted with a large amount of water, heated to about 80°C, and made slightly alkaline with soda. Any IrO2 present is precipitated with Cl2, bubbled through for a short time. The initially colloidal iridium-containing precipitate coagulates after a short time to a black flocculent deposit which settles rapidly in the yellowish-red solution. Addition of a few milliliters of alcohol produces a marked increase in the speed of separation. The more carefully the solution is neutralized (without, however, going below a pH of 7), the more complete is the separation of the unwanted oxide.

The other platinum metals, gold and the heavy base metals may be precipitated as the oxides by addition of hypochlorite. This reaction can therefore be used for the removal of all metallic impurities. The only oxide soluble in an excess of hypochlorite is the black RuO_2 (it is thereby converted to the volatile RuO_4).

The filtered platinum solution is heated in a beaker or porcelain vessel and treated with NH₄Cl. The $(NH_4)_3PtCl_6$ deposit is then filtered off and extracted by boiling with distilled water to dissolve any small quantities of $(NH_4)_3PdCl_6$ still remaining.

The very pure platinum obtained after ignition is free of all the other platinum metals, gold and the heavy base metals. If the Pt still contains a few tenths or hundredths of a percent of Ir, the purification process can be repeated.

REFERENCES:

- 1. W. von Schneider. Liebigs Ann. 5, 271 (1997).
- 2. K. Seubert, Ibid. 207, 8 (1881).
- 3. F. Mylius and F. Förster, Ber. dtsch. chem. Ges. 25, 665 (1892).
- 4. E. H. Reerink. Z. anorg. allg. Chem. 173, 45 (1928).
- 5. F. Mylius and A. Mazzucchelli, Ibid, 89, 1 (1914).

Reclaimed Platinum

In order to reclaim platinum residues from the laboratory (e.g., platinum absorbed on filter papers, scraps, filter ash, etc.), these are well ignited and then sieved through a fine screen, separating the residues into "fine" and "coarse" fractions.

The coarse fraction remaining on the screen contains the metallic residues, such as small pieces of wire, small clippings and pieces of foil. It is advisable to pass a magnet through this material to locate and remove any iron present in the form of nails, wire, etc. In some cases, it may be advisable to extract the iron from this fraction by boiling with dilute hydrochloric acid. Copper or brass residues are extracted by boiling with dilute nitric acid. The coarse material is then dissolved in aqua regia and processed to recover the Pt and its associated metals. In order to expel the nitric oxides present, the aqua regia solution is evaporated to a sirupy thickness, taken up with water and some dil. hydrochloric acid, and treated with NH₄Cl to precipitate the (NH₄)₅PtCl₆. The Pt still remaining in the mother liquor is precipitated with pure Zn.

The iron in the fine fraction is first extracted by boiling with dilute hydrochloric acid; after ignition, the residue is dissolved by heating in aqua regia. This solution is evaporated to a strupy thickness and taken up with H_{2O} and HCl; the Pt is precipitated as $(NH_{4})_{2}$ PtCle.

If aged solutions or more or less reduced salts and preparations are to be processed, Berthold's work-up method is recommended, Often dirt appears in the residue on long standing, and sometimes the Pt salts are partially reduced by alcohol on long storage. In either case the liquid is first filtered, the residue is treated with aqua regia to dissolve any platinum it may contain, and the resulting solution is filtered.

The last filtrate is not combined with the first one, but is evaporated to drive off the aqua regia. The residue is extracted with hot water and this solution added to the main (that is, the first) filtrate.

When the solution to be worked up originates from an analytical laboratory, the main impurities are likely to be salts of K. Na, Mg and NH₄. Alcohol and ether may also be present. In this case, the liquid is treated with some conc. HCl and pure Zn. If K_3PtCl_8 precipitates, it must be reduced by heating to convert it into soluble material. Any alcohol or ether present must first be driven off.

After the reduction, which is clearly indicated by the decoloration of the liquid, the supernatant is decanted; the residue is thoroughly extracted by boiling with conc. HCl and washed by decantation with hot distilled water until the wash water no longer contains any chloride.

Double saits containing a platinum and an alkali metal ion (and especially the ammonium ion) are best treated by careful calcination in a Pt crucible under a layer of NH_4Cl , extraction with bolling water acidifed with some hydrochloric acid, and reignition.

For reclaiming procedure for Pt from electrolytic Pt baths, see p. 1567.

REFERENCE:

A. Berthold. Z. angew. Chem. 14, 621 (1901).

Platinum Sponge

Platinum sponge is best produced by prolonged ignition of $(NH_{\bullet})_2$ PtCl_e in a Pt dish or bowl (dull red heat, about 600°C). The ignited sponge should be boiled with dilute hydrochloric acid, and then with distilled H₂O. Finally it is gently heated again in a Pt dish.

Platinum Black

Of the various methods of preparation given in the literature, that described by Gutbler and Maisch seems to be the best. A 5% solution of H_2PtCl_6 is heated, neutralized with Na_2CO_8 , and poured into a boiling solution of sodium formate. The black residue which precipitates immediately is washed by decantation with hot H_2O_4 . It is then filtered off with suction and freed from residual water by pressing between filter papers; it is further dried over P_2O_6 or conc. H_2SO_4 .

PROPERTIES:

Black powder, very active toward H_2 , with a maximum absorptive capacity for H_2 at 0°C.

REFERENCE:

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A. Gutbier and O. Maisch. Ber. dtsch. chem. Ges. 52, 1370 (1919).

Platinized Asbestos

As bestos is saturated with an alcoholic solution of H_2PtCI_8 . 6 H_2O (technical "platinum chloride"), thereby producing a material with a definite platinum concentration. In view of the cost of the solution, the calculated quantity of H_2PtCI_8 must be absorbed quantitatively by the asbestos; it is therefore essential to establish accurately (by preliminary experiments) the absorbance of the asbestos to be used. The H_2PtCI_8 -saturated asbestos is kneaded as uniformly as possible and the mass is ignited while being agitated with a Pt spatula or rod. This method is particularly suitable for producing asbestos with low Pt contents (0.1-1% Pt). Its advantage lies in that the product contains no foreign salts which could obstruct the pores of the asbestos fibers and adversely affect its catalytic activity.

To prepare platinized asbestos with high platinum contents (5-10%), the mass is saturated with a H_aPtCl₆ solution which does not contain alcohol. The procedure is the same as described above. The mass is made slightly alkaline by treating it with dil. sodium hydroxide, and the chloride is then reduced to fine, particulate Pt with sodium formate. The reduction is best carried out in a muffle furnace at about 300-400°C. Finally the asbestos is freed of alkali salts by thorough washing with cold water and is dried in a muffle furnace. At this point the asbestos should be light gray.

Erdmann gives another method. Asbestos saturated with conci-H₂PtCl₈ is placed in a conc. solution of NH₄Cl. The asbestos, which is thus permeated with $(NH_4)_2$ PtCl₈, is placed on a glass funnel to allow the excess solution to drain, and is then slowly heated to incandescence. This produces an asbestos with a high concentration of platinum sponge; however, the uniformity of the product leaves much to be desired. For analytical purposes the platinized asbestos fibers should be as short as possible (almost powdery). For large-scale catalytic processes, the fibers should, on the other hand, be as long as possible.

REFERENCE:

O. Erdmann. Lehrb. d. anorg. Chem. [Inorganic Chemistry Text], 5th ed., p. 175 (1910).

Handling of Platinum Equipment

Because the various chemicals used in ignition and melting processes may be corrosive, certain precautions must be observed in using platinum apparatus. Unfortunately, the use of platinum as vessel material is not a panacea for all the corrosion problems that plague the chemist.

Materials which readily form alloys with Pt (nonmetals P, As, Te, Si, B and C) or metals which melt at low temperatures (Pb or Sn) or substances which liberate these materials during ignition or melting processes can not only damage but even destroy platinum apparatus. This also holds for all meits containing potassium hydroxide, sodium nitrate, or mixtures of the alkali hydroxides or alkali carbonates with sodium nitrate; melts containing peroxides, cyanides or sulfides are particularly injurious to crucibles.

In general, ignitions should not be carried out at unnecessarily high temperatures or with reducing flames; reduction with an acetylene flame is forbidden.

Reducing conditions involving burner or flue gases, activated charcoal and the like are particularly deleterious when free silicic acid is also present. In this case, platinum-silicon alloys are formed, leading to the characteristic silicon fracture.

The critical corrosion temperature, i.e., the temperature above which serious corrosion occurs, generally lies around 700°C. However, this temperature is about 500-600°C for melts consisting mainly of KOH, Ba(OH)₂, peroxides or cyanides; for melts composed mainly of carbonates or neutral salts, it is 800°C or somewhat higher. Further details are given in the Mitteilungen aus dem Chem. Laboratorium, W. C. Heraeus Co., Hanau; publications of the Engelhardt Industries, Newark, N. J.; G. Bauer, Chemiker-Zig. <u>62</u>, 257 (1938).

CLEANING

Careful treatment of Pt vessels after use is essential. Usually the crucible contents can be easily removed by mechanical means.

In some cases, the contents can be dissolved with warm hydrochloric acid or chlorine-free nitric acid. If this does not suffice, sodium pyrosulfate is heated in the Pt crucible until liberation of SO_3 , the molten liquid is poured out, and the material still adhering to the walls is dissolved with hot water (O. Brunck). The crucible is not damaged at all by this treatment. If the edges of the orucible lid become bent out of shape, they can be smoothed out against a glass plate with a spatula made of horn or plastic. A very badly dented crucible should best be repaired by a goldsmith or other expert.

A Pt crucible that develops a small tear due to careless handling can readily be repaired in the laboratory. A small piece of thin gold foil of suitable size and shape is placed over the tear, and the spot is heated with an oxyhydrogen torch until the gold melts, after which the patch is smoothed with a burnisher. Such a crucible can still be used for most purposes. Very small tears can be heated with an oxyhydrogen torch; there is no need for a patch material in this case. Platinum wires, e.g., the leads to thermocouples or electrodes, can also be welded together quite simply with an oxyhydrogen torch: the two wires to be joined are laid close together and fused, or are welded together at a slightly lower temperature by a light tap with a hammer.

In case of serious damage, however, it is advisable to have the vessel repaired by a specialist.

Platinum Electroplating

Thin layers of platinum can easily be deposited from electrolytic baths; however, the deposition must be repeated several times to produce thicker deposits.

Böttger gives a very good bath formula: it consists of a solution of $(NH_4)_2PtCl_8$ in sodium citrate. Langbein gives the following instructions for preparing this bath: 500 g. of citric acid is dissolved in two liters of H_2O and neutralized with sodium hydroxide. This solution is heated to boiling and the $(NH_4)_2PtCl_6$, freshly precipitated from a solution of 75 g. of dry H_2PtCl_6 is added with stirring; the mixture is heated until the $(NH_4)_2PtCl_6$ is completely dissolved; the solution is then cooled and diluted with H_2O to five liters. To reduce the electrical resistance of the bath, 4-5 g. of NH_4Cl is added per liter.

The electrolysis proceeds at 3-4 volts, a current density of 0.065 amp./in.² and a temperature of 70-90 °C. Thin Pt sheet is always used as the anode in platinum plating baths; it is scarcely attacked at all. The bath must always be kept slightly alkaline; if this is no longer the case after prolonged passage of current, dilute aqueous ammonia is added until an odor of ammonia is

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noticeable. If the bath is acid, Pt sponge will rapidly precipi-

C. W. Keitel et al. give another bath formula: cis-dinitrodiammineplatinum is dissolved in ammonia, and ammonium nitrate and sodium nitrite are added to improve the conductivity of the bath.

Objects to be plated with platinum (cathodes) are prepared in exactly the same way as in any other method of electroplating. Given the cost of platinum, these objects are usually small; platinum electrolysis vessels therefore need to hold only a few liters of the solution; the vessel will thus usually be a glass or porcelain beaker or a small iron trough coated on the inside with a special alkali- and acid-resistant enamel. If the platinum deposit is too dull, it can be rubbed and scoured in the same way as gllt-ware, and then replaced in the platinum bath to deposit a further platinum layer; this treatment may be repeated until the required deposit thickness is reached.

The current efficiency in platinum coating is very small (only 30-40% of the theoretical) since large quantities of energy are consumed in liberating the great amount of H₂ that evolves. This H₂ also hardens the platinum deposits.

REFERENCE:

Pfanhauser et al. Galvanotechnik [Applied Electrochemistry], Lelpzig, 1949, pp. 939-942; gives further details on bath compositions and on other recently developed plating baths.

According to Lummer and Kurlbaum, the liquid most suitable for the platinization of electrodes for potential measurements consists of 3 g. of $H_2PtCl_6 \cdot 6 H_2O$ plus 0.10 g, of lead acetate in 97 ml. of H_3O ; the bath temperature is 20-30 °C, the potential about 4 volts. Two series-connected storage batteries are used as a power source and the current is regulated to produce a moderate gas evolution. The current is reversed, so that each electrode serves alternately as the anode and cathode. The total time for initial platinization is 10-15 minutes; usually only 1-2 minutes is sufficient for replating electrodes already covered with platinum black (before platinum plating these electrodes must be carefully cleaned; it is best to do this with chromosulfuric acid).

A thin coat of platinum (burnished platinum) can be produced on glass and porcelain by baking on either of the following special solutions:

I. A solution of 1 g. of platInic chloride $(H_2PtCl_8 \cdot 6 H_2O)$ in 3.5 ml. of absolute alcohol is mixed with 10 ml. of a concentrated alcoholic solution of boric acid and 25 ml. of a solution of Venetian turpentine in layender oil.

II. A solution of 1 g. of platinic chloride $(H_3PtCl_8 \cdot 6 H_3O)$ in the **minimum amount of absolute alcohol is added slowly (stirring) to**.

6 ml. of ice-cold lavender oil. After warming, Burgundy pitch is added to the mixture to give the required consistency.

In either case, the platinum-containing mass is spread untformly on the glass (or porcelain) and carefully heat-dried so that no bubbles develop. The coated surface is then heated to a dull red heat in a mufile furnace or in a sulfur-free blowtorch flame.

The ingredients of these solutions are not usually available in the laboratory. However, ready-for-use solutions for producing burnished platinum (with instructions) are provided by companies handling noble metals (e.g., W. C. Heraeus of Hanau or Degussa of Frankfurt or Engelhardt Industries of Newark, N. J.).

REFERENCE:

Ostwald-Luther. Physiko-Chemische Messungen [Physicochemical Measurements], 4th ed., Leipzig, 1925, pp. 158-159.

RECLAIMING PLATINUM FROM USED BATHS

If the liquid quantity is not too large, then the best method is to precipitate the platinum with H_0S (this is preferred over the procedure involving concentration of the solution and reduction of the residue to the metal). The platinum can be precipitated from larger liquid quantities with pure 2n (following acidification of the bath liquid).

Platinum Chlorides

Streicher and Krustinsons gives the following facts about the stability of chlorides of platinum as a function of temperature at 1 atm. of Cl₂ pressure:

PtCl4 (russet) stable up to 382°C.

PtCl₃ (dark green) stable between 382 and 435 °C,

PtCl₂ (greenish brown) stable between 495 and 515°C.

The existence of PtCl (pale yellow-green), 581-583*C, is not altogether certain.

REFERENCES:

S. Streicher. Thesis, Univ. of Darmstadt, 1913; J. Krustinsons, Z. Elektrochem. 44, 537 (1938).

PICL

Prepared by decomposition of $H_2PtCl_6 \cdot 6 H_2O$ in a stream of chloride. The starting material is placed in a boat set in a

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combustion tube made of high-melting glass. The temperature is increased slowly from 60 to 150°C, which drives off water. When the material is completely dry, the temperature is raised to 275-300° over a period of two hours, and held at this level for 0.5 hour. The temperature must not be allowed to rise above 360°C. After cooling to about 150°C, the product is removed, quickly ground, replaced in the combustion boat, and reheated for 0.5 hour at 275°C while a stream of Cl₂ is passed over it. The resultant chloride is placed, while still hot, in a hermetically closable storage bottle. The yield from 6 g of $H_2PtCl_5 \cdot 6 H_2O$ is 3.7 g. of $PtCl_4$.

PROPERTIES:

Red-brown, very hygroscopic crystals. Very soluble in water, sparingly soluble in alcohol. Absorbs moisture on standing in air, yielding $PtCl_4 - 5 H_3O_4$.

REFERENCES:

A. Gutbier. Z. anorg. Chem. <u>81</u>, 381 (1913); M. S. Kharasch and T. A. Ashford. J. Amer. Chem. Soc. <u>58</u>, 1736 (1936); R. N. Keller in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 247.

PtCf₂

I. Prepared by heating platinum sponge to about 500 °C in a stream of Cl₃ or, better, by thermal decomposition of PtCl₄ or $H_3PtCl_6 \cdot 6 H_3O$.

The $H_3PtCl_6 \cdot 6 H_2O$ (or the commerical product containing 40% Pt) is subjected to a preliminary decomposition over a free flame at 150°C. The resulting residue is ground and decomposed in a slow air stream at 360°C. Depending on the quantities involved, the operation may require several hours. At the end the undecomposed H_3PtCl_6 should be removed by extracting and washing with H_3O , after which the product is redried at 360°C.

PROPERTIES:

Formula weight 266.0. Greenish-brown powder. Insoluble in water. At 250°C, dry PtCl₂ forms a very volatile carbonyl chloride with CO. Thus gases containing CO should not be used in reductive ignition of platinum chloride (the same holds for the chlorides of the other platinum metals). Very sparingly soluble in dil. hydrochloric acid, yielding H_2 PtCl₄.

REFERENCE:

M. S. Kharasch and T. A. Ashford, J. Amer. Chem. Soc. <u>58</u>, 1776 (1936). II. A chocolate-brown form of platinum (II) chloride can be prepared by careful concentration of a solution of tetrachloroplatinic (II) acid (see p. 1570) in hydrochloric acid; this material is more soluble in hydrochloric acid and aqueous ammonia than the product obtained by method I.

REFERENCE:

W. E. Cooley and D. H. Busch in: T. Moeller, Inorg. Syntheses, Vol. V, New York-Toronto-London, 1957, p. 208.

Hexachloroplatinic (IV) Acid

H₂PtCl₁ · 6 H₂O

Obtained by dissolving platinum in aqua regia. To prepare large quantities, the platinum, in the form of thin shavings of foil, is dissolved in a porcelain or glass vessel and the solution poured into a porcelain dish. Hydrochloric acid is added and the solution evaporated to sirupy consistency in order to drive off the nitric acid and any PtCl₄ · 2 NOCl which may form. The thick solution is taken up with HCl and the resulting solution reevaporated to a sirup. This is repeated several times. Since the last traces of nitric oxide are very difficult to remove, finely divided Pt may also be dissolved in hydrochloric acid through which Cl_3 is bubbled (or nascent Cl_3 may be generated in the solution itself by carefully adding HClO₃ or H₂O₃ to it).

The concentrated solution is placed in a large tared dish and the percentage of platinum in the chloride is adjusted (usually to 39.5 or 40%) by controlled evaporation of the acid on a burner (check on the decrease in weight).

When the required percentage of platinum is reached, the dish is removed from the burner and allowed to stand until the chlorids solution becomes a definite slurry. The solution is then stirred with a thick glass rod until it is completely cool.

SYNONYMS:

Chloroplatinic acid, platinum chloride, platinic chloride,

PROPERTIES:

Formula weight $(H_3PtCl_8 \cdot 6 H_3O)$ 518.0. Commercial "piatinum chloride" containing 39.5-40% Pt is not a definite hydrate, but has the composition of $H_3PtCl_8 \cdot 4.5 H_3O$ and is deep orange. Starting material for the preparation of most platinum compounds: 1.34

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Tetrachtoroplatinic (II) Acid

H_PiCl.

Stable only in solution; prepared by reduction of H_3PtCl_8 with a stoichiometric quantity of $N_8H_4 + 2$ HCl:

 $2H_{*}PtCl_{*} = 6H_{*}O + N_{*}H_{*} = 2Hcl_{*} = 2H_{*}PtCl_{*} + N_{*} + 6HCl_{*} + 12H_{*}O$

Commercial platinum chloride (10 g., 40% Pt) is dissolved in 50 ml, of water in a 150-ml, beaker. Then 1.07 g. of solid $N_2H_4 \cdot 2$ HCl is added in small portions, so that the solution effervesces each time due to evolution of N_2 . Within five minutes of adding the last of the hydrazine salt, the deep red solution is heated on a steam bath until no further gas evolves; it is then filtered to remove the small quantity of platinum black which may deposit out.

PROPERTIES:

Red solution; leaves a brown deposit of $PtCl_3$ on careful eveporation. Very stable in hydrochloric acid solution. With an excess of ammonia it forms $[Pt(NH_3)_4]$ $[PtCl_4]$ or $[Pt(NH_3)_4]Cl_2$.

REFERENCE:

W. S. Cooley and D. H. Busch in: T. Moeller, Inorg. Syntheses, Vol. V, New York-Toronto-London, 1957, p. 208.

Ammonium Hexachloroplatinate (IV)

(NHL),PtCL

A dilute, weakly acidic (HCl) solution of H_2PtCl_6 is prepared and, if that is needed, oxidized with H_2O_2 . It is then reacted with an excess of NH₄Cl (at least three parts by weight of NH₄Cl to one of Pt) and slowly evaporated to dryness on a steam bath. The salt crust mixed with the resulting residue is broken up with a glass rod and the solids heated on a steam bath with continuous stirring until the powdery mass no longer gives off the odor of HCl. The dry residue is then carefully moistened with some distilled water, taken up in cold saturated NH₄Cl solution and filtered. It is washed first with NH₄Cl solution, then with alcohol. The mother liquor should be completely colorless and show only traces of Pt on reaction with H₂S and SnCl₂.

SYNONTMS:

Platinic salammoniac, ammonium platinichloride, ammonium chloroplatinate.

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PROPERTIES:

Formula weight 443.9. Lemon-yellow octahedra. A color of yellow ochre to brick red instead of lemon yellow indicates the presence of other platinum metals, particularly Pd, Ir and Ru. Greenish-yellow to green indicates that Rh is present. Completely decomposed on ignition in a platinum dish, leaving fine particles of platinum sponge. Very sparingly soluble in H₂O, less soluble in NH₄Cl solutions. Solubility (15.5 °C) 0.67 g., (100 °C) 1.25 g./100 ml. H₂O. Colorless solution in conc. ammonia. Like K₂PtCl₈, insoluble in alcohol.

Potassium Hexachloropiatinate (IV)

K₂PtCl₄

Prepared by adding a solution of KCl to H_2PtCl_6 (the ratio of solid components is 3:1). For complete precipitation of the Pt with KCl or NH₆Cl, the Pt must be completely oxidized to the +4 state and the solution must be as concentrated as possible; however, the solution should not be so concentrated that it becomes viscous while the product is being formed.

SYNONYM:

Potassium platinichloride.

PROPERTIES:

Formula weight 486.0. Pure yellow crystals; dissolve with difficulty in water; insoluble in alcohol. The color changes in the presence of the other platinum metals in the same way as does that of $(NH_4)_3$ PtCl₈. Solubility in water:

| °C | g. K ₂ PtCl ₆ /100 g. H ₂ O | | | | | | |
|-----|--|--|--|--|--|--|--|
| 0 | 0.74 | | | | | | |
| 10 | 0.90 | | | | | | |
| 20 | 1.12 | | | | | | |
| 50 | 2.16 | | | | | | |
| 80 | 3.79 | | | | | | |
| 100 | 5.13 | | | | | | |

Sodium Hexachloroplatinate (IV)

N8+PtCl., Na+PtCl. · 6 HrO

Prepared by passing Cl₂ over a mixture of platinum sponge with twice its weight of NaCl. The reaction temperature should be highles

than 500°C, but should not under any circumstances exceed 660°C. Purification is effected by solution of the product in alcohol, fiitration to remove NaCl and platinum metals, and concentration of the solution, after which the salt is dried in a drying oven.

If the reaction mixture is dissolved in water (instead of alcohol) and the solution concentrated, $Na_3PtCl_6 \cdot 6 H_3O$ is produced as triclinic, orange-colored crystals. A very pure salt is obtained by recrystallization from 1% soda solution; it loses its water of crystallization below 100°C.

SYNONYM:

Sodium platinichioride.

PROPERTIES:

Formula weight (anhydrous) 453.8. Orange crystals. Soluble in water and alcohol.

REFERENCE:

L. Wöhler and P. Balz. Z. anorg. allg. Chem. 149, 356 (1925).

Potassium Tetrachloroplatinate (II)

K,PtCL

Prepared by reduction of K₂PtCl₆ with SO₂ or N₂H₄ · 2 HCl.

L A suspension of 4.7 g, of K₂PtCl₈ in 35 ml. of H₂O is prepared in a 50-ml, beaker; small portions of freshly prepared SO2 solution are added while stirring the suspension mechanically and heating It to 85-90 °C on a water bath. About 15 additions of 0.6 ml. should be made first, followed by 10-15 additions of 0.4 ml. After each addition, 2-3 minutes (later 3-4 minutes) should be allowed until the SO₂ is consumed and its odor disappears. Toward the end of the reduction, when the suspended particles are gradually disappearing, it is necessary to proceed even more slowly. The solution remaining on complete reduction is concentrated on a water bath until crystallization begins. After cooling, it is suction-filtered, and the red KaPtCl4 is dissolved in 40 ml. of cold water, filtered to remove any small residue of KaPtCls, and the residue rinsed with 5 ml. of water. The solution is carefully transferred (rinsing with 10 ml. of water) into an 600-ml. beaker; its total volume at this point is 55-60 ml. Then 650 ml. of a 1:1 mixture of acetone and ether 18 added with stirring. This precipitates the solid chloroplatinate,

which is allowed to settle. The bright yellow liquid is decanted, and the salt is washed three times with 120 ml. of acetone-ether mixture (decantation) and then three times with 80 ml. of ether. After filtering and drying the product in air, the salt is recrystallized from hot, slightly acidified water.

II. The K₂PtCl₅ can be reduced with N₂H₄ · 2 HCl in the same way as H₂PtCl₈.

> $2 K_{s} PtCl_{s} + N_{s} H_{4} \cdot 2 HCl = 2 K_{s} PtCl_{4} + 6 HCl + N_{4}$ 105.0 972.1 830.2

The K2PtCls is suspended (brisk stirring) in 10-12 times its weight of water. With continuous stirring, the stoichiometric quantity of solid N₃H₄ · 2 HCl is added in small portions, the temperature being raised to 50°C within 10 minutes. The KaPtCla dissolves with evolution of N2. The solution is brought to the boiling point, filtered and concentrated, first over an open flame and then on a water bath, until crystallization begins. Since no foreign ions are introduced in this preparative method, recrystallization can be omitted, provided the starting materials used are pure.

An excess of N2H4 · 2 HCl leads to the formation of platinum black, while a deficiency leaves undissolved KaPtCle-

The compounds (NH4), PtCl4 and Na, PtCl6 can also be prepared in this way.

PROPERTIES:

Formula weight 415.1. Red crystals or bright red powder. Solubility in water (16°) 0.93 g., (100°C) 5.3 g./100 ml. Insoluble in alcohol; reduced in alcohol.

REFERENCES:

L. Magnus, Pogg, Ann. 14, 241 (1828).

H. R. N. Keller in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 247; N. G. Klynchnikov and R. N. Savel'eva, abstract in Chem. Abs. 51, 10288 (1957).

Platinum (II) Oxide

PiC

Wöhler's method is recommended in preference to others. Oxygen is passed at 150°C over platinum sponge that is as finely divided as possible; the temperature must not exceed 560°C.

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PROPERTIES:

Completely anhydrous black powder. Readily soluble in aqua regia. Instantly reduced by H₂ at ordinary temperatures, liberating heat and forming gray platinum sponge. Decomposes at atmospheric pressure (560°C): 2 PtO = 2 Pt + O₂.

REFERENCE:

L. Wöhler. Z. Elektrochem. 15, 136 (1909).

Platinum (IV) Oxide

PtO₁ · xH_xO

I. It is impossible to prepare completely anhydrous PtO_2 without decomposing it. In addition, even the hydrated material (which contains variable quantities of water) is not easy to obtain in pure form. The procedure of Wöhler and Frey appears to be the most suitable. Red-brown hydrated platinum dioxide is precipitated by boiling a pure, concentrated solution of H_2PtCl_8 with concentrated Na_2CO_3 solution. The precipitated solid is made acid-insoluble by heating for several hours in a drying oven at 200°C; it is then freed of chlorides by vigorous boiling with dilute sola solution and distilled water. Finally, it is freed of alkali by treatment with dilute sulfuric acid and distilled water, filtered off and dried on a water bath.

PROPERTIES;

Straw yellow after brief drying; on further drying, becomes yellow ochre and then dark brown; at this point the oxide is acidinsoluble.

BEFERENCE:

L. Wöhler. Z. anorg. Chem. 40, 436 (1904).

II. A 10% solution of H_3PtCl_6 (10 ml.) is added to 9 g. of NaNO₃ in a 50-ml. beaker. The solution is evaporated to dryness over a flame (covered with asbestos-wire gauze) while continuously stirring with a glass rod. Local melting of the mixture must be carefully avoided. Then 100 g. of NaNO₃ is heated to 520°C in a 400-ml. beaker (controlling the temperature with a thermocouple), and the dry, fine powder residue from the evaporation is added at once. The flame is then removed. The olive-brown platinum oxide is

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precipitated more or less quantitatively and settles rapidly. During cooling and solidification, the beaker is rotated, so that the contents solidify on the walls in fine particles, thus avoiding the cracking of the beaker.

The cooled melt is dissolved in about two liters of H_2O , and the residue is filtered off with suction. It is then washed repeatedly with H_2O_1 taking care that the residue remains covered with water at all times, since otherwise it passes into solution as a colloid. Finally it is dried over CaCl₂ in an evacuated desiccator.

PROPERTIES:

Heavy brown powder; insoluble in aqua regia. Blackens and settles rapidly when treated with H₂ in an alcoholic suspension (this powder is soluble in aqua regia). Very active catalyst for the hydrogenation of olefins and carbonyl groups.

REFERENCE:

V. L. Framton, J. D. Edwards, Jr., and H. R. Henze, J. Amer. Chem. Soc. <u>73</u>, 4432 (1951).

Hexahydroxyplatinates (IV)

$Na_1Pt(OH)_1 \cdot x H_1O, K_2Pt(OH)_1 \cdot x H_1O$

An aqueous solution of $Na_{2}PtCl_{8}$ or $K_{2}PtCl_{8}$ is boiled with NaOH and then treated with alcohol. The precipitate consists of small colorless crystals, which are filtered off and dried in air. Depending on the conditions of precipitation, the product contains from 0.5 to 3 moles of H₂O. Aqueous solutions of these two salts are very good electrolytes for electroplating platinum.

Platinum (II) Sulfide

PtS

Produced by heating an intimate mixture of very fine powders of platinum sponge and sulfur; may also be produced by decomposition of a boiling solution of PtCl₂ by bubbling in H₂S, or by adding to it a solution of one of the alkali sulfides. The black precipitate can be washed and dried without being altered.

PROPERTIES:

Insoluble in acids, even at the boil. Yields metallic Pt when heated in air.

Platinum (IV) Sulfide

PtS:

Produced as a dark-brown precipitate by passing H_2S through a bot solution of H_2PtCl_8 in hydrochloric acid. The precipitation can be greatly accelerated and made almost quantitative if the weakly acidic platinate solution is mixed with a 5% solution of MgCl₂ and then saturated with H_2S gas. After the excess H_2S is driven off by boiling, the PtS₂ is filtered off and carefully dried.

PROPERTIES:

Insoluble in hydrochloric and sulfuric acids, soluble in nitric acid and particularly in aqua regia. Even though Pt belongs to the group of elements forming this salts, PtS_3 is only slightly soluble in colorless alkali sulfides and yellow ammonium sulfide.

Potassium Tetracyanoplatinate (II) and Barium Tetracyanoplatinate (II) K.Pt(CN),·3H2O, B2PI(CN),·4H2O

Both salts are obtained by precipitation reactions.

| PtCl ₂ | (K ₂ PtCl ₄) | ÷ | 4 KCN | ÷ | K ₂ Pt(CN) ₄ | ÷ | 2 KCI | (4 KCl) |
|-------------------|-------------------------------------|---|------------------------------|---|------------------------------------|---|-------|---------|
| 268.0 | (4)5.1) | | 260.5 | | (3H ₂ O) 491.4 | | 149.1 | (298.2) |
| | K ₂ Pt(CN) ₄ | + | BaCl | = | BaPt(CN) | + | 2 KCi | |
| | (3H ₂ O) 431.4 | | (2H ₂ O) 244.3 | | (5 H ₁ O) 526.6 | | 149,1 | |

A solution of $PtCl_2$ or K_3PtCl_4 is added to a cold, saturated solution of KCN (use a good hood!). The precipitated $K_3Pt(CN)_4$. 3 H₂O is filtered off with suction. If it is to be used for preparing the barium salt, it is dissolved in water and treated with a concentrated aqueous solution of BaCl₂. The precipitated BaPt(CN)₄. 4 H₂O is filtered off with suction and washed with cold water.

SYNONYMS:

Potassium platinocyanide; barium platinocyanide.

PROPERTIES:

 K_2 Pt(CN)₅ · 3 H₂O: Polychromatic, blue and yellow. Readily soluble in hot water; most of it rapidly reprecipitates on cooling the solution. d 2.455.

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Ba[Pt(CN)₄] · 4 H₂O: Crystals with brilliant polychroniand (pleochroism), iridescent violet-blue on the prism faces, yellow green in the axial direction. Solubility (20°C) 3.5 g./100 g. H₂O. d 2.076.

Ammine Complexes of Platinum (II)

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(Platinum Ammines)

Magnus's Sait [Pt(NH,),][PtCL] and Reiset's First Chloride [Pt(NH,),]CL+H₂O

An excess of 50% ammonia is added to a boiling solution of H_2PtCl_4 (obtained by reduction of H_2PtCl_5 , see p. 1570). Cooling precipitates the dark-green crystals of Magnus's salt. If heating with the excess of ammonia is continued with stirring, ignoring the appearance of the precipitate, the latter redissolves and the solution becomes colorless. It now contains $(Pt(NH_3)_4)Cl_3$, Reiset's first chloride. This salt can be precipitated directly by adding alcohol whereby it is obtained as colorless crystals. However, for higher purity, the preparation should proceed via Magnus's salt.

This requires a solution of H_2 PtCl₄ in which the latter is present in a quantity exactly equivalent to the Reiset's chloride. The simplest way to achieve this is to divide a given quantity of H_2 PtCl₄ solution into two equal parts and use only one of these for conversion of the solute to [Pt(NH₃)₄]Cl₂ in the manner described above. The excess NH₃ is driven off as completely as possible by heating on a water bath. The two solutions are then gradually combined (stirring), and pure green Magnus's salt is precipitated:

 $[Pt(NH_3)_{\epsilon}]Cl_{2} + H_{2}PtCl_{4} = [Pt(NH_3)_{4}][PtCl_{4}] + 2HCl$

The precipitate is allowed to settle, the mother liquor decanted, and the solid washed with small portions of hot water (on a filter) until the wash water is free of chlorides. The Magnus's salt is now pure and can be dried.

For conversion into pure Reiset's chloride, the moist Magnus's salt is placed in a beaker, covered with some dil. hydrochlonic acid, and treated with an excess of concentrated ammonia. The mixture is boiled gently with continuous stirring, gradually dissolving the solids. The evaporating ammonia must be replaced from time to time to maintain the original volume. After the green salt is completely dissolved the solution is evaporated until only a faint odor of NH₃ remains. Then it is neutralized to litmus, 1 mi. of concentrated HCl added, and the mixture treated with 16 times its volume of 1:1 alcohol-acetone. It is allowed to stand for an tour: the white precipitate is removed, washed a few times with small portions of alcohol-acetone, and rinsed with pure acetone on a suction filter. The resulting Reiset's chloride is dried in air.

PROPERTIES:

Magnus's salt: Dark-green crystalline needles. Very difficult to dissolve in water. Rapidly transformed into trans-[PtCla(NHa)a] on dry heating to 290°C.

Reiset's first chloride: Colorless tetragonal crystals. Solubility (20°C) about 20 g./100 g. H₂O; more soluble in hot water. insoluble in alcohol, ether and acetone. Forms the hydrate (Pt(NHs), Cla H2O on recrystallization or concentration of an aqueous solution.

Reiset's Second Chloride

trans-[PtCl₂(NH₃)₂]

If Reiset's first chloride is heated at 250°C until no further NH3 is given off, the product is trans-diamminedichloroplatinum (II);

> $[Pt(NH_3)_4]Cl_2 = [PtCl_2(NH_3)_2] + 2 NH_3$ 334.1 300.1 34.1

A mixture of this chloride with NH₄ Cl is obtained by evaporating the first chloride with a large excess of concentrated HCl; the NH. Cl is extracted from the residue with cold water.

Purification is effected by recrystallization from hot water or by converting the solid to the nitrate by means of AgNO3, followed by reprecipitation of the chloride from the nitrate solution with concentrated HCl.

PROPERTIES.

Sulfur-yellow crystalline powder. Very slightly soluble in cold water; solubility (100°C) 0.7 g./100 g. H₂O. Decomposes above 340°C.

L A cold, clear solution of 20 g, of (NH₄)₂PtCl₄ in 100 ml, of H₂O is reacted with 50 ml, of 5 N ammonia and allowed to store of

29. THE PLATINUM METALS

12-48 hours in a closed flask at 0°C. The crystalline precipitate contains Peyrone's chloride and some Magnus's salt. The minister is filtered off and washed with ice water until no Magnus's salt precipitated from the filtrate with PtCl2⁻. The Peyrone's chloride on the filter is then dissolved with boiling water, and the yellow solution is mixed with 1/3 its volume of 50% hydrochloric action After standing for 24 hours, the crystalline precipitate is filtered off, washed until free of acid with ice water and then with alcohol, and finally dried in air. Yield: 10.7 g.

H. A lukewarm solution of 41 g. of K_3PtCl_4 and 27 g. of NH₄Cl in 200 ml. of H₃O is reacted with 54.4 ml. of 3.75 N ammonia (0.204 mole) and allowed to stand for two days at room temperature and for an additional day at 0°C. The precipitate which has formed is then filtered off with suction (removing the liquid as completely, as possible), thoroughly washed with ice water, and dried in air. The yield is 27.1 g. of a product which is not completely pure but contains, in addition to cis-[PtCl₃(NH₃)₃], a few percent of Magnus's salt and [PtCl(NH₃)₃]₂ [PtCl₄].

PROPERTIES:

Yellow crystalline powder (needles or platelets). Solubility, (0°C) 0.26 g., (100°C) 3 g./100 ml. H₂O. Dissolves very slowly in water at 100°C. Rapidly converted to the trans compound on dry heating to 275°C.

REFERENCES:

Gmelins Handb. d. anorg. Chem. [Gmelin's Handbook of Inorganic Chemistry]. 8th ed. (1957). Platinum. Part D, pp. 45, 53, 236.
241; S. M. Jörgensen. Z. anorg. Chem. <u>24</u>, 153 (1900); S. M. Jörgensen and S. P. L. Jörgensen. Ibid. <u>48</u>, 441 (1906); L. Ramberg. Ibid. <u>83</u>, 33 (1913); R. N. Keller in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 250.

cis-Dinitrodiammineplatinum (II)

- 3 - **3 - 3** - **3**

[Pt(NO₄)₄(NH₄)₄]

The cis form of this neutral salt complex is precipitated when an aqueous solution of potassium platinum (II) aitrite is treated, with aqueous ammonia.

The starting $K_2Pt(NO_2)_4$ can be prepared from K_2PtCl_4 which is allowed to react with an excess of alkeli nitrite, evolving nitric exide.

KsPtCls + 6 NaNOs = KsPt(NOs). + 2 NOs + 6 NaCl 488.0 414.0 457.3 350.7

H. L. GRUBE

One part by weight of K_2PtCl_0 is suspended in water and treated with a concentrated solution of 10 parts by weight of NaNO₃. The mixture is then heated with stirring. The yellow K_2PtCl_0 first dissolves giving a dark solution, and then nitric oxide is liberated as fine bubbles while the solution clears to a pale greenish yellow. When no further gas evolves the solution is cooled and, if necessary, the precipitated impurities are filtered off.

The K_2 Pt(NO₂) solution can also be prepared, in a smooth reaction, from K_2 PtC4:

 $K_{1}PtCl_{4} = 4 NaNO_{2} = K_{2}Pt(NO_{2})_{4} = 4 NaCl_{415,1} = 270.0 = 457.3 = 233.5$

To produce the desired complex $[Pt(NO_2)_2(NH_3)_2]$, the cold, filtered solution of $K_2Pt(NO_2)_4$ is reacted with a stoichiometric quantity of 20% aqueous ammonia:

 $\begin{array}{rcl} K_{2}Pt(NO_{2})_{4} & \succ & 2 \ NH_{3} & = & \left[Pt(NO_{2})_{2}(NH_{3})_{2}\right] & + & 2 \ KNO_{2} \\ & & 457.4 & 34.1 & 321.2 & 170.2 \end{array}$

After a short time the complex precipitates as a dense whitish mass of fine, needlelike crystals. After filtration and washing with cold water, it can be recrystallized from hot water; the product consists of pale-yellow needles.

PROPERTIES:

Formula weight 321.17. Pale-yellow needlelike crystals. Decompose explosively at 200°C. Sparingly soluble in water; readily soluble in aqueous ammonia, forming $[PtNO_3(NH_3)_3]NO_3$, which can be used to prepare a good platinum electroplating bath.

REFERENCE:

W. Keitel and H. E. Zschlegner. U.S. Patent 1,779,436.

Pure Palladium

₽d

In the Wilm method, very pure palladium is obtained by treating a solution of $PdCl_2$ or Na_2PdCl_4 with NH_4Cl in order to precipitate as $(NH_4)_2PtCl_6$ any slight Pt impurity which may be present. The filtrate is boiled with an excess of NH_3 , filtered again if necessary, and acidified with HCl. A yellow precipitate of very pure $(PdCl_2(NH_3)_3)$ should form. If the salt has a duil, dirty yellow color.

Strandar (No.)

it contains a small quantity of $[RhCl(NH_3)_5]Cl_2$, which is insoluble in cold ammonia. The salt is therefore digested with cold aqueous ammonia; completely pure palladodiammine chloride $[PdCl_2(NH_2)_2]$ is obtained from the filtrate by a second precipitation with hydrochloric acid; it is a bright-yellow crystalline salt. This is reduced by ignition in a stream of H₂ to light gray palladium sponge.

PROPERTIES:

M.p. 1554°C; d 11.97. Absorbs large quantities of many gases, especially H_2 .

REFERENCE:

Th. Wilm. Ber. dtsch. chem. Ges. 15, 241 (1882).

Colloidal Palladium

A solution of 2 g, of sodium protablinate (the sodium salt of protablinic or lysablinic acid) in 50 ml, of water is prepared; aqueous NaOH is added in slight excess, followed by a solution of 1.6 g of PdCl₂ (equivalent to 1 g, of Pd) in 25 mi, of H₂O. Then N₂H₄ · H₂O is added dropwise to the tesulting clear red-brown liquid, producing immediate reduction (foaming). After standing for three hours, the black solution is dialyzed against water to remove the excess NaOH, N₂H₄ · H₂O and NaCl; this is continued until the dialyzing water no longer gives a reaction for N₂H₄ · H₂O and NaCl. The purified solution is concentrated at 60-70°C and dried in vacuum over H₂SO₄. The product consists of shiny black platelets, which dissolve in water leaving no residue.

PROPERTIES:

Stable when dry. Its solution appears opaque and black in incident light; thin layers are clear black-brown with a greenish tings in transmitted light. One volume of the product (about 50% Pd) contained in this colloidal solution can absorb approximately 3000 volumes of H_{2} .

REFERENCES:

C. Paal and C. Amberger. Ber. dtsch. chem. Ges. <u>37</u>, 124 (1904); P. Stecher et al. Merck Index. 7th ed., p. 623 under "lysalibinic acid."

Palladium Black

The Böttger method for preparing palladium black consists in reducing an aqueous solution of a Pd (II) salt with sodium formated The reaction occurs slowly at room temperature and is instantaneous at 50°C.

PROPERTIES:

According to C. Paal, an aqueous suspension of palladium black absorbs 12,000 times its volume of H_3 ; the dry material absorbs only 870 times its volume.

REFERENCE:

Jahresber. d. phys. Vereins Frankfurt a.M. [Annual Report of the Frankfurt a.M. Physics Society], 1872-73, p. 11.

Palladized Asbestos

Palladized asbestos is prepared in exactly the same way as platinized asbestos (see p. 1563).

Palladium (II) Cloride

PdCl₂

The anhydrous salt is prepared by heating loose palladium sponge (contained in a porcelain boat set in a glass tube) to a dull red heat in a stream of Cl_{2^*} . According to Krustinsons, the decomposition pressure of PdCl₂ reaches 1 atm. at 738°C.

By dissolving finely divided Pd in conc. HCl through which Cl_3 is bubbled, one obtains a solution in which both H_3PdCl_4 and H_3PdCl_6 can be detected. Concentrating the solution also yields a residue of $PdCl_3$.

PdCl₂ Solution for the Detection of CO

Winkler gives the following method for preparing this solution. Pure Pd (0.2 g.) is dissolved with gentle heating in about 10 ml. of aqua regia. The solution is evaporated to dryness in a 50-ml. porcelain dish placed on a steam bath. The residue is dissolved in 10 ml. of 20% hydrochloric acid and the solution is again evaporated to dryness; this last procedure is repeated three times. The resulting residue, which is now completely nitrate-free, is mixed with 2 g. of KBr and dissolved (gentle heating) in 10 ml. of 1 N HCl. After dilution to about 150 ml. with water, a few particles of pumice and 1 ml. of alcohol are added to the solution, which is then boiled for about 10 minutes in an Erlenmeyer flask in order

to reduce any Pd (IV) not decomposed during the drying to Pd (II) and to drive off the excess alcohol. After cooling, 2.5 g, of $CH_3COONa \cdot 3 H_2O$ is dissolved in the liquid. The solution is filtered through a small wad of cotton wool and diluted to 200 ml. with the water used for washing the cotton wool. The clear, reddish-brown liquid, which contains 0.1% pailadium, is stable when stored in a flask provided with a ground-glass stopper. To be on the safe side, it is best to filter the solution before use; it should be stored in the dark.

REFERENCES:

J. Krustinsons. Z. Elektrochem. <u>44</u>, 537 (1938); L. Winkler, Z. anal. Chem. <u>100</u>, 321 (1935); <u>97</u>, 18 (1934); also describes analytical methods for detecting CO with PdCl₂ solutions. Explicit directions for the preparation of palladium catalysts using PdCl₂ are given by R. Mozingo in Organic Syntheses, collective vol. III, p. 685 (Wiley, New York, 1955).

Palladium (II) Oxide

PdO

A reasonably pure PdO, particularly suitable for catalytic purposes, can be prepared by decomposition of palladium nitrate. Sodium nitrate (50 g.) and a solution of PdCl₃ containing 2 g. of Pd are mixed and evaporated to dryness. The dry mixture is then heated (it fuses in the process), first for some time at 270-280°C, then at 350-370°C, until evolution of nitric oxides ceases; finally, it is heated to 575-600°C for a short time. The melt is extracted with 200 ml. of water, leaving behind the PdO. This is washed with a 1% NaNO₃ solution and dried in vacuum over H_2SO_4 . The product still contains about 1.5% H_3O and 2.5% alkali salts. The pure material can be obtained by ignition in O_8 , but this causes a loss of catalytic activity.

PROPERTIES:

Black powder; tetragonal crystals. Stable in air up to about 700°C, in O_3 to about 800°C. Insoluble in aqua regia; soluble in conc. HBr. d 8.7.

REFERENCES:

Gmelin, Handb. d. anorg. Chem. [Gmelin's Handbook of Inorganio Chemistry], 8th ed., System No. 65, Berlin, 1942; R. L. Shriner and R. Adams, J. Amer. Chem. Soc. 46, 1685 (1994).

Tetrachloropailadates (II)

K.PdCl., Na,PdCl., (NH.),PdCl.

 $PdCl_{t} + 2 KCl (2 NaCl, 2 NH_{t}Cl) = K_{0}PdCl_{t} [Na_{1}PdCl_{t}, (NH_{t})_{2}PdCl_{t}]$ 320.4(294.2)284.3107.01 149.1 (116.9 177.3

These three salts are obtained as well-formed crystals by treating PdCl₂ solutions with stoichiometric quantities of the respective alkali chlorides and slowly evaporating the solutions.

SYNONYMS:

Potassium, sodium and ammonium palladochlorides.

PROPERTIES:

K-PdCL: Crystallizes in dark yellow or brownish prisms. Readily soluble in hot water, soluble with difficulty in cold water. Precipitated in golden yellow lamellae by addition of alcohol to a hot aqueous solution.

Na₂PdCl₄: Brown, deliquescent; also soluble in alcohol.

(NH₄)₂PdCl₄: Crystallizes in long olive-colored prisms; can be recrystallized from water.

Hexachloropolladates {|V}

K₂PdCl₆, (NH₄)₂PdCl₆

A solution of PdCl₂ with an excess of KCl (NH₄ Cl) is prepared, from which bright red K₂PdCl_e [(NH₄)₂PdCl_e] is precipitated on introduction of chlorine. This is rapidly suction-filtered, washed quickly with KCl (NH+Cl)-containing water, and rinsed with alcohol.

SYNONYMS:

Potassium and ammonium palladium (IV) chlorides.

PROPERTIES;

Contraction of the second Bright red crystals. Soluble with difficulty in water, even less soluble in KCl and NH, Cl solutions. Crystal structure: KaPtCla type,

Diamminepolladium (II) Salts

[PdCl₂(NH₃)₂], [PdBr₂(NH₃)₂]

If a slight excess of ammonia is added to a fairly dilute, cold solution of $PdCl_2$, a red precipitate known as Vauquelin's sait is formed. After drying, this becomes a crystalline, flesh-colored to dark-red powder, corresponding to the formula $[Pd(NH_3)_4]*$ $[PdCl_4]$ (analogous to Magnus's green platinum sait). On boiling in water, most of it dissolves; the solution precipitates small yellow octahedral crystals on cooling; this is trans- $[PdCl_2(NH_3)_3]$. Larger quantities can be easily prepared via methods described in the section on the preparation of pure palladium (p. 1580).

A PdBr₂ solution behaves in an exactly parallel manner upon addition of ammonia: a red, crystalline precipitate of $[Pd(NH_3)_4]_{4} = [PdBr_4]$ is obtained from the mixture. This undergoes the same transformation as the chloride to give yellow octahedral crystals of $[PdBr_2(NH_3)_2]_{4}$.

Pure Rhodium

Rh

I. Reasonably pure sodium or potassium hexachiororhodate (see p. 1588 for preparation) is the starting material. The sait is dissolved in water; the solution is bolled with an excess of ammonia and concentrated. This gives the so called purpureo salt [RhCl(NH₈)_B]Cla as a straw-colored powder, which must be purified. The salt is first digested for a long time in hot 50% hydrochloric acid, is then suction filtered (removing as much water as possible) and dried. The lumps are carefully broken up with a broad glass spatula and transferred to a container of cold, concentrated H2SO4 (salts H_2SO_4 ratio = 1:1.5). Too large an excess of H_2SO_4 should be avoided, and the mixture should be warmed very carefully, since otherwise an insoluble sulfate will result. Upon addition of the powder, small lumps, not wetted by the HaSOA, are easily formed; these must be broken up with the glass spatula. The powder must be added in small portions with continuous stirring; the HOL escapes in bubbles, so that the mass foams. It is digested until at becomes a honeylike, viscous, lump-free yellowish paste. Not water is added and the mass is filtered; the filtrate is allowed to run into concentrated HCl so that the resulting solution is approximately 50% in hydrochloric acid. The purified purpureo salt precipitates as a dense, yellowish-white residue. It is filtered off with suction, washed, dried, ground with a glass spatule, and holied

for two hours with five times its quantity of concentrated HNO₃, after which the solution is mixed with an equal volume of water. The nitrate is allowed to crystallize overnight; it is then filtered off, washed and recrystallized once from water. It is then redissolved in water, the solution is filtered, and the filtrate is again allowed to run into hydrochloric acid. The salt is washed with liquids whose compositions approximate those of the respective mother liquors. Since the salt is only slightly soluble in cold H_2O , it is given a final rapid wash with cold H_2O , preferably on a filter in this way is placed in a covered quartz crucible set inside a graphite crucible and ignited carefully in a gas-heated or muffle furnace.

II. According to Wichers and Glichrist, pure rhodium can be prepared as follows. The finely divided, impure metallic raw material is mixed intimately with 1.5 times its weight of NaCl and heated at 600°C in a stream of Cl₂ for 2-4 hours. It is then cooled in the stream of Cla, and the fused mass is dissolved in H2O. The insoluble residue is again treated with chlorine until all of the rhodium becomes soluble. The solution is then diluted to a concentration of 40 g. of Rh/liter and filtered. The filtrate is heated on a steam bath and NaNO₂ is added until the color changes from red to yellow; this requires about 500-550 g. of NaNO, per 100 g. of Rh. Finally the solution is boiled for an hour. The platinum metals and some of the base metals are converted into soluble double nitrites, while other base metals are precipitated as hydroxides or basic salts. The mixture is filtered; the cold solution is treated with Na₂S and allowed to stand overnight (5-10 g, of Na2S is sufficient for a solution containing several hundred g, of Rh). The odor of HaS indicates the end of the reaction, which precipitates Pb and small quantities of Pd, Pt and Ir. The filtrate is boiled to decompose the excess Na₃S. The purified solution is again treated with 30-50 g. of NaNO2 per 100 g. of Rh (to convert the rhodium completely to the double nitrite). The cooled solution is treated with a saturated solution of NH4 Cl, which precipitates the sparingly soluble $(NH_4)_3[Rh(NO_2)_6]$, which is white when pure. This product is allowed to react with hydrochloric acid. The resulting hydrochloric acid solution of rhodium chloride is treated with NaNO3 (after evaporating the excess of the acid) and treated again as described above, except that smaller additions of Na₂S are made in the successive purifications. Finally, the concentrated solution of rhodium chloride in hydrochloric acid is converted to (NHa) aRhCla · H2O by addition of a small excess of NH, Cl, and the mixture is treated with 95% alcohol. The precipitate is filtered off and washed with alcohol. The (NH4)3 RhCle · H2O may be redissolved in water and reprecipitated with alcohol.

The $(NH_4)_3RhCl_6 \cdot H_2O$ is ignited to rhodium sponge and postreduced with hydrogen.

PROPERTIES;

M.p. 1970°C. Harder and more difficult to work than Pt. The solid metal and the fine rhodium black powder obtained by reduction from salt solutions differ in their solubility in acids. The solid metal is insoluble in all acids and mixtures of acids, and is not attacked by molten NaOH even if KNO_3 is added at dull red heat. If Rh is fused with $KHSO_4$, it slowly forms the water-soluble potassium rhodium sulfate, which imparts a dark-red color to the melt; at high Rh concentrations, the melt becomes black.

REFERENCE:

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E. Wichers and R. Gilchrist, Trans. Amer. Inst. Mining Metallurg. Eng. <u>76</u>, 619 (1928).

Rhodium (III) Chloride

RhCl₃

The anhydrous chloride is prepared by heating the metal in a stream of Cl_2 at about 400°C. Above 800°C, it redecomposes to the metal and chlorine. This chloride is red and insoluble in water and acids.

However, the hydrated rhodium (III) oxide mentioned on page 1588 dissolves readily in hydrochloric acid, giving a yellow solution. On evaporation of this solution, a residue of the hydrated chloride RhCl₃ \cdot xH₂O (x = 3-4) is left as a red deliquescent mass, which is called "water-soluble rhodium chloride" to distinguish it from the first product. Heating above 200°C converts this product to the water-insoluble RhCl₃.

Hexachiororhodates (III)

Sodium hexachlororhodate (III), Na;RhCl. 12 H.O

First RhCl₃ is prepared by passing Cl₂ over very fine rhodium powder at about 400°C. One part by weight of the product RhCl₃ is carefully mixed with 2-3 parts by weight of NaCl and heated to about 300°C in a stream of Cl₂. The aqueous solution of this chlorination product is filtered; after concentration, Na₃RhCl₆. 12 H₂O crystallizes out as deep-red, monoclinic prismatic crystals.

Potassium hexachlororhodate [III], K_RhCle H2O, K2[RbCl3(H2O)]

A solution of the potassium salt is prepared in exactly the same way as that of the sodium salt. On concentration, the first crystallization yields $K_2[RhCl_5(H_2O)]$. This salt is dissolved in an almost saturated aqueous KCl solution and the solution concentrated; the hexachlororhodate $K_3RhCl_8 \cdot H_2O$ crystallizes out on cooling. Both of the above compounds form dark-red crystals.

Ammonium hexachlororhodate (III), (NH4)3RhCl4+H3O, (NH4)3[RhCl4(H2O)]

Concentration of a platinum-rhodium solution which has been freed of platinum by the addition of NH₄Cl yields crystals of the red (NH₄)₃RhCl₆ · H₂O. Green crystals occasionally obtained are (NH₄)₃PtCl₆ containing Rh as an impurity.

A better method starts with soluble rhodium chloride (see page 1587), which is evaporated together with an excess of aqueous $NH_{A}Cl$.

If the $(NH_4)_3 RhCl_5 \cdot H_3O$ is taken up in water and heated to a high temperature, the much less soluble $(NH_4)_3(RhCl_5(H_3O))$ crystallizes out on cooling.

REFERENCE

M. Delépine. Bull, Soc. Chim. Belgique 36, 114 (1927).

Rhodium (III) Oxide

Rh₂O₃

L Very pure Rh_2O_3 is obtained by heating $RhCl_3$ to 750-800°C in a stream of O_3 until Cl_2 is no longer given off.

II. The highly hydrated compound $Rh_2O_3 \cdot 5 H_2O$ is obtained when concentrated KOH is added slowly to solutions of rhodium salts. A lemon-yellow compound precipitates; after washing and drying, it becomes a pale-yellow powder. This material is not completely alkali-free and is insoluble in water; however, it dissolves readily in acids and on ignition reverts to nonhydrated Rh_2O_3 , which is insoluble in acids.

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STNONYM:

Rb₂O₃ · 5 H₂O: Rhodium hydroxide.

REFERENCES;

- I. Gmelin, Handb. d. anorg. Chem. [Gmelin's Handbook of Inorganic Chemistry], 8th ed., Rhodium, p. 46; L. Wöhler and W. Müller. Z. anorg. allg. Chem. <u>149</u>, 132 (1925).
- II. F. Krauss and H. Umbach. Z. anorg. allg. Chem. <u>180</u>, 47 (1929); G. Grube and G. Bau-Tschang Gu. Z. Elektrochem. <u>43</u>, 398 (1937).

Rhodium Sulfate

Rh₂(SO₄)₂ ' x H₂O

According to Krauss and Umbach, attempts to prepare rhodium sulfate from rhodium hydroxide and sulfuric acid lead to two different products, depending on the conditions: these are yellow rhodium sulfate $Rh_2(SO_4)_3 \cdot 15 H_3O$ and red rhodium sulfate $Rh_2(SO_4)_3 \cdot 4 H_3O$.

Rh₂(SO₄)₁ · 15 H₂O

The yellow sulfate is produced on solution of moist hydrated rhodium (III) oxide (rhodium hydroxide) in dilute (1:10) sulfuric acid at temperatures not exceeding 50°C. Then the hydrated Rh (III) oxide is precipitated from the cold solution with KOH (avoiding an excess of the latter) and washed on a membrane filter until the coiloidal hydroxide passes through. Suction is then applied and as much water as possible is removed; the residue is dissolved without heating in dilute sulfuric acid.

The solid salt is obtained by evaporating this solution in vacuum, dissolving the residue in absolute alcohol, and precipitating with 10-20 times its volume of ether; this gives a pale-yellow, fine, flocculent residue. After filtration, washing and drying, this becomes a light, yellowish-white powder. The yield is always poor, at most 20%.

Rh₂(SO₄)₂ · 4 H₂O

Red, amorphous rhodium sulfate is obtained either by evaporating a solution of the isomeric yellow salt or by precipitating hydrated Rh (III) exide from a RhCl₃ solution at the boiling point, washing the precipitate with hot water, dissolving it in hot dilute sulfuric acid, and evaporating the mixture. To remove the excess H_3SO_4 , the product is dissolved in H_2O and $Ba(OH)_2$ is added until Rh (III) hydroxide begins to precipitate. The solution is filtered and again evaporated.

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The two sulfates undergo quite different precipitation reactions. Barium chloride precipitates the $50\frac{3}{4}$ almost quantitatively from solutions of the yellow salt prepared in the cold. These are acidic and KOH precipitates the rhodium from such solutions. On the other hand, the red salt solutions prepared under the same conditions either fail to give these reactions, or react only gradually, but in any case, not quantitatively. We must therefore conclude that in this last case we are dealing with a complex in which the bonds are stronger than in the yellow salt.

REFERENCE

F. Krauss and H. Umbach. Z. anorg. allg. Chem. 180, 42 (1929).

Chioropentaamminerhodium Salts [RhCl(NH₃)₃]Cl₃, [RhCl(NH₃)₅](NO₅)₂

The preparation of the chloride and nitrate of these compounds, which are also known as purpureo salts, is given in the section on the preparation of pure rhodium (p. 1585 ff.).

Pure Iridium

Ir

Chemically pure iridium is best prepared by ignition of $(NH_4)_2IrCl_6$. To obtain especially pure material, the metal should be reconverted to $(NH_4)_2IrCl_6$ (see p. 1594), which is then reignited.

PROPERTIES:

Very hard, fairly brittle metal; m.p. 2454 °C. On ignition in air, forms small quantities of a volatile unstable oxide, IrO_3 ; thus, under conditions of oxidizing ignition the weight of Pt-Ir alloys does not remain constant. Extraordinarily resistant to acids; insoluble even in aqua regia. Attacked with comparative ease by Cl_2 , particularly in the presence of NaCl, with which the nascent chloride forms a double salt.

Iridium (IV) Oxide

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In the method of Wöhler and Streicher, IrO_3 is prepared from green $IrCl_3$ which can be readily oxidized in a stream of O_3 at 600°C, giving blue-black IrO_2 .

The exidation of fine iridium powder in a stream of air or exygen does not give IrO_2 quantitatively.

PROPERTIES:

Black to blue-black powder, insoluble in acids. Crystal structure: rutile type.

REFERENCE:

L. Wöhler and S. Streicher. Ber. dtsch. chem. Ges. <u>46</u>, 1721 (1913).

Hydrated Iridium (IV) Oxide

IrO, 2HtO

I. An aqueous solution of $IrCl_{\bullet}$ or $H_{\bullet}IrCl_{\bullet}$, prepared by the old method of Vauquelin (see $H_{\bullet}IrCl_{\bullet}$, method I, p. 1593), is evaporated several times to a sirupy consistency in a vacuum at 40 °C. After each evaporation, the sirup is redissolved in water; this treatment completely removes the excess of HCl. The final concentrate is again diluted, and dilute aqueous KOH is added in drops to the boiling solution until the color changes from dark red-brown to green and then to blue. The solution is then held at the b.p. for some time to oxidize any Ir (III) which may be present and to complete the precipitation of the hydrated Ir (IV) oxide. The residue of deep-blue coarse floc is filtered off, washed with water, then with absolute alcohol, and dried in a vacuum desiccator.

II. Gerlach's method consists in adding the KOH solution in drops to a boiling solution of Na_2IrCl_8 , to give the alkali-free hydrated oxide. The use of excess hydroxide leads to a product which contains alkali. Purification is the same as in method I.

PROPERTIES:

Very dark-blue powder. The hydrated oxide prepared by method I may be converted to IrO_2 at 350 °C in a stream of N₂. Freshly precipitated $IrO_2 \cdot 2 H_3O$ is soluble in acids.

REFERENCES:

I. F. Krauss and H. Gerlach. Z. enorg. allg. Chem. <u>143</u>, 126 (1925).
 H. Gerlach. Thesis, Tech. Hochschule, Braunschweig, 1925; pp. 4, 42; N. K. Pschenizyn and S. E. Krassikow, abstract in Gierry Zentr. <u>1933</u>, I, 3911.

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Hydrated Iridium (III) Oxide

IrrO, 'x H,O

A solution of Na_3IrCl_6 is prepared either in the same way as in method II for $K_5IrCl_6 \cdot 3 H_2O$ (see p. 1594) or, better, as suggested by Ogawa, from a solution of Na_3IrCl_6 and sodium oxalate at 50°C according to the equation

 $2 \operatorname{Na}_{2}[\operatorname{IrCl}_{3}] + \operatorname{Na}_{2}C_{2}O_{4} = 2 \operatorname{Na}_{3}[\operatorname{IrCl}_{4}] + 2 \operatorname{CO}_{2}$

In either case the solution is treated with potassium hydroxide or potassium carbonate solution in a stream of CO_2 . The separation, washing and drying of the hydrated oxide must be carried out under an inert gas (CO_2 or N_2). The alkali cannot be completely removed from the product.

PROPERTIES:

Pale-green to dark powder, depending on the precipitation conditions and water content; oxidized in air to the hydrated Ir (IV) oxide, particularly when damp. The Ir (III) compounds are more stable in acid solutions than the Ir (IV) salts; the reverse is true in alkaline solutions.

REFERENCES:

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L. Wöhler and W. Witzmann, Z. anorg. Chem. <u>57</u>, 334 (1908); Preparation of Na₃IrCl₆ solution; E. Ogawa. J. Chem. Soc. Japan <u>50</u>, 246 (1929).

Iridium (III) Chloride

IrCl_a

 $Ir + 1^{1}/_{\ell} Cl_{\ell} = IrCl_{0}$ 192.2 106.4 298.6

Fine initial powder is placed in a porcelain boat set in an open-end glass combustion tube. The gas inlet side of the tube is drawn to a small-diameter tubing, while the other end carries a ground-glass joint. An O_2 -free stream of chlorine, containing a small percentage of CO, is passed through the tube, which is heated to about 600°C with a burner and illuminated either with direct sunlight or light from a burning magnesium ribbon. The chlorination is complete in about 15 minutes.

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H. Alternatively, IrO₂ · 2 H₂O is heated to 240°C in a stream of Cl₂ and illuminated with sunlight or a burning magnesium phboms

III. Finally, (NH₄)₃lrCl₈ may be decomposed in a stream of Cl₃ at 440-550°C; the conversion of 0.5 g, requires two hours.

PROPERTIES;

Dark olive-green powder. Stable up to 760°C under a Ci₂ pressure of 1 atm. (Streicher); at 700°C the color changes to bright yellow.

REFERENCES:

F. Krauss and H. Gerlach. Z. anorg. allg. Chem. <u>147</u>, 265 (1925); L. Wöhler and S. Streicher. Ber. dtsch. chem. Ges. <u>46</u>, 1720₄; 1582 (1913); S. Streicher. Thesis, Univ. of Darmstadt, 1913.

Hexachloroiridic (IV) Acid

H_tLCl_t

I. A solution of $(NH_4)_2$ IrCl₈ is decomposed by bubbling Cl₂ through it at about 4°C; then the liquid is concentrated at 40°C (12-15 mm.)until a dark-brown sirupy mass results. This is allowed to stand for some time in an evacuated desiccator containing CaO (until it congeals and crystallizes). The low temperatures mentioned must be maintained to avoid the formation of NCl₂.

II. A solution of $(NH_4)_3$ IrCle is heated with aqua regia on a water bath (approximately 10 hours) until the NH⁺ is completely split off: the solution is repeatedly concentrated with cone. HCl until the HNO₃ is completely removed.

REFERENCES:

I. Vauquelin. Liebigs Ann. <u>89</u>, 150, 225 (1845); A. Gutbier, and F. Lindner, Z. phys. Chem. <u>69</u>, 304 (1909).

H. S. C. Woo and D. M. Yost. J. Amer. Chem. Soc. 51, 884 (1931).

Potassium Hexachloroiridate (IV) * _____

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K_sIrCl_e

L A mixture of fine iridium powder and twice its weight of KOL is heated in a porcelain boat almost to red heat while chlorine is passed over it. After cooling, the excess KCl is extracted by washing with the least possible quantity of cold water. Then the double salt is dissolved in bolling water and filtered free of unconverted Ir. The solution is slowly evaporated in a porcelain dish. The K_2IrCl_6 crystallizes as small, shiny, red-black octabedra, which yield a red powder on grinding.

In the above extraction with boiling water it is best to add a few drops of nitric acid in order to prevent the formation of K_3IrCl_8 and convert any Ir (III) present to Ir (IV).

II. According to Puche, better results are obtained by allowing Na_3IrCl_8 solution to react with solid KCl while a stream of Cl_2 is bubbled through the mixture. The crystalline deposit is filtered off with suction and washed several times with dilute alcohol. It is then rapidly washed with some water. The product is dried in a drying oven at about 100°C.

PROPERTIES:

Deep dark-red octahedra. Solubility (20°C) 1.12 g./100 g. $H_{2}O$. Insoluble in alcohol. d 3.5.

REFERENCES:

I. Old process of Berzelius: G. Gire, Ann. Chim. 4, 210 (1925).

H. F. Puche. Ibid. 9, 270 (1938).

Ammonium Hexachloroiridate (IV)

(NH4),IrCL

A mixture of iridium metal powder plus twice its weight of NaCl is converted to Na₂IrCl₆ by heating to 400 °C in a stream of Cl₂ (compare the preparation of the analogous K_2 IrCl₆); this salt is dissolved in some water. Addition of NH₄ Cl to this solution [or to other solutions of Ir (IV)] leads to the formation of (NH₄) ₂IrCl₆; the latter is only slightly soluble.

SYNONYM:

Ammonium iridium (IV) chloride.

PROPERTIES:

Dark-red octahedra. Solubility (cold) about 5 g., (100 °C) about 10 g./100 mi. H_2O . d 3.03. Crystal structure: K_2PtCl_8 type.

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REFERENCE:

A. Gutbier. Z. phys. Chem. 69, 307 (1909).

29. THE PLATINUM METALS

Potassium Hexachloroiridate (11)

K,lrCl, 3H,O

I. A hydrogen stream is passed over gently heated (not over 150° C) K₃IrCl_e placed in a quartz or porcelain boat; the reduction proceeds according to the equation

 $3 K_1 IrCl_5 + 3 H_2 = 2 K_1 IrCl_4 + Ir + 6 HCi$

II. A solution of K_3 IrCl₆ (the concentration should be as high as possible) in freshly prepared H_3 S water is heated until the color turns olive-green. Then KCl is added and crystals of K_3 IrCl₆ · 3 H_3 O deposit out; these can be dehydrated, if need be. The K_3 IrCl₆ can be reduced with SO₃ in the same manner, but the product must be neutralized with K_3 CO₃.

Alternate method: Reduction with oxalate; see section on $Ir_{n}O_{3} \cdot xH_{2}O$ (p. 1592).

SYNONYM:

Potassium iridium (III) chloride.

PROPERTIES:

Dark olive-green crystals. Readily soluble in water, insoluble in alcohol.

REFERENCE:

I. F. Puche. Ann. Chim. 9, 273 (1938).

Pure Ruthenium

Ru

Guthier and Trenkner give the following method for the preparation tion of the pure metal. To start with, 30 g. of the fine metal powder. It is heated to dull red heat for three hours in a stream of O_3 in order to volatilize Os, which is often present as an impurity. The partially oxidized Ru is then reduced in a stream of H_3 ; then a mixture of the metal, the purest KOH, and the purest KNO's (3:25:3 by weight) is prepared and fused in a flat sliver dish: The green melt is kept in the liquid state for half an hour. It is then cooled, and the reaction product is broken into small lumps and dissolved in lukewarm water. The orange-yellow solution is poured into a large retort, the neck of which is joined to a 2-m.long glass tube in such a way that the neck of the retort projects as far as possible into the tube. That tube is placed in a metal trough of about the same length filled with an ice-salt mixture. The other end of the tube is connected to a flask half-filled with 30% KOH. Then a fast stream of dry Cl_2 is introduced through the filler tube of the retort. So much heat of reaction is evolved that the RuO₄ distills over in a very short time. It is in the form of golden-yellow drops which solidify as a yellowish-red mass in the cooled condenser tube.

As soon as the formation of the tetroxide subsides, the contents of the retort are heated to 80-90 °C with a microburner while continuing to introduce Cl_2 ; the whole operation is stopped only when a yellow vapor (a mixture of RuO₄ and Cl_2) can be seen in the attached flask. Since only ruthenium is capable of forming volatile compounds under these conditions (the osmium having been removed previously), all the other impurities remain in the retort.

To convert the tetroxide to the metal, the RuO₄ is washed out from the tube with lukewarm water, transferred to a porcelain dish and, when completely dissolved, reduced immediately with pure alcohol (if the alcohol is added before solution is complete a violent explosion may occur!). The resulting inky liquid is concentrated on a water bath and the residue reduced to elemental Ru with pure H_2 .

Alternate method: A method which is related to the analytical procedure of Wichers et al. separates the osmium by distillation of a nitric acid solution of the products of the alkali fusion step. The residue from this distillation is made alkaline and ruthenium is then distilled off, using Cl_3 as above. Regarding the danger of explosions, see the properties of RuO₄.

PROPERTIES:

M. p. ~ 2400 °C; d 12.43. Very hard and brittle; can be pulverized. When melted, part of the metal oxidizes and volatilizes as RuO₄, which is stable at very high temperatures and gives off a peculiar choking odor.

REFERENCES:

A. Gutbier and C. Trenkner. Z. anorg. Chem. <u>54</u>, 167 (1905); E. Wichers, R. Gilchrist and W. H. Swanger. Trans. Amer. Inst. Mining Metallurg. Eng. <u>76</u>, 626 (1928).

Barris Strates

Ruthenium (IV) Hydroxychioride

Ru(OH)Cl

Heating of RuO₄ with conc. HCl on a water bath gives a darkbrown solution; according to Remy and Wagner, this contains the Ru (IV) chloride. If inhibited, the reaction (which involves the splitting off of Cl_2) can be started by addition of a few drops of alcohol. The product solution is evaporated and a dark-brown product [Ru(OH)Cl₃] is obtained. On the basis of an early incorrect assumption, this is often called "water-soluble ruthenium trichloride."

PROPERTIES:

Dark-brown salt. Very readily soluble in water. A certain proportion is apparently always present as RuCl₃.

REFERENCES:

A. Gutbier and C. Trenkner. Z. anorg. Chem. <u>45</u>, 167 (1905). H. Remy and A. Lührs. Ber. dtsch. chem. Ges. <u>61</u>, 917 (1928); <u>62</u>, 201 (1929); H. Remy. Ibid. <u>61</u>, 2110 (1928).

Ruthanium (III) Chloride

RuCl₂, RuCl₂ H₁O

RuCl,

L In the method of Remy et al., a mixture of carefully predried Cl_2 and CO (initial ratio of 1:4) is passed over a boat containing ruthenium powder and placed in a Vycor combustion tube. After displacing all the air from the tube, the latter is heated to 700-800°C, and the fraction of Cl_2 in the gas stream is simultaneously increased. The beginning of the reaction is clearly marked by a considerable swelling of the material. At the end of the reaction the boat is kept for half an hour at bright red heat, and the CQ throughput is gradually reduced and finally stopped. Cooling in the Cl_2 stream yields a well-crystallized product.

II. In the method of Wöhler and Balz, RuCl₃ is prepared without the use of CO. A mixture of the metal and NaCl is heated at 700°C in a stream of Cl₃, after which the products are reduced with H₃ at 400°C and extracted with H₃O. The finely divided, velvety-black metal obtained in this way is chlorinated at 800°C.

PROPERTIES:

Formula weight 207.5. Method I gives good crystals in the form of shiny black platelets. Insoluble in water.

REFERENCES:

H. Remy (with M. Köhn). Z. anorg. allg. Chem. <u>137</u>, 365 (1924);
 H. Remy and Th. Wagner. Ibid. <u>168</u>, 2 (1928).

II. L. Wöhler and P. Balz. Ibid. 139, 413 (1924).

RuCl, H₂O

Since warm hydrochloric acid solutions of Ru (III) are partly oxidized by atmospheric oxygen (for example, on concentration) commercial "water-soluble ruthenium trichloride" is not free of Ru (IV). A pure product corresponding to the formula $RuCl_3 \cdot H_2O$ can be obtained from this material by electrolytic reduction.

A cathode of platinized Pt foil $(40 \times 35 \text{ mm.})$ and an anode of polished Pt foil are suspended inside a small porous clay cylinder placed inside a rectangular, 200-ml. glass trough. The cathode liquid is a 0.03 M solution of commercial RuCl₃ [or a solution of an evaporation residue which corresponds approximately to Ru(OH)Cl₃] which is 2N in HCl; the anode liquid is 2N HCl. Efficient stirring is necessary. The electrolysis is carried out at 0.03-0.1 amp., with separate control of the cathode potential. The initial darkbrown color of the solution gradually clears. The electrolysis is stopped when the cathode potential becomes constant at 0.01 volt and H₂ evolution commences. The reduced solution should be red. A blue color indicates the formation of the undesirable Ru (II).

The RuCl₃ solution must be concentrated to crystallization in the absence of air, in order to prevent reoxidation by atmospheric oxygen. The evaporation is carried out in a round-bottom flask fitted with a dropping funnel; the flask is purged of air with HCl gas. The reduced solution is then introduced via the dropping funnel; with HCl continuously passing over it, it is evaporated at the boiling point to a sirupy thickness, and finally to dryness at 80-100°C. It is finally dried to constant weight in a vacuum desiccator over H_2SO_4 .

The salt obtained in this way is free of Ru (IV) and has the composition indicated by the formula,

REFERENCE:

G. Grube and G. Fromm. Z. Elektrochem. 46,661 (1940).

Ammonium Hexachlororuthenate (IV)

(NH₄)₂RuCl₆

A concentrated solution of NH₄Cl is added to a ruthenium chloride solution and the resultant mixture concentrated in air. The dark-red crystalline powder is not homogeneous: it contains $(NH_4)_2[Ru(OH)Cl_5]$.

SYNONYM:

Ammonium ruthenium (IV) chloride,

Ruthenium (IV) Oxide

RuO₂

In the method of Remy and Köhn, RuO_2 is prepared by heating fine ruthenium powder at about 1000°C in a stream of carefully predried O_2 . It can also be prepared by ignition of RuS_2 in air (the RuS_2 is obtained by precipitation of ruthenium chloride solutions with H_2S). Wöhler et al. suggest heating pure $RuCl_2$ at 600-700°C in a stream of O_2 .

PROPERTIES:

Dark-gray powder with a metallic luster, irideaces green and blue. Insoluble in acids. Readily reduced by H_2 even at moderate heating. d 7.0. Crystal structure: rutile type.

REFERENCES:

H. Remy (with M. Kóhn). Z. anorg. allg. Chem. 137, 361 (1924); L. Wóhler, P. Balz and L. Metz. Ibid, <u>139</u>, 213 (1924).

Ruthenium (VIII) Oxide

RaO4

Chiorine is passed through a solution of an alkali ruthenate, as described earlier in the section on the purification of ruthenium.

In another method (Ruff and Vidic) mixtures of ruthenium powder with KMnO₄ and KOH are fused; the ruthenate produced in this way is decomposed with H₃SO₄ while still hot; a CO₃ stream is simultaneously passed through the reaction vessel and the RuO₄ distills off. A mixture of Ru, KMnO₄ and KOH (1:2:20 by weight) is fused to a mobile liquid. The dark-green melt is kept liquid for 0.5-1 hour after all the permanganate has been added. After cooling, the melt is dissolved in water and placed, with one additional part of KMnO₄, in a flask fitted with a dropping funnel and containing 1:3 H₃SO₄. An ice-cooled flask containing some water is used as the first receiver (no alcohol! see properties), followed by a flask containing some 7% NaOH. Sulfuric acid is introduced until the color changes from green to red; then further H₃SO₄ (1/3 of the total liquid volume) is added. After this a fast air stream is bubbled through while the solution is heated to 40-50°C. Long golden-yellow needles of RuO₄ soon form in the ice-cooled flask. Later, ruthenate is formed in the NaOH solution, producing an orange-red color. Finally the solution is heated to boiling in order to steam-distill any remaining RuO₄. The yield is almost quantitative.

PROPERTIES:

Formula weight 497.1. A solid composed of golden-yellow rhombic prisms. Very volatile, subliming even at room temperature. Characteristic odor comparable to nitric oxide or ozone; very irritating to the respiratory tract. Less irritating to the eyes than OSO_4 . Melts at 25°C to an orange-red liquid. Solubility (20°C); 20.3 g./liter of H₂O. Vapors and concentrated solutions tend to react explosively with organic substances, such as alcohol, filter fibers, etc. Distillation must therefore be carried out in perfectly clean equipment.

REFERENCE:

O. R. Ruff and E. Vidic. Z. anorg. allg. Chem. 136, 49 (1924).

Potassium Ruthenate and Potassium Perruthenate

K2RuO4 H2O, KRuO4

A dark-green melt is obtained by heating a mixture of Ru powder with KOH and adding KClO₃ or KNO₃; this readily takes up water, giving an orange-red solution. On evaporation, $K_2RuO_4 \cdot H_3O$ crystallizes in iridescent green prisms which appear red when spread in thin layers and viewed by transmitted light. If Cl₂ is introduced into the red solution, the latter becomes green due to the formation of perruthenate. Continued passage of Cl₂ yields RuO₄. However, if the Cl₂ stream is shut off at the right moment, KRuO₅ is precipitated on cooling as small black tetragonal crystals. In contrast to the ruthenates, the perruthenates are not stable above 200°C.

REFERENCES:

A. Gutbier, F. Falco and H. Zwicker. Z. anorg. Chem. <u>22</u>, 490 (1909); F. Krauss. Z. anorg. allg. Chem. <u>132</u>, 306 (1924).

Pure Osmium

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Osmium powder is purified by fusion in an oxidizing alkali melt. Nitric acid liberates the volatile OsO₄ from an aqueous solution of this melt; the OsO₄ is distilled in a stream of air into a receiver containing aqueous NaOH and is absorbed. The osmium is then reprecipitated as OsS₃ and filtered off. It is reduced to the metal in a stream of hydrogen.

The procedure is almost the same as in the purification of ruthenium. The fine metal powder is mixed with KOH and KNO₃ and fused at red heat. After cooling, the melt is dissolved in water in a retort. Nitric acid is added until the solution becomes acidic, and the OSO₄ liberated is carried in an air or oxygen stream to a receiver containing aqueous NaOH, in which it is absorbed. The solution is treated with H_2S , which precipitates the osmium quantitatively (as OsS₂). The precipitate is filtered off and reduced in a stream of hydrogen.

Since the sulfur is difficult to extract from the metal after the hydrogen reduction, the distillation receiver can also be charged with aqueous KOH (instead of NaOH), the resulting osmic acid salt may be reduced to K_2OsO_4 with alcohol, and the K_2OsO_4 reduced to Os with H₂.

PROPERTIES:

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M.p. > 3000 °C. Very hard and brittle, readily pulverized. The powder always retains the characteristic odor of OsO₄, since traces of the latter are formed in air even at room temperatures. Heating in air leads to complete combustion to OsO₄.

Osmium (IV) Chloride

OsCl₄

 $O_5 + 2 Cl_2 = O_5 Cl_4$ 190.2 141.8 332.1

Small quantities of Os (prepared, for instance, by reduction of OsO_2 with H_2) are heated to 850-700°C in a porcelain best set in

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a glass combustion tube, while a slow stream of very pure Cl_3 is passed through. The tube is constricted beyond the boat and lagged for 20 cm, with asbestos to produce a zone of gradual temperature drop. About 2 hours are required for 0.2-0.5 g. of Os to react. The chloride precipitates in various forms (crusts to powders) and in various colors (black to red-brown). It deposits in the reactor tube at and beyond the construction. The tube is melt-sealed at the constriction, and the part of the tube containing the chloride is evacuated, a cooling trap being inserted before the pump. The material is sublimed in vacuum, using the same tube, and deposited in a further section of the tube.

PROPERTIES:

Black crust with a metallic luster, or red-brown powder. Insoluble in water and other solvents and in concentrated oxidizing acids. Slowly hydrolyzed by water. The above product does not correspond exactly to the composition given by the formula.

REFERENCE:

O. Ruff and F. Bornemann. Z. anorg. Chem, 65, 446 (1910).

Sodium Hexachloroosmate (IV)

NazOsCl, 2H2O

In the method of Gutbier and Maisch, fine osmium powder and NaCl are mixed in a 1:1 ratio and the mixture heated in a porcelain boat in a stream of Cl_3 for half an hour, at which point the temperature should correspond to a dull red heat. The conversion to Na₂OsCl₈ is almost complete. The sintered contents of the boat are dissolved in the minimum quantity of cold dilute hydrochloric acid. The unreacted metal is filtered off and the filtrate is saturated with HCl (careful cooling). Most of the excess NaCl is thus separated although part of the Na₂OsCl₈ also precipitates out.

Gradually evaporation of the filtrate yields Na_3OsCl_8 as beautiful crystals, which, however, obstinately retain traces of NaCl even after repeated crystallization from dilute hydrochloric acid.

REFERENCE:

A. Gutbier and K. Maisch. Ber. disch. chem. Ges. <u>42</u>, 4239 (1909).

Ammonium Hexachloroosmate (IV)

(NH4)2OsCl

In the method of Guthier and Maisch, this salt is precipitated by allowing a dilute alcoholic solution of NH_4 Cl to react with the stoichiometric quantity of Na_2OsCl_6 (also in alcoholic solution). The precipitate is a fine, dark-red powder. It crystallizes from dilute hydrochloric acid (or from a mother liquor consisting of the components) in beautiful, shiny black octahedra which are opaque under the microscope.

Gutbler claims that $(NH_4)_3OsCl_6$ is also obtained by dissolving in HCl the sublimates from osmium fusion, concentrating the solution, and mixing the filtered liquid with NH₄Cl.

REFERENCE:

A. Gutbler and K. Maisch. Ber. dtsch. chem. Ges. 42, 4239 (1909).

Osmium (IV) Oxide

OsO₇

Osmium (VIII) oxide is reduced in the cold by a stream of H_{2^*} . If, however, the OsO₄ is heated in the H_2 stream, the product is the metal. Osmium (IV) oxide can also be prepared by heating a fine powder consisting of a mixture of K_2OsCl_8 and three times its amount of Na₂CO₃. The temperature should be lower than red heat; the cooled product is extracted with water which is slightly acidified with dilute hydrochloric acid. The product is perfectly pure OsO_{2*}

Alternate method: Heating of Os to 600-610°C in a nitrogen stream saturated with OsO, vapor. Unreacted OsO, is reclaimed from the nitrogen stream by cooling it to a low temperature [O. Ruff and H. Rathsburg, Ber. dtsch. chem. Ges. <u>50</u>, 495 (1917)].

PROPERTIES:

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Formula weight 222.2. d 11.4. Black powder. Insoluble in water, and acids. Forms OsO, on heating in air; readily reduced to the metal by H_2 . Crystal structure: rutile type.

Osmium (VIII) Oxide

OsO,

 $O_S + 2O_z = O_SO_4$ 190.2 64.0 254.2

Pure OsO, is best prepared by a dry method. Osmium powder is heated in a boat placed in a glass or quartz tube through which a

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stream of dry oxygen is passed. The metal burns to OsO₄, which deposits beyond the heated zone of the tube or, better, in a bulb fused to the tube and cooled in ice. The deposit consists of white shiny crystals, though at first it may be a liquid (occasionally pale yellow in color), which forms a crystalline solid on cooling. Two or three receivers, preferably connected via ground-glass joints, are fitted to the glass tube beyond the bulb. They are halffilled with KOH to absorb the OsO₄ vapor entrained by the oxygen. The OsO₄ in the receivers is reclaimed by reduction to potassium osmate (violet-blue octahedra); this is accomplished by treating the combined caustic liquors from the receivers with an equal quantity of alcohol.

The temperature at the boat is increased gradually so that the reaction does not proceed too vigorously, heating initially to 300°C and gradually increasing the temperature to 800°C. The temperature is then slowly reduced, and the product allowed to cool in the tube. The heating is most conveniently carried out in a small tubular electric furnace.

PROPERTIES:

M.p. 40.6-40.7°C, b.p. 130°C; d 4.9. Soluble in water without decomposition; may be volatilized in steam. Dissolves slowly. Decomposed by conc. HCl with evolution of Cl_{2} . A solution of OsO₄ is not decomposed by light and can be indefinitely stored in transparent bottles. Toxic; the vapor first irritates the respiratory passages and (particularly) the eyes. Decomposed in a stream of H₂ at red heat, forming a mirror.

Potassium Osmate (VI)

K₂O₅O₄ · 2 H₂O

A solution of OsO_4 in potassium hydroxide solution is reduced with alcohol.

Osmium powder (2 g.) is heated with 5 g. of KOH and 3 g. of KNO₃ in a silver dish to form a smoothly flowing melt. After cooling, the brown solid is dissolved in 50 ml. of water. The gray-violet crude salt is precipitated by adding twice the volume of alcohol. It is readily decomposed and cannot be recrystallized from water. It is decomposed by heating with 5 g. of CrO₃ and conc. H_2SO_4 , the OsO₄ distilling off is collected in 10% KOH, and K₂OsO₄ · 2 H₂O is precipitated from the resulting solution by adding an equal volume of alcohol. The solid is filtered off with suction, washed with 50% alcohol and with absolute alcohol, and dried in vacuum over H_2SO_4 .

In a simpler method, osmium powder is heated directly in a stream of O_2 (compare preparation of OsO₄), and the OsO₄ vapor is collected in 10% KOH.

PROPERTIES:

Pale violet-red octahedra. Readily soluble in water, insoluble in alcohol and ether. Stable only in dry air. The water of crystallization is removed by heating to 200°C in an inert gas. Heating in air produces OsO_4 .

REFERENCE:

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Potassium Osmiamate

K(OsO₁N)

 $O_{5}O_{4} + KOH + NH_{3} = K(O_{5}O_{2}N) + 2H_{2}O$ 254.2 50.1 17.0 291.3 36.0

In the method of Joly, 100 g, of OsQ, is dissolved in a solution of 100 g, of KOH in 50 ml, of H_0O ; the solution is heated to 40°C and dilute ammonia is added; this clears the dark-brown liquid and precipitates K(OsO₃N) as a granular, yellow crystalline powder.

Excess ammonia should be avoided because it may produce NH_4 (OSO₃N). The product is washed with some cold water and recrystallized. Larger crystals may be obtained by gradual evaporation of the solution; however, these crystals are dark due to incipient decomposition.

PROPERTIES;

Fine, granular, yellow crystals. Readily soluble in water, only slightly soluble in alcohol. Darkens on heating to 180°C, with decrepitation at higher temperatures. d 4.5. Tetragonal crystals.

REFERENCE:

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Part III Special Compounds

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SECTION 1

Adsorbents and Catalysts

R.WAGNER

Introduction

Solid adsorbents or catalysts must possess large surface areas to allow contact with large quantities of reactants. Large surface areas can be obtained via two methods:

1) SUBDIVISION OF THE SOLID

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The solid is subdivided into very small granules so that a large fraction of the total crystal lattice structure becomes exposed as particle surface. Comparison of x-ray and ultramicroscopic data then shows whether the resulting granules are primary particles (i.e., coherently diffracting single crystals) or secondary particles (i.e., a mosaic consisting of several primary crystals).

2) CREATION OF A NETWORK OF INTERNAL PORES

In this case, the solid is permeated by a system of pores (interconnected or not), somewhat in the manner of a sponge. The net result is the creation of a large internal surface. The pore openings of such active solids should not be too narrow since they must allow the gases to penetrate into the interior (see [8]).

The two methods of achieving high surface may be illustrated on the classic catalyst, platinum; thus, platinum black is the subdivided solid, while platinum sponge is the porous form.

Active substances not only must have a large surface area, but must also possess a proper surface structure. As a general rule, one can expect the surface lattice of metals and ionic compounds to differ from the interior lattice of the crystal [12, 13, 14]. Thus, the active surface is very readily affected by external agents (such as impurities), and is also subject to other influences, such as the method of preparation, etc. In addition, it is often found that the same particle may carry several crystallographically differing surfaces. Obviously, these will differ not only in their chemical properties [2, 4, 5] but also in their catalytic activity [7, 9, 11]. This fact, as well as the presence of intrinsic and impurity defects in the lattice, results in an overall surface which is usually very heterogenous; this, in turn, affects its adsorptive and catalytic behavior.

The methods of controlling particle size, surface area and surface structure during preparation of various adsorbents and catalysts are given in the preparative directions for individual substances, as well as in the general notes. A more extensive treatment of these problems is given in Ref. [A], especially in the articles in Vol. 4. The usual methods are frequently employed to obtain substances whose activity is not only related to their particle size and surface structure, but is also a direct consequence of other factors such as lattice defects, amorphism, the existence of unstable modifications [1, 10], etc.

We have seen in the above that the activated state of solids. which is the result of the existence of special conditions in the material, is rather unstable and can easily be destroyed. In the preparation of activated solids, this state is fixed by removing the conditions favorable to a transition to a more stable form (for example, slow aging at preparative conditions); i.e., the solid is "frozen" in the activated state. This may be done, for example, by rapid quenching, quick removal of supernatant mother liquors, etc. The active state also implies higher than normal surface energies. For this reason, active materials are generally very reactive, and are frequently used in heterogeneous reactions (solid-solid, solid-liquid, or solid-gas). They are more readily decomposed chemically than inactive preparations; thus, active metals oxidize faster, oxides hydrate more easily, hydroxides and hydrated oxides are more sensitive to CO₂. All of these solids decrease in activity with time, due to a slow healing of surface defects and an eventual increase in grain size. The kinetics of such aging processes are in some ways analogous to those of the ion-hole processes in semiconductors. Aging proceeds via a series of individual steps and, depending on the activation energy of these steps, different optimum temperatures are required if the aging is to proceed at a significant rate. The temperature scale of Hüttig [6], derived as an extension of the work of Tammann (see table), is based on studies of metals and ionic compounds and provides a useful rule-of-thumb guide to the temperatures at which these processes take place.

It is seen from the table that some healing of surface defects is possible without undue reduction of particle size. In general, however, the temperature of any heat treatment of active materials must be strictly controlled to avoid deleterious effects. In heterogeneous gas catalysis, reaction temperatures exceeding those recommended in the table are often unavoidable; this leads to a

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| Period | α* | Processes occurring in the catalytic material | | | |
|--|-----------|---|--|--|--|
| Initial surface degradation | < 0,23 | Reduction in adsorbing surface; degradation of those surface de- fects which possess the highest energy. | | | |
| Surface activation | 0.23~0.36 | Degradation of surface defects. | | | |
| Deactivation of the surface | 0.33-0.45 | Formation of a surface which is stable in a thermal equilibrium; beginning of particle sintering. | | | |
| Activation of the crystal center | 0.37-0.53 | Degradation of defects in the in- terior of the crystal. | | | |
| Deactivation of the interior of the crystal | 0.48-0.8 | Accretive crystallization. | | | |
| Relaxation and disintegration of the crystal | > 0.8 | Stage prior to melting. | | | |

 $*\alpha = T/T_m$, where T is the temperature of the experiment and T_m the melting point of the substance (°K).

rapid inactivation of the catalyst. In such cases a stabilization of the surface and of the remainder of the defect structure may be achieved by precipitating the catalyst onto a suitable carrier substance. This method is also used to transform into a quasi-solid form substances that, when pure, normally exist only in a subdivided form.

Such carriers must have good accessibility to gases, combined with reasonable mechanical strength and thermal stability. The frequently used carriers are:

NATURAL MATERIALS

Pumice, kleselgur, various silicates (asbestos, meerschaum, etc.), adsorbent clays, etc.

SYNTHETIC MATERIALS

Magnesium oxide, γ -aluminum oxide, synthetic rutile, thorium dioxide, silica gels, barium sulfate, activated carbons, metallic network supporting structures, various silicates (especially of Mg, Al), etc.

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Natural materials are transformed into carriers in a variety of ways such as slurrying, washing and treatment with acids or alkalies; or they may have to be fractionated to separate the most active structures before the catalyst itself is deposited. Catalytic substances containing alumina, silica, thoria and similar carriers may also be obtained by coprecipitation.

It is frequently observed that the activity of a catalyst varies with the carrier and substrate and that certain catalyst-substrate combinations give especially good results (see [3]). This is a particular case of catalyst promotion which is frequently observed in mixed catalysts. This phenomenon is of great practical importance. It permits the creation of catalyst mixtures that are very active and capable of influencing reactions in a very specific manner. something that the individual components of the combination cannot achieve qualitatively or quantitatively.

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1. ADSORBENTS AND CATALYSTS

ACTIVE METALS

The usual methods for the preparation of active metals fall into three groups, which are characterized by common preparative methodology and the same type of defect structure of the products.

PREPARATION BY REACTIONS OF SOLIDS

These reactions should be carried out topochemically; i.e., the active metal should be formed in the boundary region of the solid starting substances and not via a reaction between dissolved or gaseous particles. It is also desirable to avoid transport of the atoms of the solid from the initial reaction site; thus, any regrouping of atoms due to the reaction should involve minimum displacement. The desired product should be a loose network of mutually joined primary crystallites. The lower the temperature, the shorter the exposure of the material to high temperature; and the looser the structure of the starting material, the closer the approach to this ideal condition.

Reactions of this type include:

 Reduction of solids with gaseous agents (see preparation of pyrophoric cobalt, p. 1615; Ni-Mg mixed oxalate catalyst, p. 1615).

2) Reduction of solids with solid reducing agents, solid-solid reactions (see tungsten, p. 1622).

3) Reduction of solids with solutions of reducing agents (see "molecular" silver, p. 1623).

4) Leaching out one component from a solid mixture (see Raney Ni, p. 1625).

5) Thermal decomposition of solids, resulting in liberation of a metal (see nickel formate-paraffin catalyst, p. 1631).

PREPARATION OF ACTIVE METALS BY DEPOSITION FROM A HOMOGENEOUS MEDIUM

These reactions give materials with a broad particle size distribution, which does not follow a predetermined probability function, but is controlled by the processes of nucleation and phase formation. A precondition for such a distribution is a high degree of supersaturation of the homogeneous phase, something which is readily achieved given the poor solubility and high boiling of metalls. One thus obtains many nuclei. Local supersaturation is insufficient and is to be avoided. Processes of this kind involve:

1) Reductions of compounds from the gaseous phase and from homogeneous solutions (see active copper, p. 1633).

2) Thermal decomposition of volatile metal compounds, especially carbonyls (see carbonyl iron, p. 1636).

PREPARATION BY PRECIPITATION ON INTERFACES

The structure of such precipitates can be influenced by the carrier. Thus, oriented deposits are known in which the crystallites of the deposit are preferentially attached to a specific crystal plane of the carrier. Further, there exists the phenomenon of epitaxy, in which the crystal axes of the individual deposit particles have a definite spatial and geometric relationship to each other and to the crystal axes of the carrier. Under such conditions, there may occur significant changes in the relative proportions of some crystal surfaces to the total surface area. Precipitation on a surface is not necessarily preceded by a chemical reaction.

Among such methods of preparations are:

1) Electrolytic preparation of finely divided and active metals (see explosive antimony, p. 1638).

2) Electrochemical reduction, cementation (see silver, p. 1641).

3) Deposition from a vapor (see metallic deposits from a vapor, p. 1643).

Pure metallic preparations normally do not have a very high intrinsic activity; the total activity of a catalyst depends very much on the development of the surface. Lattice imperfections are usually observed only in the presence of impurities (incomplete reaction of starting materials) or in metals supported on carriers. The carriers prevent sintering of metal particles [73] on heat treatment during preparation or use, and in addition they stabilize crystal modifications beyond their normal range of existence.

The extremely active metals are pyrophoric; that is, they oxidize spontaneously on contact with air or in a high-temperature environment, becoming brightly incandescent (spontaneous and latent pyrophoric tendencies, respectively). The spontaneous pyrophoric tendency. which causes some obvious difficulties in the handling of these materials, may be converted to the latent one by mixing the products with a 0.5% solution of acetyl cellulose in acetone or a very dilute solution of polystyrene in benzene, followed by evaporation of the solvent. Frequently, a spontaneously pyrophoric metal may be sufficiently deactivated either by shaking it for some time with pure benzene, petroleum ether, ethanol or a similar substance, or by allowing such a liquid to evaporate from the mixture. On such treatment the particle surfaces become covered with a thin layer of oxide due to slow diffusion of oxygen through the liquid or due to slow exposure on evaporation. Because the exposure is slow and the particle is at least partly submerged in a heat-removing liquid, the heat generated by the oxidation does not increase the temperature to the point of ignition.

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Pyrophoric Cobalt

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$$\frac{2 \operatorname{CoO}(\mathrm{OH}) + 3 \operatorname{H}_{t}}{183.9} + \frac{3 \operatorname{H}_{t}}{67.2!} = 2 \operatorname{Co} + 4 \operatorname{H}_{t} \operatorname{O}$$

Cobalt (III) hydroxide (prepared as on p. 1520) is placed in a porcelain boat and reduced in a stream of hydrogen. The boat is heated by a tubular electric furnace whose temperature is regulated by a thermocoupie connected to an on-off relay. For practical purposes, a temperature exceeding 300°C gives a sufficiently high reduction rate. The crystal structure and pyrophoric nature of the product (at room temperature) are related to the reduction temperature as follows:

| Temperature, °C | 300 | 400 | 500 | 600 | 700 | 800 | |
|--------------------------------------|--|-----|--------|----------------|-----|-----|--|
| Crystal structure | α -Co (hexagonal [49]), β -Co (cubic) | | | | | | |
| Pyrophoric tendency (see p. 1614) | spontaneous | | latent | not pyrophoric | | | |

U. CARRIER-SUPPORTED PYROPHORIC COBALT, BY REDUCTION OF A COPRECIPITATE

A solution of 75.0 g, of Al(NO₃)₃ • 9 H₂O (0,2 moles) in 300 ml. of water is prepared and 200 ml, of 20% sodium hydroxide solution is added with efficient stirring. The initial precipitate is redissolved and a solution of 29.1 g, of Co(NOs) a · 6 H2O (0.1 moles) and 20 ml. of conc. HNO₃ (d 1,40) in 500 ml, of water is immediately poured in (thin stream, good agitation). The violet-rose precipitate is allowed to settle and then is washed 4 or 5 times by decanting with pure water. It is then centrifuged off and dried in an oven at 75 °C. The coprecipitate is then ground under water and boiled several times with water (250 ml, each time) until the absence of nitrate in the product can be established by some qualitative test reaction. The product is again collected by centrifugation and dried at 75°C, then at 100°C. Reduction of such coprecipates by method I yields spontaneously pyrophoric materials even at the highest reaction temperatures. While 6-Co prepared by method I is converted more or less completely to the a-form on grinding in the absence of air in an agate mortar, materials prepared via method II remain completely unchanged [17] on such grinding. The β -form appears to be the more active hydrogenation catalyst [56]. ۰.

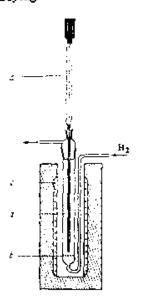
Ni-Mg Mixed Oxalate Catalyst (1:1)

(Ni, Mg)C2O4 2 H2O (H1) Ni/MgC2O4

In the Langenbeck method [34] a solution of 15 g, of Ni(NO₃)₂ \cdot 6 H₂O and 70 g, of Mg(NO₃)₂ \cdot 6 H₂O in 600 ml, of water is heated

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to 50°C and the mixed oxalate precipitated by addition of a solution of 29.6 g. of $H_9C_9O_4 \cdot 2 H_2O$ in 400 ml, of water (constant stirring). The mixture is then left standing for 12 hours to complete the crystallization. The compound is collected by suction filtration and the light-green crystals washed with water until free of nitrates. Drying at 100°C yields 16 g. of the mixed oxalate.



The material is reductively decomposed in the apparatus of Fig. 336. The sample is placed over the fritted-glass plate b (which acts as a distributor). When the hydrogen stream is adjusted to 10 liters/hour at STP, the mixed oxalate should form a stable fluidized bed. The temperature is then raised to 350°C. The decomposition takes 150 minutes.

PROPERTIES:

Black, pyrophoric powder. Aside from the metallic Ni produced in the decomposition, contains a nearly unchanged magnesium oxalate carrier [32]. Extremely active hydrogenation catalyst.

GENERAL :

The reduction of oxygenated compounds to active metals presented above is a very general method. Hydrogen is frequently the only useful gaseous reducing agent. It possesses a high thermal conductivity, and therefore the heat of reaction tends to be removed as fast as it is generated. This is important in systems where the metal, once produced, catalyzes another further reaction [2, 52]. Apart

from this, fewer undesirable side reactions can be expected with hydrogen than with other (possibly) useful gases such as CO, the lower hydrocarbons and NH_3 , with which formation of carbonyls and contamination with carbides and nitrides is possible [20]. The flow rate must be sufficiently high to remove the volatile decomposition products as fast as they are formed; otherwise the reaction may be inhibited and the activity of the final product may be less than the optimum [56, 69, 71]. If necessary, the exit gas composition

Fig. 336. Preparation of mixed salt catalysts by fluidized bed decomposition of oxygen-containing compounds. α reactor, b fritted-glass plate (distributor), c electric heating coil, d thermometer connected to an on-off relay in the heater circuit, may be monitored [2]; a continuous monitoring system based on the thermal conductivity of the gas can be especially useful [8].

The oxygenated starting material must also be carefully chosen. In the following, we shall present some remarks pertaining to individual classes of starting materials.

OXIDES

The best starting materials are active oxides, possibly produced in situ, preferably from hydroxides, hydrated oxides or carbonates. In some cases it may be necessary to start with a very well-defined oxide modification in order to obtain an active catalyst [29]. Occasionally, the required starting oxides are produced by thermal decomposition of nitrates. However, the activity of such products is not very high and their maximum specific surface does not exceed a few m.²/g. For this reason, altrate decomposition is important only for the production of supported catalysts (see below). Oxides calcined at a high temperature, as well as spineltype materials, should be avoided, since their reduction times tend to be extremely long [2].

FORMATES AND OXALATES

Heavy-metal salts in this class may reduced directly since their anions also are reducing agents and thus promote the overall reaction [36]. In some cases (see p. 1665), simple thermal decomposition of the formate or oxalate will yield the metal; in such cases the hydrogen acts only as a protective gas which prevents reoxidation. Metals obtained by this method are not always completely free from carbon [33, 37]. The nature of the starting material may influence the activity of the product metal catalyst to some extent; this is especially true if the material is reduced at a temporature just sufficient to effect the reaction [42].

The following methods apply to the production of carriersupported catalysts:

a) Precipitation of the compound to be reduced (hydroxide and carbonate by precipitation from solution, oxide by nitrate decomposition) on the desired carrier. The major methods involved are those of Sabatier [60, 61] and that illustrated by the case of active copper [47] (see copper tower, p. 459). Many industrial catalysts are prepared in this manner; it is especially recommended for cases where the active material must participate in a stoichiometric reaction.

b) Coprecipitation. In this case, the noble and the base metal are both attached to the same type of anion. The noble metal is in the form of a compound which yields the actual catalyst upon reduction, while the base-metal compound yields the carrier upon

reductive decomposition. The coprecipitation must be carried out in such a way as to avoid possible fractionation of the two components [66]. Thus, it is desirable that the coprecipitants form compounds or solid solutions under the mother liquor. It is known for instance, that divalent metal couples (Co/Zn; Ni/Zn [12]) as well as mixed bi- and trivalent metal couples (Mn/Al; Co/AI [13]; Ni/Al [13, 43, 44, 46]; Cu/Al [5]) can form double hydroxides. Solid solutions (or mixed crystals) tend to give especially finely divided active metal catalysts, because this subdivision tends to exist in the material even prior to the reduction. Systematic studies by Langenbeck have shown that mixed formate and oxalate crystals tend to give especially active catalysts. Such mixed salts decompose at low temperatures and the active metal exists in a finely divided form [56]. The specific surface in such cases is high (in isolated cases it may exceed 200 m.²/g. [54, 56]).

To achieve homogeneity with these relatively soluble compounds, which, however, have different solubilities, the mixed formates must be prepared by a special spray-drying technique [31]. The mixed oxalates, which are precipitated with oxalic acid and ammonium oxalate rather than with alkali oxalates (this tends to give more active catalysts), yield, as a rule, homogeneous materials via a simple precipitation. Complex oxalates are just as usable as the mixed oxalates [33].

c) Activation of the surface of suitably shaped metals by surface oxidation and reduction. This process may have to be repeated; highest activation is usually obtained after 3-4 cycles [21]. The product particle consists of a small solid metal nucleus—the carrier—to which the reduced metal, in finely divided or porous form, adheres tightly. The roughening of the surface accompanying this process leads to a useful increase in specific surface. The starting materials are usually thin metal foils, but sometimes oxidized wire cuttings (see CuO "wire" [45]) give a useful catalyst with a carrier of exceptionally high thermal conductivity. This is a useful feature because it helps achieve a uniform temperature distribution within a closely packed catalyst mass.

The above methods may also be used for the production of alloy powders and solid metallic solutions. However, the mechanical properties [24], the tendency to lattice imperfections [25], and the catalytic activity [4, 68] of such preparations are not simple functions of the composition.

The hydrogen reduction method is also used for the preparation of active forms of lower oxides and sulfides of multivalent metals. However, these materials require a much longer time to achieve reduction, even though the procedure is otherwise identical.

The optimum reduction temperature depends on a variety of factors. Among these the nature of the metal is, of course, of primary importance. However, the type of the anion, the purity of

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the starting material [51], the degree of decomposition and the defect state of the compound to be reduced are also important determinants of the optimum temperature. The deposition on a carrier or the presence of admixtures [11, 55, 62] may decisively influence the reductive behavior. The lowest reduction temperatures are achieved with specially purified gases (carefully dried H₂ [56], CO free from CO₂), if necessary, at reduced pressure [48].

| Metal or alloy | | Starting material for the reduction | | | | | | |
|-------------------------|--------------|-------------------------------------|----------------------------|----------------------------------|-----------------|---|---------------------------|--|
| | | Oxide | Nitrate | Hydroxide | Car- bonate | Formate | Oxelate | |
| Fe | | [28] | _ | (18) a, b (29) | . | (3) | {3, 6, 37] | |
| FeCr FeMn | I | [28] | | | _ ! | → | _ | |
| Fe-Co Fe-Ni | I I II | | [59] | | [68] a [20] | [3,38,40) [38] | [25] | |
| Fe-Cu | ï | = | _ | [57] | #[10] | _ | (94) - | |
| Fe-Ag Fe-Au Fe-Ph | 1 | | _ | [57] | - | — | - | |
| Co Co—Ni | 1 11 1 | | [53,59] n [59] {53} | [17] 5 [17] — | a [27] | [39,41,42,58] b [58] [38,40] | [39, 49] b [34] | |
| Ni | 1 | [41] c [70] | [15, 42, 53] a [64, 65] | [19, 41, 42] b [14, 50, 63] | [4,19] a (7] | [39, 41, 42] a [58] b [30, 31, 35, 54] | [9,39,41] b [32,34,35] | |
| Ni—Cu | [| _ | [53] | - | [4] | | - | |
| Cu | ן נ | [16] c [1,21] | a [26,67] | a [16, 47] | (18) | b [38] | [72] 6 [38] | |
| w | Į | [22,23] | <u> </u> | | <u> </u> | <u> </u> | <u> </u> | |

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I: free metal or free alloy.

II: metal on supported carriers: a deposited by precipitation; b deposited by coprecipitation; c obtained by activation (see text).

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Tungston

 $WO_n + 3Zn = W + 3ZnO$ 244.1 196.1 183,9 231.9

Small amounts of a homogeneous mixture of 50 g. of finely powdered calcined WO3 (prepared from analytical grade sodium tungstate) and 150 g, of fine zinc dust (containing as little oxide as possible and dried at 150°C) are pressed into unglazed porcelain crucibles. An unglazed porcelain tube may be used when a larger batch is to be prepared; the tube, centered vertically in the crucible, provides better heat conduction. The mixture is then covered with a 1- to 2-cm, layer of zinc dust, and the crucible is then closed with a closely fitting asbestos lid. To initiate the reaction, the crucible is heated to 500-520°C in an electric furnace, As soon as the mixture ignites and a bright glow is visible through a small hole in the asbestos cover, the current is cut off. The reaction is completed within a few minutes and the crucible may then be removed from the furnace. After complete cooling, the crucible is broken up and the product added (in small portions) to cold, dilute (1:4) hydrochloric acid. The mixture is boiled until hydrogen evolution ceases and the supernatant is of Zn-free acid must be added from time to time). The product is washed in a centrifuge with oxygen-free water; at the end, the wash liquors must be free of chloride ion. Toward the end of the washing procedure, the metal begins to form a colloidal suspension. It should be covered with water at all times to avoid reoxidation. After washing, the water is displaced with ethanol, under which the

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product may be stored in active form; or it is inactivated with benzone (see p. 1614) and dried in vacuum over P2O. In the latter case, the product consists of coarse lumps, which may be cautiously triturated under benzene to give a fine powder upon drying [1, 3, 5].

PROPERTIES:

High density black powder which consists of 99% W, provided the workup has been rapid and no oxygen contacted the product. The avorage size of the primary particles is about 400 A, with the individual crystallites showing a slight lattice distortion [3]. Preparations which are not inactivated prior to storage oxidize in air, evolving heat; after this, they show oxygen bands in the powder pattern.

GENERAL:

This method is obviously applicable only to very high-melting metals which retain their subdivision and defect state in spite of the high reaction temperature. The retention of these properties is aided by the fact that the particles of the reaction product are embedded in ZnO, which, together with the unreacted Zn, gives effective protection against penetration of atmospheric oxygen during cooling. This form of tungsten, as well as the analogously prepared molybdenum [4], consists of such small particles that it gives colloidal solutions on peptization by the etching method (alternate treatment with dilute acids and bases).

Other solid reducing agents include metal hydrides (for example, CaH₂) [2] and carbon. However, reduction with carbon does not yield solid oxidation products and introduces the danger of carbide formation.

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"Molecular" Silver

 $2 \text{AgCl} + \text{Zn} = 2 \text{Ag} + \text{ZnCl}_{1}$ 65.4 215.8 286.5

In the method of Gomberg and Cohne [3], pure, thoroughly washed silver chloride is placed in a beaker and covered with

water. A platinum disk, attached to a thoroughly flame-cleaned platinum wire, is embedded in the AgCl. A porous clay cell, closed at the bottom and containing some water and a few Zn rods, is placed on top of the AgCl. The reaction starts as soon as the protruding platinum wire is connected to the zinc rods. To increase the reaction rate, a few drops of HCl are added to the clay cell. Reduction of 250 g, of AgCl requires a few days. To decrease the migration of impurities from the zinc into the silver, the liquid level in the clay cell is always kept below that in the beaker. After completion of the reaction, the product (a metal-containing sludge) is washed with water, ammonium hydroxide, again with a large quantity of water, alcohol and finally ether.

PROPERTIES:

High-density gray powder. The individual particles are permeated with many pores (pore radius of the order of 10^4 A); the interconnected single grains are primary particles [8].

GENERAL:

The reduction of a suspended solid is applicable only to noble metals, but under favorable reaction conditions it produces highly dispersed materials [2]. Here again it pays to use very active starting materials, preferably prepared (by precipitation) immediately prior to use. Apart from the galvanic reduction method, one can use dissolved reducing agents. However, these must be absorbed to some extent by the precipitate to be reduced. If the precipitate is unable to absorb the reducing agent, the ions are reduced in solution, with consequent loss of the topochemical nature of the reaction [5].

Reactions of the above type give Cu from hydrated Cu oxide and N₂H₄ [2]; Ag from Ag₂O and H₂O₂ [7]; Ag from AgCl and H₂CO [9]. NH₂OH [5], N₂H₄ [6], Cr ²⁴ [4]; Pt from PtO₂ and H₂[1]. Platinum-asbestos and palladium-asbestos may also be prepared by this method (see p. 1563).

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Raney Nickel

1. METHOD OF PAUL AND HILLY [29]

A fireclay crucible is charged with 400 g. of Al. It is then heated to 1200°C, and 300 g. of nickel cubes are added at once to the Al melt. Nickel cubes are especially useful in this case since the material is porous and thus quickly dissolved at the initial, comparatively low temperature. The nickel dissolves in a vigorous reaction which raises the temperature of the melt to 1500°C. The alloy must be prepared under a salt melt layer or in an inert atmosphere to protect the Al from oxidation.

After cooling, the alloy is broken up or cut on a lathe (however, it is best to grind it in a ball mill). Then, 250 g, of the powder is added in small portions to one liter of ice-cold, 25% aqueous NaOH. During the initial vigorous reaction the flack is kept in ice; then, the mixture is gradually heated to $90-100^{\circ}$ C and this temperature is maintained until hydrogen evolution ceases. The solid is allowed to settle, the spent hydroxide solution is removed, and the process is repeated twice, each time with one liter of fresh base. The Ni sludge is then washed by decantation with water until the wash water is neutral to phenolphthalein. At the end, the water is displaced with ethanol or dioxane.

II. BANEY NICKEL, W-6 [2]

The reactor is a two-liter Erlenmeyer flask equipped with a thermometer and a stainless steel stirrer. This flask is charged with 160 g. of NaOH and 600 ml, of water. The solid is dissolved with intensive stirring and the solution is cooled in an ice bath to 50°C. Then, 150 g. of Raney nickel-aluminum alloy (1:1) is added in small pieces. The rate of addition should be such that the temperature of the mixture remains constant at $50 \pm 2^{\circ}$ C. The addition takes 20-30 minutes. The solution is then stirred for an additional 50 minutes while the temperature is kept at 50°C (first by cooling and later by heating on a water bath). The catalyst sludge product is washed three times by decontation with water. It is immediately placed in the washing tube c of the apparatus in Fig. 337 (the last of the product is transferred into c with a stream of water from a wash bottle). Tube c and the one-neck Woulfe flask b are filled with water and the apparatus is assembled as quickly as possible. All rubber stoppers and tubing should be held in place with clamps or wires. Then, O_2 -free hydrogen is introduced via e until the entire apparatus is under a gage pressure of 0.5 atm. This pressure is then maintained while stirring at such a rate that the catalyst is fluidized to a height of 18-20 cm. above the bottom of tube c and the wash water flow rate from b is 250 mL/min. When the water reservoir b is nearly empty, stopcocks g and a (the latter is connected to a large pressurized water reservoir) are simultaneously opened, and b is replenished at the same rate as water runs out at g (the flow rate is checked by a differential manometer).

In this way, 15 liters of H_2O are allowed to pass through c. The stirrer motion and wash water flow are then stopped, the pressure is released, and the apparatus is disassembled. The water layer above the catalyst is decanted and the solid transferred into a 250ml, centrifuge tube by flushing with 95% ethanol. The material is washed three times by stirring (not shaking) with 95% ethanol (150 ml, each time) and the same number of times with absolute ethanol. If centrifuged after each washing at 1500-2000 r.p.m., one to two minutes are usually sufficient to settle out the product. The product catalyst is stored under absolute ethanol in a refrigerator. It cannot be stored indefinitely.

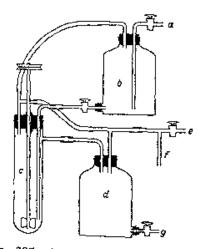


Fig. 337. Apparatus for continuous washing of Raney nickel in the absence of air. a water inlet; b water reservoir; c wash vessel; d discarded wash water; e hydrogen inlet; f nozzle for attaching a manometer; g waste water outlet.

All the above operations should be carried out as rapidly as possible. The time from the beginning of the run to the final placing of the catalyst into cold storage should not exceed three hours.

PROPERTIES:

Very dense grayish-black powder. Used as a hydrogenation catalyst [34]; it can also serve, just as Raney iron or cobait, as the starting material for the production of the corresponding carbonyl compounds [19]. Also used as a catalyst carrier [9]; can be efficiently activated by treatment with metals of the platinum group [4].

The individual catalyst particles are very porous. The primary particle size ranges from 10 to 100 A [18, 42]. Raney Ni W-6 contains 12.7% Al [20]; its specific surface was determined as 87 m. 2 /g. [44].

GENERAL:

The intermediate stages of Raney's [33] general method for the preparation of catalytically active metal skeletons can be varied over a wide range, making possible products of widely varying activities. Let us discuss these individual stages.

The storting ofloy is usually prepared by fusion of the components; this fusion should yield as homogeneous a structure as possible [39]. In another method, a fine powder of the pure catalytic metal is mixed with Al powder; the mixture is pressed into tablets and sintered for some time at moderate (of the order of 700°C) temperatures [46]. The Raney alloys can also be obtained by aluminothermic synthesis [11].

The optimum composition of the starting alloy, which determines the catalytic properties to some extent [36], is controlled by several considerations, namely: a) alloys with too high a content of catalytic metal yield products of low activity [6]; the upper limit of allowable active metal content varies from metal to metal, b) Catalysts obtained from alloys of differing active metal contents have somewhat different selectivities in the same reactions [6, 7]. c) Alloys with a definite composition such as NiAl may be so resistant to the leaching solvest used that no useful catalyst, results. The use of ordered solid solutions (e.g., Ni₂Al₃) does not offer any advantages, since the Ni atoms tend to regroup interal undesirable configuration after the Al is leached out [42].

Decomposition of the clicy should expose the skeletal metal structure. However, complete removal of the alloying metal (which accompanies the active one) requires drastic conditions and leads to products of poor activity [3]. For this reason the decomposition conditions are selected so as to leave some Al In. 8. WAGNER

the catalyst. The milder the conditions under which the decomposition takes place, the more active the catalyst and the larger the percentage of Al in the final product. In some case, it is sufficient to leach out the surface Al [40, 41; see also 34]. This also permits activation of the walls of the catalyst-containing reactor [38]. It is improbable that the Al in the catalyst is present as Al_2O_3 [20, 45].

| Literature references for the preparation of active metals |
|--|
| by the Raney process. |
| |

| Skeletal metal | Second metal (weight %) | Leaching fluid | References | |
|--|--|--|---|--|
| Fe | Al (20/80) Al | Aqueous NaOH Aqueous NaOH | [17, 30, 34] [15] | |
| Co | Al | Aqueous NaOH | [5, 11, 12, 34] | |
| Ni W-1 W-2 W-3, -4 W-5, ~6, -7 W-8 | Al (50/50) Al (50/50) Al (50/50) Al (50/50) Al (50/50) Al Mg (50/50) | Aqueous NaOH Aqueous NaOH Aqueous NaOH Aqueous NaOH Aqueous NaOH Aqueous NaOH Acueous NaOH | [8] [27] [32] [2] [25] [6, 29, 39] [28] | |
| Cu | Zn Al, Zn (50/45/5) (Devarda's alloy) | Aqueous NaOH Aqueous NaOH | [24] [10, 26] | |
| CoNI | Al (2/48/50) (5/45/50) SI (25/25/50) | Aqueous NaOH Aqueous NaOH | [35] | |

As far as the effect of the decomposition conditions is concerned, the following can be reported. The activity of the product is proportional to the rate of the decomposition and varies inversely with the decomposition temperature. The rate can be enhanced by starting with as fine metal powder as possible and adding the latter as rapidly as possible to the decomposing medium [6]. The primary particle size of the catalyst (as determined by x-ray analysis) always increases with the hydroxide concentration and the temperature [23]. However, the hydroxide concentration has little effect on the activity of the catalyst. Adkins [1] has presented a number of conclusions on the effect of these external conditions of the preparation of Raney Ni.

MISCELLANEOUS CONSIDERATIONS

In addition to the Al, the ready Raney nickel catalyst also contains hydrogen, to which the pyrophoric nature of the product [22] is due. For the nature of bonding of the hydrogen, see [13, 14, 16, 37, 43]. The removal of hydrogen leads to loss of catalytic activity, which can not be restored by renewed treatment with hvdrogen, even though the powder patterns of hydrogen-treated inactive preparations do not differ from those of active ones [22]. Since the catalyst must contain hydrogen, a special technique is required if it is to be used in deuteration reactions [25].

This general method for preparation of catalytically active structures is also applicable to metals other than Ni. It is also useful with alloys [31, 34]. In addition to Al, the alloy component which is leached out may be Si [12], Zn [24] and occasionally Mg [28] (dilute acetic acid is used as the leaching fluid). In determining the optimum composition of the Raney alloy for a specific purpose, one must also take into account the effect of the second metal.

Highly active skeletal Si was obtained by multistage removal of Ca from CaSi; the silicon metal was arranged in the form of a network consisting of six-membered rings [21].

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Nickel Formate-Paraffin Catalyst

$\frac{\text{Ni}(\text{HCOO})_{t} \cdot 2 \text{ H}_{t}O}{184.9} = \frac{\text{Ni}}{58.7} + 3 \text{ H}_{t}O + CO_{t} + CO_{t} + CO_{t}$

Dry, precipitated NiCO3 is dissolved in a 20% stoichiometric excess of 50% formic acid (80°C). The salt that crystallizes on cooling is filtered and dried at 110°C. Then, 100 g. of this formate is placed in a 500-ml, round-bottom flask equipped with a 12-mm. I.D. condenser tube (method of Allison et al. [1]) and slowly heated in aspirator vacuum together with 100 g. of paraffin wax and 20 g. of paraffin oil. The evolving gases are washed three times with paraffin oil to trap entrained paraffin wax which might plug the tubing. The product is then held for one hour at 170-80°C to remove the water of crystallization, and then the temperature is raised to 245-255° to decompose the formate; the termination of the reaction after an additional four hours can be recognized by a decrease in pressure. The reaction product is poured onto a metal sheet while still hot. After cooling as much as possible, the top paraffin layer is scraped off and the remaining very black mass is broken up into coarse pieces. Immediately before use, these paraffin-coated pieces are treated on a large Buchner funnel with a large quantity of hot water to remove most of the paraffin, The residue is dehydrated with pure ethanol; it is then immersed several times in petroleum other, removing the petroleum other by suction.

PROPERTIES:

Loose, black, nonpyrophoric powder; relatively stable in air, provided the paraffin is completely removed and well wetted by water. Shows an activity level similar to that of Raney Ni in hydrogenation of aromatic nitro compounds in aqueous solutions.

GENERAL:

Thermal decomposition of some metal compounds whose anions are reducing agents gives the metal, which may have a very high catalytic activity. The active metal may then react with air or with gaseous reaction products. If air is not allowed to penetrate (the reaction is conducted in an inert liquid), and the nascent gaseous products are quickly removed (use of high vacuum or a stream of inert gas—see use of H₂, p. 1615), it is sometimes possible to obtain the metal in its active form.

The following starting metal compounds can be used in this procedure. Hydrides, for example, CuH [16], ZnH₂ [15], CeH₃ [5], UH₃ [8] and so forth; these are decomposed in high vacuum at relatively low temperatures. Active uranium prepared from UH₂ has the remarkable ability to absorb large quantities of H₂, O₂, N₂, CO, CO₂ and other "base" gases; it can thus be used for the purification of "inert" gases, especially in closed systems [4].

Formates, for example, those of Co [17], Ni [2, 9, 17] and Cu [17]. Decomposition of these compounds yields a very porous active metal structure of crystallites; the same is true of Ni and Co oxalates {3, 13]. The decomposition of these salts is, to a large extent, a topochemical reaction, in which the nascent freemetal atoms regroup themselves within a very small region. To obtain these metals in the form of carrier-supported catalysts, one can start with a mixture of salts [3].

A number of other organometallic compounds among them several acetylides [7] and nitrides, give the metal in a more or less pure form on thermal decomposition.

Finally, active, sometimes even pyrophoric metals can be obtained by thermal decompositions of amolgoms. Thus, fine powders of Be [14], Cr [6] and Ni [9, 10] are obtained from their amalgams upon removal of Hg by distillation. Since electrochemically obtained Fe and Co amalgams [10, 11, 12] decompose spontaneously, the active metal can be separated by simple mechanical means. This type of cobalt is an extremely active hydrogenation catalyst, while Ni produced from an amalgam is totally inactive [10].

Highly active noble metals may also be generated from other compounds. Thus, Pd, Ir and Pt "sponges" are obtained upon calcination of their ammoniumhexachloro complex salts (see p. 1562).

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Active Copper

10

- 15

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$Cu^{2+} + 2Cr^{2+} = Cu + 2Cr^{2+}$ 63.5 104.0

A fresh solution (800 ml.) of anhydrous Zn-free CrCi₂ (80 g.) is prepared in water strongly acidified with HCl (see p. 1367). Carbon dioxide is bubbled through and the solution is cooled to 0° C. Then, an ice-cold solution of 60 g. of CuSO₄ • 5 H₂O in 350 ml. of water is added with vigorous stirring. The reduction starts immediately and ends in a short while. The precipitated copper powder is washed several times by decanting with water. The water is then displaced with ethanol. The alcohol is, in turn, displaced with ether or benzene. The product may be stored upder either of these liquids, unless it must be inactivated before use (see p. 1614).

PROPERTIES:

Extremely fine red powder with no metallic luster. Very useful as a catalyst in organic chemistry [16, 17].

GENERAL:

The usefulness of this homogeneous phase reduction is restricted to the more noble metals. The range of reducing agents which can be used here is quite wide: cations of low valence (Gran Fe^{2+} , Ti^{3+} and others), reducing anions ($S_2O_4^{-3-}$, $PH_2O_2^{--}$, $HCOO^{-}$), as well as H_2O_2 , N_3H_4 , NH_2OH , H_2CO and so forth may all be employed.

These reductions require, as a rule, guite specific reaction conditions, especially as far as the hydrogen ion concentration and temperature are concerned. Both of the latter factors also affect the particle size of the product: the temperature does so in the way one would expect, but the pH in a less predictable fashion. Thus, for instance, gold precipitates from alkaline solutions in smaller primary crystallites than those obtained from acidic solution [8]. Certain reactions require above-atmospheric pressures [6, 10].

Homogeneous phase reductions have also been carried out in liquid NH₃ [1-5, 22-30]. The use of this solvent extends the general method to less noble metals, whose halides may thus he reduced with alkali metals. The intermediate compounds used are frequently metal ammines; these are carefully decomposed to give the active metal. The activity of the product increases with the atomic weight of the reducing alkali metal (26); it is frequently maximum when Ca is the reducing agent [4, 5]. Many metals obtained via this procedure have remarkable catalytic activities. The use of the method is restricted by the tendency of many of the metals to combine with the reducing agent under the reaction conditions. Also, some of these metals undergo irreversible reactions with the solvent [2]. Solid solutions may be precipitated from solutions which contain two easily reduced cations (see below). Since the free energy of the less noble metals decreases as a result of formation of mixed crystals with more noble metals, the aqueous-solution procedure is not restricted to the alloys of noble metals. If the more readily reduced metal is also quite insoluble under the reaction conditions, it yields the nuclei upon which the remainder of the precipitate crystallizes. Such precipitates are, in general, finer and have a much narrower particle size distribution than chemically uniform materials [14, 24].

| Metal | Reducing agent | Reaction medium | References |
|---------------------------|---|---|----------------------------|
| Cu | Cr ² + | acid | [7,16,17] |
| Ní | S ₂ O ₄ ²⁻ PH ₂ O ₂ | ammoniacal neutral; | [9] [6,10] |
| Ag Pt (Pt black) Au | H₂O₂ | ammoniacal ammoniacal neutral alkaline | [19] see p. 1562 [8] |
| Ag-Au | NH ₃ OH Fe ²⁺ | acid | [20] [14] |
| Ag-Hg | H ² CO H ² CO | alkaline alkaline | [12] [11] |

Precipitation from aqueous solutions:

I. ADSORBENTS AND CATALYSTS

| Metal | Reducing agent | References | Metal | Reducing Agent | References | |
|----------------|-------------------------------------|-------------------------------------|------------------------------|--------------------------|-----------------------------------|--|
| Fe Co Ni | K K K Li, Na, K, Rb, Cs | [23] [25] [5, 22, 24] [26] | Ru, Rh, Pd Ag ir Pt | K Na, K, Ca K K | [29] [1, 3, 4] [28] [27] | |

Precipitation from solutions in liquid ammonia:

Homogeneous reductions may also be carried out in the goseous phase. In this case, the product metal must form a sufficiently volatile reducible compound (chlorides are frequently useful in this respect) and the reduction temperature must not be too high. Suitable reducing agents are the vapors of easily volatile base metals or hydrogen:

> $SiCl_{4} + 2Zn = 2ZnCl_{3} + Si$ [15] TiCl_{4} + 4Na = 4NnCl + Ti [18] VCl_{4} + 2H_{3} = 4HCl + V [13]

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R. WAGNER

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Carbonyl Iron

 $Fe(CO)_{s} \approx Fe + 5 CO$ 195.9 55.9 140.1

I. "FIBROUS" IRON

In the method of Beischer [1], a nitrogen stream saturated with $Fe(CO)_{g}$ at some temperature is combined in the bulb-shaped reactor of the apparatus shown in Fig. 338 with a stream of very hot nitrogen. The hot-gas quantity is always several times that of the cold one. Thus, for example, if the carbonyl-saturated N₂ flows at a rate of 2 liters/hour, the flow rate of the hot N₃ must be 40-100 liters/hour. If the reaction temperature is maintained between 200 and 700°C and the Fs concentration in the decomposition zone does not exceed 10 mg./liter, a uniform, fibrous product collects in the settling chamber.

PROPERTIES:

Fibrous carbonyl iron, prepared at 200°C and at a reactor concentration of 1 mg. of Fe/liter, quickly absorbs 10-15% of its weight in O_2 upon exposure to air; it must therefore be handled

2

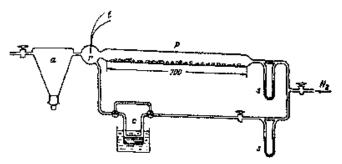


Fig. 338. Preparation of very fine iron powder with fibrous particles. a settling chamber; r reactor (30 mm. I.D.); t thermocouple; p nitrogen heating tube (20 mm. diameter), filled with small porcelain pieces, and heated either electrically or with a series burner; s flowmeter; c carbonyl storage.

and used in an N_3 atmosphere. The individual fibers reach a length of 10⁶ A at a rather uniform thickness of about 2000 A. They consist of primary particles 70-90 A long (as determined by x-ray analysis).

11. IRON GLOBULES

In the method of Beischer [1] iron globules are formed at the maximum possible $Fe(CO)_s$ concentration in the decomposition zone. The apparatus of Fig. 339 is used. The air is flushed out with a moderately fast stream of N₂ introduced via the inlet tube to a. Then the liquid carbonyl compound is vaporized at a rate of 30 ml/hr, and the vapor fed into the decomposition chamber, which is heated to 200-600°C (depending on the reaction conditions). At this point the N₂ flow is either reduced or shut off completely. The tubing from the distillation flask to the decomposition tube (which is surrounded by a vertical heater) must be well insulated or maintained at about 110°C by means of a small electric cofil or tape in order to avoid decomposition of the iron carbonyl. The first crop of product does not have the desired properties. A uniform powder consisting of microscopic globules is obtained only after a certain induction period.

PROPERTIES:

The individual globules have a diameter of 10^{4} - 10^{8} A and a peculiar structure similar to onion skin [5]. They contain (probably due to catalytic decomposition of CO on their surface) about

14 C, and they pick up 1-2% O₂ on exposure to air. The particles grow rapidly when heated to above 350 °C [4]. Because of its particle size carbonyl iron is useful in solid-solid reactions (e.g. in metallurgical sintering processes).

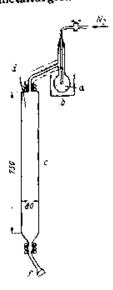


Fig. 339. Preparation of very fine iron powder with globular particles. a iron carbonyl distillation flask; b oil bath; c decomposition reactor and furnace; d thermocouple; f filter. GENERAL:

The process may also be used with other metals that form volatile, readily decomposed carbonyls. The optimum reaction conditions vary from case to case. In some instances, suppression of carbide formation is the major probiem [2].

A material with a developed inner structure (i.e., porous) is developed if the decomposition is carried outcompletely in the reactor chamber (whereby the heat is supplied by radiation or hot gases). If the reacting gases are also made to follow a vortex path, then uniform, small particles are obtained [3]. However, any undecomposed carbonyl which reaches the wall of the vessel decomposes on it, precipitating the metal in the form of a tenaciously adhering mirror or in lavers of leaflets (see p. Incomplete removal of air 1644). or deliberate addition of oxygen to the reactor may produce fine metal oxide aerosols (see p. 1669),

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Explosive Antimony

A 25% solution of SbCl₃ in 10% hydrochloric acid is electrolyzed at 20°C in the apparatus shown in Fig. 340 [6]. The solution is obtained by adding 300 ml. of conc. HCl to 500 ml. of water, dissolving 250 g. of $SbCl_3$ in this mixture, and adding water to make up one liter. The electrolysis vessel, placed in a constant-temperature bath, is either a 650-ml. three-neck Woulfe flask or a oneliter filter jar [7]. The anode a con-

sists of very high-purity antimony; if it is short and does not protrude from the electrolysis jar, it is extended with a olatinum wire, the remaining length being supplied with a copper wire. The cathode c is best prepared from a 10cm.-long piece of 1-mm.-diameter Pt wire, but copper [7] or manganin [18] wires of the same diameter are also suitable; the cathode c is bent to a U shape and rigidly attached to the stirrer (with the two free ends directed downward). The electrical connection is made via a drop of mercury placed inside the hollow stirrer shaft; this pool contacts a sealed-in platinum wire, which in turn makes contact with the cathode wire.

The electrolysis is started at a very low current; after five minutes the current is increased to give a cathode density of approximately 0.3 amp./in?, while stirring at a rate of 1000 r.p.m. Since the cathode surface gradually increases during the run due to deposition

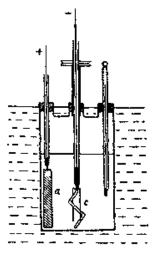


Fig. 340. Preparation of explosive antimony. *a* ance of pure antimony; *c* cathode of platinum wire.

of the smooth, shiny metal, the current must be gradually increased (25% in two hours). A two-hour run yields about 400 mg. of metal deposit, sufficient for demonstration purposes. After completion of the electrolysis the cathode is carefully removed (avoid bumping against the vessel wall), washed with conc. HCl, then with water, and rinsed with alcohol and ether.

PROPERTIES:

f

X-ray analysis [8, 10, 11] indicates that explosive antimony is amorphous, with a crystal structure almost like that of a liquid except for some short-range ordering of the atoms. This state is stabilized by small amounts of SbCl₃ or SbOCl, which contaminate the precipitate. The electrical conductivity is 4-5 orders of magnitude smaller than that of the pure element [4, 18]. Crystallization, which is a first-order reaction [4], may be initiated by scratching the walls, by slight heating, or by an electric discharge. Due to a "heat of crystallization" of 2.5 kcal./g.-atom [5, 7], the trichloride is vaporized and becomes visible as a fog.

GENERAL:

Good cathodic deposition of metal powder or sponge is controlled by a number of factors which depend on the material itself and on the experimental conditions employed [14, 20, 21].

a) Cathode surface conditions. A low concentration of the deposited ion in the cathode surface film tends to prevent the formation of a solid deposit layer, as the crystals then tend to grow away from the surface. Low surface concentrations are enhanced by the use of a dilute electrolyte, complexes in which the metal is firmly bound, the presence of high concentrations of neutral salts, low solution temperatures, and high current density in an unagitated electrolyte.

b) iow overvoltage of the metal to be deposited; this causes needlelike and dendritic deposits which are easily crushed to a crystalline powder, e.g., Cd [19]. The overvoltage of the metals generally increases with complex formation and decreases with increasing temperature. These factors therefore work in a direction exactly opposite to that cited under (a).

c) Coprecipitation of bosic saits from the cathode film also gives a porous precipitate, a condition favored by the use of neutral or weakly acid solutions (depending on the tendency of the metal ion to hydrolyze). It is, however, also possible to remove H^+ from the cathode film; this can be done by electrolytic deposition of electron-bearing ions (low cathode current yield)—a factor which may be enhanced by metallic impurities or low hydrogen overvoltage—or by oxidizing agents which use up H^+ while accepting electrons. The effect of temperature on this coprecipitation varies: higher temperatures favor hydrolysis, but also favor the increased supply of hydrogen ions from the solution by increasing the diffusion rate.

An appropriate selection and balance of these factors should permit electrolytic production of powders of every metal that can be deposited from aqueous solution. The particle size of the cathode deposit can be reduced by the use of ultrasound [2, 3].

The simultaneous evolution of H_2 , which is not absolutely essential for the preparation of metal powder, nevertheless causes a certain fluffing of the metal precipitates, allowing them to occlude considerable amounts of nonmetallic impurities from the electrolyte. Thus Cu or Ag precipitates may, under proper electrolysis conditions, occlude several percent of citric or tartaric acids (or their salts), as well as asparagine, and so forth. In this state the powders have lower negative potentials than the pure metals [15], in the same way as explosive antimony [18]. Fused salts (fluorides, chlorides) easily yield metal powders [1] because they have virtually no overvoltage as long as the bath temperatures are kept low.

The following metal powders have been obtained by electrolysis of aqueous solutions: Fe [12, 20, 21], Ni [12, 20, 21], Cu [12, 16, 20, 21], Zn [12, 13, 20, 21], Ag [17], Cd [19, 20, 21], Sn, Pb [12], Ni-Pd alloy [9].

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Şilver

(Active Agent for Reductors)

 $2 \text{ AgNO}_3 + \text{Cu} [\text{Zn}] = 2 \text{ Ag} + \text{Cu}(\text{NO}_3)_3 [\text{Zn}(\text{NO}_3)_3]$ 339.8 63.5 (85.4) 235.8

A sheet of electrolytic copper [7] or several zinc rods [2] are suspended in a well-stirred solution of 29 g. of AgNO₃ in 400 ml. R. WAGNER

of water acidified with a few drops of HNO_3 . The reaction starts immediately. When the solution is free from Ag^+ , the copper sheet and the stirrer are removed and the silver sludge is washed several times with dilute sulfuric acid (decantation). This removes most of the copper (zinc); the sludge is then transferred to the reductor tube and further washed with dilute sulfuric acid until free from Cu (Zn). The sulfuric acid is then displaced with 1N HCl: the acid must always cover the silver in the reductor, whether it is being used or just stored. Any air bubbles present are removed by shaking.

The regeneration of the silver in the reductor proceeds via method of Wislicenus [9]. A small piece of zinc is placed on top of the silver filling of the column (this column packing is blackened for about 3/4 of its length by superficial chloride formation). The reductor should be filled with dilute sulfuric acid. The reduction of the AgCl proceeds rapidly if the Zn makes good contact with the reductor material.

PROPERTIES:

Fine silver-gray powder; used in analytical chemistry as a packing for Jones reductors (reductions in hydrochloric acid solutions).

GENERAL:

This process does not usually yield very pure products [4, 6]. The less noble metals (e.g., Cu [4]) become pyrophoric at low temperatures. The somewhat higher energy level of these preparations is due to the large surface area and to lattice defects. Some metals tend to form fibrous structures [8] with appropriate reducing metals and solvents.

Zinc can also be used as a reducing agent for the preparation of Cu [4, 5], Ni [3] and Sn [1].

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Deposition of Metals from the Vapor Phase

Deposits of metals from the vapor phase [2, 5, 6, 10] are especially useful for studies of very pure materials, where it is desired to correlate the structure and the electronic state of a solid with its catalytic activity. Metal deposits can be investigated by electron diffraction, conductivity measurements, and optical and magnetic techniques even while they are covered with a layer of adsorbed material or while actually participating in a catalytic process.

The experimental apparatus varies with the type of study. In general, the parts of a glass apparatus should be fused together so as to avoid greased glass joints. This means that not only the reaction vessels proper but all the auxiliary devices such as gas receivers, cold traps, manometers and so forth must be fused to the apparatus prior to the start of a run. To obtain reproducible results, the catalyst carrier is carefully purified prior to sealing the apparatus, heated slowly to 400-500°C, and baked at this temperature for several hours in a high vacuum. Only then is the carrier temperature adjusted to the level required for condensation and the deposition of the metal vapor started. All these operations must be carried out in the vacuum of a running pump. Fresh metal deposits adsorb gases extremely readily. For this reason all gases other than those actually needed in the process (especially those which may be catalyst poisons) should be removed from the apparatus prior to the start of deposition.

Reaction vessels: The inside wall is usually used as the support for the deposit. The vessels, which are made of quartz or glass, are of two common types: spherical flasks for adsorption measurements $\{1, 29\}$ and cylinders, which are especially suited for experiments in catalysis $\{5, 22\}$. Since the studies are usually conducted at constant temperature, the wall must have good thermal conductivity. The vessel is either immersed in a bath or surrounded by a jacket filled with a heat transfer medium.

Ŗ

Vaporization of the metal. The metal must be melted in vacuum. Aside from this requirement, which applies in all cases, the experimenter can choose from a variety of options. The usual procedure involves resistance heating of a suitably shaped wire coil. This method can be used where the metal has a sufficiently high volatility below the melting point to produce the vapor at an appreciable rate. In other cases it may be necessary to vaporize the metal at or above its m.p. In these cases, it is vaporized from the surface of a resistance-heated spiral or boat made of a high-melting metal (W, Mo or Ta). The current leads are sealed to the glass vessel; if necessary, they may be introduced in water-cooled ground joints. Suitable sheet-metal screens prevent condensation of metal in unwanted places.

Additional possible heating methods include high-frequency induction heating and cathode sputtering. However, one should remember that deposits obtained from a vapor and from a sputtered cathode differ somewhat in structure [14].

Condensation. In general, the condensation conditions greatly affect the secondary structure and the catalytic activity of the metallic deposit [7]. Depending on condensation conditions, the metal layers deposited on amorphous supports (glasses) at low temperatures may be either crystallographically disordered (random) or oriented [5, 25]. In an oriented layer the crystallites adhere to the support in a uniform fashion, the boundary with the support being the simply indexed crystal lattice plane that has the lowest atomic (or molecular) density. The crystallite arrangement in all other directions is totally random. Epitaxial growth may occur on crystalline material, with deviations of up to 15% in the lattice dimensions [8, 24, 34]. Metastable crystal modifications have also been observed in vapor deposits [11].

Condensation at low temperatures favors the formation of homogeneous mirrors, which remain stable at room temperature. Under these conditions mirrors are formed even by metals that otherwise would appear dull [28]. The specific surface area, which is controlled primarily by the melting point of the metal, is slightly higher in deposits obtained at low temperatures than in those produced at 0°C [32]. Higher condensation temperatures or the presence of inert gases (noble gases can be used in all cases, nitrogen sometimes, while hydrogen is completely unsuitable; see [12]) results in a decrease of the orientation of the crystallites (the latter cease to be oriented at sufficiently high condensation temperatures). An additional phenomenon appearing at high condensation temperatures or in the presence of gases is that the individual crystallites become smaller while retaining their normal lattice constants [20] and the deposits become dull black. In contrast to mirrors, they show a strong small-angle x-ray scattering [9].

Simultaneous deposition of lattice-distorting substances (NaCl, H_2O) has been recommended for obtaining defect structures [12].

Metal deposits which are useful for preparative purposes may be obtained by thermol decomposition of suitable volatile metal compounds (hydrides, carbonyls) on hot surfaces. For instance, decomposition of Ni(CO)₄ on Pyrex glass wool at 150 °C produces a deposit of very finely divided nickel, which is an excellent catalyst for gas-phase hydrogenation of olefinic double bonds [4].

1. ADSORBENTS AND CATALYSTS

| Metal | Studies on the properties of the deposit | Adsorption measurements | Catalytic studies |
|----------|--|----------------------------|--------------------------|
| Fe Co | [13, 14, 32] [13] | [3, 21, 33] | [18, 27] |
| Ni | [5, 7, 11, 13, 20, 25] | [21] [5, 7, 26, 29, 33] | [5, 15, 16, 17, 18, |
| Cu | [9, 13, 19, 28] | [1] | 22, 23, 27, 30] |
| Rh | [32] | | [16, 17, 18] |
| Pd W | [32] | [31, 33] | [16, 17] {17, 18, 27] |

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HYDRATED OXIDE GELS

The hydrated oxides used as adsorbents are called, more precisely, xerogels* or aerogels. They are prepared by drying the corresponding hydrogels. The adsorptive capacity of the xerogels depends on the drying process used. The starting hydrogels are prepared by the following methods:

PRECIPITATION REACTIONS

The molecules of precipitated hydrogels are usually arranged in a random order. However, ordered structures may form if the conditions are such that basic salts or aggregated anions can be produced during the precipitation or when such starting materials are used. The surface properties and pore structure of these gels, which show aggregates of submicroscopic globular particles under the electron microscope, depend on the precipitation reaction used. Among these reactions are:

1) Precipitation with an acid or a base (see hydrated chromium oxide gel, p. 1648; silica gel, p. 1648).

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[&]quot;Translation Editor's Note: In American practice the term "xerogel" is little used, although more precise. We prefer "resin" for organic materials and "dry gel" for inorganic ones.

2) Hydrolyses of alkoxides that give preparations free of electrolytes (see aluminum hydroxide gel p. 1652).

REACTIONS OF SOLIDS

These reactions should be topochemical and may use preformed starting materials. Among the preparative methods of this class are:

1) Topochemical hydroxide formation [see "glimmering" iron (III) hydrated oxide, p. 1654].

2) Leaching out one component of a solid mixture (see p. 1656).

The preparation of gels by controlled coagulation of sols is used more rarely. However, it may still be of interest in special cases. For instance, globular gel particles, which are useful as fluidized bed catalysts, are obtained by allowing the sol to drop into a medium which causes its spontaneous coagulation.

On simple drying in air or heating (if necessary), gels obtained by precipitation reactions show a much higher shrinkage than those obtained by reactions of solids. The shrinkage may, however, be avoided to a large extent if instead of drying the material one displaces the water with organic solvents of low surface tension. These are then removed by evaporation. In general, the pore volume increases as the surface tension of the liquid used decreases [7].

Aerogels with an especially high surface activity and specific surface (up to 800 m?/g. [4]) are obtained via the procedure of Kistler [5, 6]. In this case, the water in the hydrogel is displaced with an organic liquid which is miscible with water. The preparation is then heated in an autoclave to a point above the critical temperature of the solvent where the supercritical vapor is released, Gels prepared by this method retain the volume and the structure that existed prior to drying. In the preparation of hydrated oxide gels, one must remember that the reaction products age rapidly on contact with the aqueous mother liquor; in addition the aging process is markedly affected by the electrolyte content of the solution. Only a few precipitates remain amorphous for any length of time; most convert fairly rapidly to crystalline hydroxides or hydrated oxides [2, 3]. However, their gel nature initially remains almost the same. Some hydrated oxide gels must not be heated above a certain temperature during drying to avoid spontaneous crystallization with glimmering deflagration (compare also metamictic minerals [1, 8, 9]).

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Hydrated Chromium Oxide Gel

 $2 Cr(NO_3)_3 + 6 NH_2 = Cr_2O_3 \cdot (aq) + 6 NH_4NO_3$ (9 H-O) 152.0 800.4

Slightly more than one liter of 0.12M NH₃ solution is added with efficient stirring to one liter of 0.04M Cr(NO3)3 (the excess of NH3 favors the formation of a floculent precipitate). The precipitate is washed 10 times by decantation with water, filtered and dried at 150°C [5].

PROPERTIES:

Dark-green glasslike granules. The N2 absorption isotherm gives a specific surface of 310 m²/g. (BET method) [5]. Used as a hydrogenation and dehydrogenation catalyst [18].

Silica Gel

To start with, 3.4 liters of sodium silicate solution (sodium waterglass, d²⁰ 1.37) is diluted with one liter of water (mechanical stirring). Then, 10N HCl is added at a rate of 10 ml./min. until thymol blue shows an acid reaction (pH 2-2.8). (After addition of 400 ml. of the acid the mixture becomes viscous and rubberlike. The acid addition is interrupted and the mass is broken up. It is then manually stirred while acid is added in drops. The mixing is continued until a thin suspension is obtained. The remainder of the acid is then added at the original rate until the desired pH is reached.) The mixture is then stirred for two additional hours at room temperature, suction-filtered and washed until the wash liquid is no longer acid. The gel is dried at 200°C for 12 hours, ground to the desired particle size, and finally washed free of Cl .

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PROPERTIES:

Dull-white gel granules; hardness approximately that of glass; high specific surface (500 m^2/g_*). Gels prepared according to the above directions are especially useful for chromatographic purposes [11].

GENERAL:

Many other hydroxide precipitates may be obtained in a way similar to that used for the hydrated chromium oxide gel. However, when selecting the starting metal salts one must remember that anions of multivalent acids, especially SO4⁸⁻, are frequently difficult to remove from the product by washing. For this reason nitrates, chlorides and perchlorates are preferred. In addition, hydrated oxides obtained from sulfates frequently have a very high tendency to spontaneous deflagration. Isomeric hydrated salts, such as chromium (III) chloride hydrates, may give a variety of hydroxide precipitates ([10]; see p. 1345). The base is usually a freshly prepared, carbonate-free NH3 solution. In cases when the metal ion forms stable ammine complexes which make a quantitative precipitation difficult, the precipitation may be carried out with ammonium acetate or tetramethylammonium hydroxide solutions [22]. In addition to these agents and the various alkali metal hydroxides, active MgO and alkaline earth hydroxides may also be used as precipitants. The impurity cations that are adsorbed on the precipitate may, under certain circumstances, act as catalyst or adsorption promoters. Hydrated oxide gels of amphoteric metals may also be obtained by careful neutralization of the corresponding alkali hydroxometallate solutions. As a rule, such precipitates are microcrystalline and contaminated with large amounts of alkali ions. Hydrated oxides of cations with a high ionic potential, such as Ti⁴⁺, may also be obtained by hydrolysis of their salts, whereby a dialyzer may also be used [28, 33, 34].

The quantity of the precipitating agent has a large effect on the properties of the product gel. Incomplete precipitations (final acidic solution in the case of hydrated metal oxide gels, final alkaline solution in the case of silica gels) produce soft, friable; strongly opalescent gels with a wide range of pore sizes and low specific surfaces. An excess of the precipitating agent, on the other hand, usually causes the condensation reaction to go to completion. As a result, the gel products are thoroughly crosslinked and the presence of the three-dimensional network makes them hard, elastic and translucent, with fairly uniform pore size. The properties of the product gels depend also on the reaction temperature, as well as the order and rate of addition of the reagent solutions. If the precipitating agent is added slowly to the salt solution, there is a possibility of forming an intermediate basic sait [12, 24]; these may then precipitate as well defined compounds [6]. On the other hand, slow addition of the precipitant may yield isopolyanions (polysilicate ions and so forth); these last may also be added beforehand to obtain special effects. Such precipitation products are aged in a specific way compared with gels obtained by fast addition of the salt solution to the precipitant [17, 20].

The adsorptive selectivity of the gels may be influenced to a certain extent by the preparative conditions. One may, for instance, produce silica gels which adsorb a specific dye of characteristic molecular shape and charge distribution. This is done by dispersing this dye in the silicate solution and the precipitating the gel in the presence of the dye [2, 4, 9]. Similar experiments have been carried out with optically active compounds ([3], see also [1]). The silica gel surface may also be modified in a specific way by adsorbing on it appropriate substances; this yields preparations with completely new adsorptive properties [14, 19].

The adsorptive activity of gels is reduced not only by heat but also by grinding. Grinding produces a slight reduction in the specific surface. This is occasionally accompanied by a reduction of the average pore radius [16].

The above general remarks apply also to mixed precipitates of metal hydroxides as well as to silica-hydrated metal oxide mixed gels. As would be expected, products obtained by simultaneous precipitation of two (or more) compounds differ from those obtained by mechanical mixing of finished gels; both of these types of gels are in turn different from mixed gels produced by sequential precipitation in the same solution. Finally, we should mention the so-called chalky silica gels (see p. 1656).

To summarize, the quality of the final product gels depends on the history of the preparation. In view of the many possible slight variations in the procedure which affect the reactions involved, it is not surprising that the products vary in quality.

The product gels may be freed from impurity ions (usually present in large amounts) by dialysis or electrodialysis. However, even this procedure does not yield gels completely free from electrolytes. If completely pure products are desired, it is best to use the hydrolysis of alkoxides presented on p. 1652.

Finally, let us cite a number of new publications dealing with the preparation and testing of hydrated oxide gels: hydrated aluminum oxides [30, 32]; silica gels, unmodified [11, 13, 16, 21, 27]; silica gels, modified [1-4, 9, 14, 19]; hydrated titanium oxides [8, 15, 28, 33, 34]; hydrated chromium oxides [5, 10, 18, 23-25]; hydrated iron oxides [7, 17, 20, 23, 29]; hydrated zirconium oxide [26]; hydrated tin oxide [31]; hydrated thorium oxides [8].

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Aluminum Hydroxide Gel

α-GEL BY THE METHOD OF WILLSTÄTTER AND KRAUT

 $A!(OC_tH_s)_s + 3H_sO = A!(OH)_s + 3C_tH_sOH$

In the method of Schmäh [25], 400 ml of CO_2 -free doubledistilled water is placed in a one-liter, three-neck flask, whose center neck carries a mercury-seal stirrer. One side neck is closed off with a soda lime tube. The other is fitted with a dropping funnel with an ungreased stopcock from which a solution of 3 g, of aluminum ethoxide in 200 ml. of absolute ethanol is allowed to run in a thin stream into the vigorously stirred water (the aluminum ethoxide is prepared from SI- and Fe-free 99,99% Al by one of the methods given on page 640 and is then dissolved by refluxing with the required amount of ethanol). During the hydrolysis of the ethoxide, the temperature rises by 6-8°. The precipitate is washed by decantation with double-distilled water (the settling may be speeded up by centrifugation).

PROPERTIES:

The α -gel is completely free of electrolytes; its surface is quite alkaline. The fresh gel is completely amorphous [19]; it ages rapidly to bayerite via the intermediate stage of böhmite, the alkalinity of the surface decreasing considerably in the process [16, 17]. Aluminum oxides prepared from this gel are more active than the usual aluminum oxide catalysts [1].

GENERAL:

This method of preparation allows some latitude in the hydrolysis conditions as well as in the alcohol moiety of the alkouide. The hydrolysis may be carried out in absolute ethanol

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solution, the hydrolysis agent being atmospheric moisture (stirring in air). Alternatively, aqueous alcohol may be added to the ethanoi solution, or the hydrolysis may be carried out in the reverse fashion. by addition of the alcoholic solution to water (the water may be hot, if required). Ammonia solution may be used instead of water. Solid alkoxides (such as some methexides) may be hydrolyzed in a stream of moist air with heating if required [27]. Since the hydrolysis of alkoxides of metals of variable valence may proceed in steps [2, 5, 11], the most active products are obtained on fast precipitation.

The ability of the alkoxide to undergo hydrolysis depends on the nature of the alcohol moiety. This ability decreases with increase in the molecular weight of the organic part and increases in the order of primary to tertiary alcohol (as shown by zirconium and titanium alkoxides [6, 8, 26]). The volatility of the alkoxides increases in the same order. This fact is of some importance, because with elements having a high atomic number, it is often only the tert-alkoxides that can be distilled (and thus purified), even in high vacuum (for example, Th [10]).

A high hydrolysis temperature accelerates the aging process, so much so that in some cases the amorphous hydrated oxide cannot be isolated.

| Metai | Method of preparation of the alkoxide | Hydrolysis and products of hydrolysis | |
|---------------|--|--|--|
| Al | p. 840 this handbook | [1, 3, 16, 17, 19, 21, 25] | |
| St | [7], see p. 702 | (2, 18, 22, 32), see p. 698 | |
| Ti | [4, 7, 11, 24, 26, 27] | [5, 11, 15, 18, 20, 23, 26, 27] | |
| \mathbf{Cr} | [30] | [30] | |
| Fe | [24, 28, 29] | [29] | |
| Zr | [6-8, 24] | [6] 6 | |
| Nb | [14] | e e sta | |
| Sn | [24, 31] | [31] | |
| Ce | [13] | | |
| Hf | . [9] | | |
| Та | (12) |] | |
| Th | [10, 13] | - 44 | |

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"Glimmering" Hydrated Iron (III) Oxide

In the method of Kohlschütter et al. [3], 20 g, of $FeSO_4 \cdot 7 H_2O$ (analytical grade) is boiled for 40-60 minutes in a Kjeldahl flask

with 200 ml. of pure 70% H2SO4. The water vapor is allowed to escape in order to concentrate the acid. Following the reaction the tablet-shaped crystals (which range in size up to 2 mm.) are collected on a fritted-glass filter. They are washed with some water, then several times with acetone, and are then dried in vacuum. The dry crystals are reacted (vigorous stirring) with 200 ml. of 2N aqueous ammonia (or correspondingly less of a more concentrated solution). The reaction is over in 10-15 minutes. The product is allowed to settle, the mother liquor is decanted, and the residue washed 4-5 times by decantation with water. The hydrated oxide is collected on a filter, rinsed several times with water, and dried with acetone and ether.

To obtain a preparation with a particularly impressive glimmer, the substance is predried with ether (as above) and then carefully heated at 300°C for 30 minutes.

PROPERTIES:

Contains, even after baking at high temperature, a considerable amount of water. Single, freely flowing particles retaining the external shape of sulfate crystals. Amorphous on x-ray analysis; the hydroxide framework is permeated by numerous pores. Crystallizes spontaneously and with glowing to α -Fe₂O₂ on heating to 350°C.

GENERAL:

The ability of the system to undergo a topochemical reaction depends on several prerequisites: the solid should not dissolve too rapidly (otherwise the reaction does not occur at the interface but in solution). This prerequisite is often fulfilled by sulfates of trivalent metals. If necessary, the rate of solution may be reduced by adding a sufficient quantity of an organic substance to the aqueous solution. The organic substance may be acetone, giveol; glycerol, dioxane and so forth, or in the case of hydroxide "precipitations," it may be pyridine, mono-, di- or triethanolamine, morpholine and so forth (see [6]).

The reaction product, which is formed on the surface of the reacting crystals, should not form a solid film: it must be post meable to all reagents present in solution so as to allow the completion of the reaction throughout the individual crystallites.

Instead of simple saits, one can use double saits with readily soluble components. Thus, $KAl(SO_4)_2 \cdot 12 H_2O$ yields a granular hydrated aluminum oxide with a very porous structure [6]. Basic saits may also be reacted topochemically to yield hydrated oxides. The "glimmering" was also observed in hydrated oxides of the saits
Ti, Zr [1, 10], Sc. Nb, Ta [10] and others.

Another topochemical method for preparation of hydrated oxides consists of an extension of the procedure proposed by Raney in the case of metals. The required starting mixtures may be obtained by fusion of the components or by coprecipitation. A commercial fusion procedure yields Vycor glasses with interesting adsorptive and catalytic properties [4, 5, 9]. The fusion procedure is also used to obtain sodium ferrite-aluminate mixed crystals; these then yield bydrated iron (III) oxide skeletal structures showing considerable chemical activity (reacting with hot aqueous NaOH) provided the starting mixture contains an excess of aluminate [7]. The activity of such structures is due both to the small particle size of the product and to a strongly distorted crystal lattice due to "frozen" thermal vibrations [8].

Coprecipitation of silicic acid with hydrated oxides of metals such as Fe. Al, Cr, Ca, Cu, Ni and so forth yields silica gels that, after washing, drying and activation by leaching with hydrochloric acid, give chalky materials (provided the metal concentration in the starting mixtures is high [2]).

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ACTIVE METAL OXIDES

The methods of preparing active metal oxides may be grouped according to similarities of procedure or of structure of the product.

PREPARATION BY TOPOCHEMICAL REACTIONS

The topochemical reactions that give activated oxides are essentially thermal decompositions of suitable compounds:

1) Debydration of hydroxides [see aluminum oxide, p. 1660; o-iros (III) oxide, p. 1661]. 2) Thermal decomposition of nitrates, carbonates, exalates and

so forth (see magnesium oxide, p. 1663; zinc oxide, p. 1664). 3) Dehydration of hydrated oxides in the mother liquor [see lead (IV) oxide, p. 1668].

The products prepared under mild conditions are usually (porcus) pseudomorphs of the particles of the starting material (see [17]). Reproducible preparation of active oxides requires not only constant decomposition conditions, but also consistently uniform starting materials (constant conditions during precipitation and so forth). The effects of the chemical composition and the physical structure of the starting material on the properties of the final product decreases with increasing decomposition temperature. The extent of this decrease is proportional to the extent of ageing of the products during reaction conditions.

Kinetic measurements on thermal decomposition reactions vield several empirical equations. In general, these may be interpreted as follows:

1. If the order of the reaction is 1/3, the process is diffusioncontrolled.

2. If the order of the reaction is 2/3, the process is a decomposition reaction which progresses from the outside to the center.

If the specific surfaces of the products are plotted against the decomposition temperature (at constant decomposition time), typical curves are obtained [3]. From these, once cannot only read off the optimum conditions for creation of maximum surface but one can also obtain some indication of the mechanism of the decomposition Complete explanation of these phase relations (in reaction. some cases, an extremely complicated problem) requires the use of x-ray and IR spectroscopy and thermogravimetric methods.

In practice the decomposition temperature must be exactly maintained. Thus one cannot employ a shorter reaction time at higher temperature without incurring a loss of activity in the material. The effect of the atmosphere in which the reaction proceeds is especially remarkable. In some cases it was possible to reduce the activation energies for the decomposition by 10-15 kcal/mole (by comparison with those needed in air or vacuum) by proper choice of the gaseous atmosphere. In many cases, a property chosen gaseous atmosphere allows the decomposition to proceed at unusually low temperatures; this in turn gives high active preparations [2].

PREPARATION BY CONDENSATION FROM A HOMOGENEOUS PHASE

S. 2. The only oxides that can be condensed from the gas phose are those that are vaporized products of a chemical reaction occurring immediately prior to the condensation. Otherwise,

vaporization of oxides is usually impossible due to the high boiling points involved.

Colloidal suspensions of oxides in air (smokes, see p. 1669) usually are very nonuniform because of the randomness of nuclei formation [1, 6]. The individual particles are usually globular. The growth of particles from the gas phase occurs in two stages:

Primary growth, which is exceedingly rapid and produces particles 500-1000 A in diameter. In this stage, the only material condensed is that which finds itself within the confines of a "sphere of influence" of a nucleus.

Secondary growth, which is much slower and depends mainly on the vapor pressure of the material under the temperature conditions prevailing during growth. This stage, corresponding to the aging of precipitates under mother liquors, can be suppressed by quenching of the material.

PREPARATION BY INTERFACE REACTIONS

Under some conditions, the texture of oxide growth layers is determined by epitaxy with the support. Such layers are obtained by:

1) Surface oxidation of metals and alloys (e.g., bluing layers by heat treatment).

2) Oxidation of metal layers deposited electrolytically or from a vapor on carriers other than the metal itself. Occasionally, such surface layers show oxide modifications which are not known to occur in the pure material. In some metals the colored layers formed by strong oxidation are covered with needles or leaflets of the oxide [9]. The dimensions of these depend on the duration and the temperature of the oxidation. The rough surface thus produced may sometimes offer twice the normal specific surface [1].

Because these processes are related to catalysis, they have recently been studied by many investigators. This is especially true of the initiation reaction and the process kinetics [5, 7].

In view of the enormous complexity of the subject, the methods for the preparation of mixed and corrier-supported oxide catalysts can only be summarized here. They include:

1. Mechanical mixing (dry, in an atmosphere laden with moisture, under special gases, in suspension, and so forth [10]).

2. Coprecipitation, especially when solids of definite composition are desired; it is also applicable to the more rarely used solid solutions.

3. Precipitation of one component onto a carrier which is itself

4. Adsorption of ions of one component from a solution and so forth [8].

The interaction of the components of a mixed catalyst (promotion of catalytic activity), which in general requires thermal activition for development of the full effect, is a very complex process; occasionally, it yields very active and very specific catalysts.

The two special effects accompanying such an interaction are:

1. Alteration of the semiconductor properties of an oxide by inclusion of other oxides with different valences in the crystal lattice [5, 16]; this may also alter the activation energy of a catalytic process [14].

2. Adaptation of valence. The metal in the precipitated oxides of some transition metals adapts to the valence of the metal in the oxide carrier. Thus, transition metals preferably deposit on MgO in divalent forms while on γ -Al₂O₃ they are trivalent and on TiO₂ (rutile) tetravalent [15]. This is because the oxide precipitate attempts to continue the crystal lattice of the carrier.

Various methods are available for shoping the oxide catalysts [4]. The following methods are used in laboratories:

The material, which may be moist if required, is pressed into a sheet. After drying, it is broken up and sieved. However, the high pressure applied during sheet forming produces a large decrease in the average pore size. This may lead to a considerable reduction of the catalytic activity of such preparation, especially at large reagent throughputs (the diffusion, which controls the overall process rate, becomes hindered by the small pore size [12]).

In the second method the dry powder is made into a paste with 80% ethanol. The paste is then rolled (without applying any high pressure) into a thin sheet, which is thenforced through a polished copper or nickel screen of suitable mesh size (1-2 mm.). After drying, the granulated material may be scraped off from the reverse side of the screen. If the dilute ethanol does not yield stable granules, the paste may be made with a saturated aqueous solution of the corresponding metal nitrate. In this case, the granules are shaped as above, dried and baked at 200-220°C until nitrous fumes cease to evolve [13].

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Aluminum Oxide

Depending on the conditions, certain aluminum hydroxides yield active y-oxides on thermal decomposition. These possess interesting adsorptive and catalytic properties.

1. ADSORBING ACENT

$$2 \operatorname{Al}(OH)_3 = \operatorname{Al}_2O_3 + 3 \operatorname{H}_2O_156.0$$
 101.9

An aluminum oxide which is especially suitable for use as an adsorbing agent is obtained by heating aluminum hydroxide gel (see p. 1652) or hydrargillite (see p. 820; for preparation of an almost completely alkali-free material, see [18]) for several hours at 250-300°C. The heating proceeds in vacuum or in a stream of dry gas, and is continued until the concentration of the water has bound in the crystals decreases to 6-8 wt. %.

PROPERTIES:

Fine, white powder which flows like sand; specific surface: 250-300 m.²/g. [26]. The powder pattern shown böhmite lines, aithough the water content differs significantly from that of böhmite (15,02%). The thermodynamic potential, amounting to several kcal./mole, is due to the large surface and the defect lattice 27].

IL CATALYSTS

Aluminum oxide catalysts are prepared by heating hydrargillite at 550-659°C (other aluminum oxides give less active preparations); the content of water of crystallization is 1% or slightly less.

1. ADSORBENTS AND CATALYSTS

PROPERTIES:

Hygroscopic powder, very similar in appearance to the above described adsorption agent. The particles show a honeycomb-like secondary structure; the preparations show very uniform powder patterns (according to Glemser [17], they consist of ϵ -phase). Any water adsorbed during use is incorporated in the form of OH groups and thus causes rehydration [18].

a-Iron (III) Oxide

For chromatographic adsorption

In the method of Glemser and Rieck [19] a solution of 1000 g. of $Fe(NO_3)_3 \cdot 9 H_2O$ (A.R. or pure) in 2.4 liters of water is added with constant stirring to 2.4 liters of 6% aqueous ammonia. The precipitate is centrifuged off and washed with water until the wash liquor is free of nitrates. It is then dried at 50°C. After two days at this temperature it is broken up and freed of dust on a U.S. 400 standard screen. Long heating (10-16 hours) of this crude product at high temperatures gives preparations with other activities. The maximum activity is usually reached by heating at 180-220°C for 10 hours.

GENERAL:

The rate of dehydration of hydroxides and hydrated oxides may be varied within limits by choice of suitable experimental conditions. Aside from the obvious effect of temperature, the following dehydration procedures are open to the experimenter and give better products than does simple heating in open dishes or crucibles:

1. Removal of the water by means of a dry stream of air of other gas. The dehydrating action of the various gases is quite specific; hydrogen is an especially efficient dehydrating gas [25].

2. Reduction of the vapor pressure of water in the atmosphere surrounding the solid by operating under vacuum or using drying agents. If a drying agent is used, the material may be placed in drying platol instead of a desiccator. In this case, the samples may be heated to a high temperature while cooling the drying agent. This produces a large water vapor pressure gradient. It should be remembered that the pressure of water in equilibrium with active oxides is much lower than that encountered in equilibrium with inactive materials. In many cases it is impossible to obtain completely dry oxides without reducing the activity to level considerably below the maximum. R, WAGNER

One remarkable phenomenon, which has been proved over and over again, is the fact that dehydrations of the above type do not after the shape and size of secondary particles, while the size of the primary particles is subject to sharp variations [29].

Dehydration in hydroxides and hydrated oxides is often quite sensitive to impurities [1]. To obtain reproducible results, one should always use starting materials of the same purity.

Literature references for the preparation of active metal oxides by dehydration of hydroxides:

| Oxide | Starting material | References |
|----------------------------------|---|--------------------------|
| BeO | α-Be(OH) ₂ (see p. 894) | [9] |
| MgO | Mg(OH); (see p. 912) | [10, 23] |
| γ-Al ₂ O ₃ | Al(OH) ₃ , amorphous (see p, 1652) | [24, 26] |
| | Al(OH) ₃ , hydrargillite (see p. 820) | [2, 18, 20, 26, 27] |
| | Al(OH) ₃ , bayerite (see p. 821) | [4, 18, 20, 27] |
| | AlOOH, böhmite (see p. 821) | [12, 13, 18, 26, 27, 29] |
| TiO ₂ | Hydrated titanium (IV) oxide | [21] |
| C7 203 | Hydrated chromium (III) oxide, amorphous (see p. 1648) | [3, 25] |
| α-Fe ₂ O ₃ | Hydrated iron (III) oxide, amorphous | [6, 8, 14, 19, 22] |
| γ≁Fe ₂ O ₃ | α-FeOOH (see p. 1499) γ-FeOOH (see p. 1500) | [6] [15, 16] |
| NiO | Ni(OH) 2 (see p. 1549) | [28] |
| ZnO | €-Zn(OH)₃ (see p. 1074) Other crystalline hydroxides | [5] [11] |
| CdO | Cd(OH) ₂ (see p. 1097) | [7] |

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Magnesium Oxide

Active MgO is prepared by calcination of the basic carbonate (for preparation, see p. 911). The following particle sizes have been observed, depending on the temperature and the duration of the calcination, [12]:

| - | | | | | |
|---|---|-------------------------------------|--|--|--|
| | Heating | Particle size in A | | | |
| Temp., °C | dme, br. | Determined by x-ray analysis | Observed by altra- microscope | | |
| 870 725 820 920 980 1200 | $ \begin{array}{c} 60 \\ 1 - 4 \\ 1 - 4 \\ 1 - 4 \\ 1 - 4 \\ 1 - 4 \\ 4 \end{array} $ | 30 48 50 300 200 300 | 100 100 100 900-300 500-500 1000-3000 | | |

Since commercial basic magnesium carbonates are not welldefined compounds, the properties of the oxides vary to some extent. To obtain preparations with reproducible properties it is better start with well-defined compounds such as fine crystalline $Mg(OH)_2$ (for preparation, see p. 912) or with $MgCO_3 \cdot 3 H_2O$ [3, 22].

Zinc Oxide

 $Z_{n}C_{s}O_{4} \cdot 2 H_{s}O = Z_{n}C_{s}O_{4} + 2 H_{s}O$ 189.4 153.4 $Z_{n}C_{4}O_{4} = Z_{n}O + CO_{2} + CO$ 153.4 81.4

A solution of 27.3 g. of anhydrous $ZnCl_2$ is in 200 ml. of water and 2.5 ml. of 2N HCl is prepared. Another solution, containing 31.3 g. of $(NH_4)_2C_2O_4 \cdot H_3O$ in 2.0 ml. of water and 2.5 ml. of 2N aqueous NH₃ solution, is prepared separately. Both solutions are beated to 70°C, and the oxalate solution is then poured in a thin stream into the vigorously stirred zinc salt solution. The oxalate precipitate is washed by decantation with water until it is free of chlorides. It is then placed on a filter and dried by suction. The $ZnC_3O_4 \cdot 2 H_3O$ is then transferred to a flat pan which is placed in a drying oven. The temperature is then raised to 240°C over a period of 6 hours and is then maintained at this level for an additional 12 hours. This treatment removes nearly all of the water of crystallization. The anhydrous oxalate is then converted to ZnO by heating at 400°C for 4 hours.

PROPERTIES:

Fine, white powder; untamped bulk density (pouring into a cylinder) 0.85 g./ml. The primary particles, whose lattice still contains defects, are larger than 500 A [18].

GENERAL:

Oxides of metals exhibiting low basicity may be obtained by thermal decomposition of their salts with volatile or readily decomposed acids. Such salts include nitrates, carbonates, formates and oxalates. In order to obtain active preparations, the decomposition conditions should be as mild as possible. The decomposition proceeds faster in vacuum than in air, so that the reaction temperature may be lower (for the same yield per unit time). An even stronger influence on the reaction rate is sometimes exerted by an appropriate gaseous atmosphere (see below).

1. ADSORBENTS AND CATALYSTS

NITRATES

Hydrates of most heavy metal nitrates have low melting points. Thus, on heating, they liquefy, decompose and leave sintered or foamed oxides of low surface area. The product may sometimes be improved by starting with lower hydrates or basic nitrates. Nitrate decomposition is important primarily in the production of carrier substances.

In compounds possessing several oxidation stages (e.g., elements of the manganese series), nitrate decomposition always yields the highest oxide possible at the given reaction temperature.

CARBONATES

Vacuum decomposition of carbonates is often used to obtain metal oxides where the metal is at the oxidation stage corresponding to that in the starting carbonate. However, with air present, at least partial oxidation is possible, sometimes even after the material has been cooled to room temperature. In addition to carbonates and their hydrates, as well as basic carbonates, this method is suitable for the decomposition of double carbonates where ammonium is one of the cations [for example, MgCO₃ · (NH₄)₂CO₃ · 4 H₂O]. When the conditions are mild, very fine oxide powders are frequently obtained.

The decomposition of magnesite has been studied very thoroughly and proves to follow 2/3 order kinetics (see p. 1657 and [17, 21]). The effect of a gaseous atmosphere on the kinetics of this reaction consists mainly in the change in the activation energy for decomposition which it causes [8, 9].

| Atmosphere | Dry air | Vacuum | H3 | Moist air | H ₂ O |
|------------------------------------|---------|--------|-------|-----------|------------------|
| Activation energy in kcal./mole | 42,15 | 36,13 | 27.89 | 27.22 | 26.79 |

The preparative decomposition of magnesite may be carried out . even at 500 °C when a suitable atmosphere, e.g., air containing $H_{\pm}O$ and NH₃ at a total partial pressure of 40 mm., is provided [13]. The gaseous atmosphere over the preparation also affects the particle size of the nascent solid phase. Thus, given identical det composition temperatures, the particle size of MgO crystals formed from magnesite will decrease with decrease of the CO₂ pressure during the decomposition [10].

FORMATES AND OXALATES

The nature of the thermal decomposition of formates and oxalates is not uniformly the same. Depending on the basicity of

the metal and the degree to which it approaches the noble metals, one may obtain carbonates, oxides or the metals themselves, provided secondary oxidation reactions are prevented (the production of metals is due to reduction by the organic anions or their decomposition products). According to presently available data, formates and oxalates behave in this respect in practically identical fashion. As far as is known, the composition of products obtained on vacuum decomposition is identical to that of the primary products of decomposition in air. The following data are available on some of the divalent metals:

| Formate or oxalate of | Decomposition products in vacuum and primary products of decom- position in air | Terminal products of decomposition in air |
|---|--|---|
| Mg* Mn Fe Co Ni Cu Zn | MgO MnO FeO Co Ni Cu ZnO | MgO Higher oxides α- and γ-Fe ₂ O ₃ Higher oxides NiO ₁ +x CuO ZnO |

*At the mild decomposition temperatures assumed in this table, the salts of the heavier alkaline earths always produce carbonates.

Under certain decomposition conditions, Cd and Pb (II) oxalates give a mixture of oxide and metal [6, 11, 15]. In contrast to the corresponding formates, the oxalates of the metals mentioned here are rather insoluble in water; in general, they are readily obtained by precipitation, which usually gives a fine powder well suited as a starting material for decomposition. Provided the solvent is cautiously removed, hydrated or solvated compounds also yield suitable starting materials, and decomposition of these gives products with high activities.

Ultramicroscopic and x-ray studies show that oxides obtained from carbonates and oxalates at low decomposition temperatures are pseudomorphous with the crystals of the starting material [10, 12]. Since the molar volume of the new substance is as a rule considerably smaller than that of the starting material, the particles of the product are usually very porous, that is, provided the reduced decomposition temperature $T/T_m < 1/3$ (compare p. 1611). If the decomposition temperature is higher, aggregate crystallization can be expected to an increasing degree [19], except when the starting substance (which must in this case be a uniform fine powder) is heated for such a short time that only the desired reaction occurs and no time is left for the material to undergo aggregation [20]. Fast cooling from the decomposition temperature may help in this case.

The following are literature references for the preparation of active oxides by thermal decomposition of suitable compounds:

| - | | | | |
|------------------|--------------------------|--------------------------|---------|-------------------------|
| Preparation | Nitrate | Carbonate | Formate | Oxalate |
| BeO | | See p. 893 | f | |
| MgO | | [3, 7, 22] | [25] | [16, 23] |
| Mn oxides | [9]; see p. 1458 | See p. 1456 | [25] | [23]; see p. 1456 |
| Fe oxides | | | [5] | [5, 23]; see p. 1497 |
| Co oxides | | See p. 1519 | [25] | [23] |
| Ni oxides | [14, 26]; see p. 1548 | [14, 24]; see p. 1548 | [25] | [1, 23] |
| CuO | [24]; see p. 1012 | | [25] | |
| ZnO | [18] | [18, 27] | [25] | [18, 23] |
| CdO | | | [25] | [11, 15] |
| ThO ₂ | See p. 1221 | | | [2, 13]; see p. 1221 |

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Lead (IV) Oxide

 $Pb(CH_sCOO)_t + 2H_sO = PbO_s + 4CH_sCOOH$ 239.2 443.4

The instructions given on p. 767 are used to prepare 50 g. of Pb(CH3COO)4. The material is then crushed and triturated with 460 ml. of water in centrifuge tubes until all tetraacetate is converted to brown PbO2. The fine suspension is then centrifuged. The deposit is stirred four times with water (500 ml. each time); the suspension is centrifuged each time before decanting the liquid. The last wash water should not be acid. The PbOg is then suspended in 50 ml. of water, filtered with suction, and washed on the filter with 50 ml, of water. Then the material is washed on the funnel with four 25-ml, portions of acetone to displace the water. The acetone is then displaced by washing with four 25-ml. portions of ether. This imparts the final color to the material. The product is immediately placed in a vacuum desiccator [5].

PROPERTIES:

Very fine, dense powder with a light brown, coffeelike color; reacts with dil. HCl to give chlorine. Its physical state, characterized by small particle size, lattice defects and occlusions of admixtures which prove to be amorphous and on x-ray analysis are recognizable under an ultramicroscope [6], causes an extraordinary high chemical activity. Especially useful in dehydrogenation of aromatic dihydroxy compounds to the corresponding quinones. Pure preparations age with release of O₂, losing their activity (5% in 15 hours, 8-11% in 7 days).

1.4

GENERAL:

Spontaneous dehydration of hydroxides is occasionally also observed in precipitations with alkali hydroxide solutions. The method is especially useful in preparation of CuO [2, 7], ZnO [3] and Ag₂O [4]. The products thus obtained are usually fine powders and quite frequently contain occluded admixtures which prove amorphous on x-ray analysis. The rate of dehydration depends on the particle size of the precipitated hydroxide and on the possible formation of intermediate basic salts. The latter may inhibit the dehydration to a considerable extent. An especially useful starting material for preparation of CuO is Cu(NO₃)₂ [1].

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Colloidal Suspensions of Oxides in Gases (Smokes)

Oxides of especially small particle size (smokes) may be obtained under appropriate reaction conditions. Such reactions are nearly always described in conjunction with special investigations where only very small amounts of compound are necessary. Only occasional literature references to work on a preparative scale are available. However, these may be supplemented, by data and descriptions from the patent literature, since oxide smokes are prepared on an industrial scale. The following methods are the most useful for generation of oxide smokes:

1) Burning of the metal (e.g., Mg. Zn. Cd and so forth); however, this procedure frequently converts only part of the oxide to the desired colloidal (smoke) dispersion.

2) Oxidation of a metal volatilized in an electric are. This simple method is frequently used to demonstrate the present phenomenon. The procedure consists of striking an arc between two electrodes made of the desired metal. However, it is only rarely useful for preparative purposes, since the quantity of product is very small due to the high thermal conductivity of the electrodes and the frequent shifts in the arc focus.

A much higher efficiency is reached in the apparatus developed by V. Kohlschütter [5] (see Fig. 340), comprising an arc furnace with vertical electrodes. The bottom electrode has an indentation for the metal to be volatilized. The arc is struck between the metal and the top (movable) electrode. Usually the vaporization proceeds very smoothly if the metal is the anode. The optimum conditions for the operation of the arc and for removal of the vapors from the electrodes vary somewhat from metal to metal.

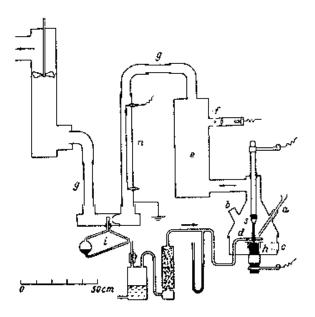


Fig. 340. Preparation of active metal oxides by oxidation of metal vapor. a funnel for addition of metal; b observation port; c side port; d circular nozzle for air intake; e first chamber with lateral observation ports (these are not shown); / illuminating device; g glass tubes (the remaining parts of the apparatus are made from sheet iron); h carbon electrodes; i flow meter activated by differential pressure; n precipitation cell; s movable carbon electrode.

3) Thermal or photochemical decomposition of volatilized metal compounds in the presence of oxygen. Metal compounds that are usable in such reactions are carbonyls and certain metals. hydrides or organometallic compounds, for example, alloying metals. To avoid explosions, the reaction must be carried out at very low pressures or the partial pressure of the reagents must be reduced by appropriate dilution with an inert gas. The reactions may be carried out either in closed systems [4, 10] or in a gas stream [11]. The continuous apparatus is shown in Fig. 338.

The decomposition of $Fe(CO)_{s}$ has been investigated very thoroughly. It was found that it oxidizes according to the following equation:

 $\begin{array}{cccc} 4 \ \operatorname{Fe}(\operatorname{CO})_5 & \stackrel{(O_2)}{\longrightarrow} & 2 \ \operatorname{Fe}_2 O_5 & + \ \operatorname{xCO}_2 & + \ \operatorname{yCO}_{738.6} & & 319.4 \end{array}$

Low O_2 concentrations in the starting mixture, high temperatures and short reaction times give thoroughly crystalline γ -Fe₂O₃; this material gives sharp powder patterns. Lower decomposition temperatures and higher oxygen partial pressures produce smaller smoke particles; however, the particles show powder patterns which are less distinct [11]. Similar investigations have also been carried out on the decomposition of Pb(CH₃)₄ [6].

4) Decomposition of holide vopors. Readily vaporized halides, especially the chlorides of elements such as Al, Si, Ti, Zr, Sn and so forth, may also be converted to oxides in the gas phase. This may be done in either of the following ways:

a) Saturation of a stream of an inert gas with the chloride, followed by reaction with steam. External heating is required in this case.

b) Combustion of the chloride together with hydrogen or with a combustible gas which contains bound hydrogen, e.g.:

 $2 \operatorname{SiCl}_{4} + 2 \operatorname{CH}_{4} \xrightarrow{(O_{3})} 2 \operatorname{SiO}_{2} + 8 \operatorname{HCl}_{1} + \operatorname{xCO}_{3} + \operatorname{yCO}_{2}$ 339.8 32.1 120.1

The second gas may be preheated or the combustion mixture may be diluted with an inert gas (to avoid excessive temperatures), depending on circumstances.

Under suitable reaction conditions this procedure yields tremely fine oxide powders which are used industrially as active, white fillers [2, 7].

Some difficulties in the preparation of oxide smokes arises the separation and collection of the smoke particles. The apparatus of Kohlschütter solves the problem partially by the a dust collector and a Cottrell precipitator. However, the are still heavy due to elutriation of the smallest particles. The following are literature references for the preparation of oxide smokes from metals or carbonyls:

| Oxide | MgO | ALO. | CrrO, | Fe-O1 | NiO | CuO | ZnO | CdO | SnO ₂ | PbO | Bi₅O, |
|------------------|-----|------|-------|-------------------|-------|-----|-------|---------|------------------|-----|-------|
| črnen metal | (11 | [3] | [5] | [1, 9] | [1,5] | [5] | (1,5) | [1.3,5] | [5] | [5] | [3] |
| trom carbonyl | | | | [1, 4, 8, 10, 11] | | | | | | | |

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Copper-Chromium Oxide

 $\begin{array}{rl} (\mathrm{NH}_4)_2\mathrm{Cr}_2\mathrm{O}_7 + 4\,\mathrm{NH}_3 + 3\,\mathrm{H}_2\mathrm{O} + 2\,\mathrm{Cu}(\mathrm{NO}_3)_2 = 2\,\mathrm{Cu}(\mathrm{OH})\mathrm{NH}_4\mathrm{Cr}\mathrm{O}_4 \\ & (3\,\mathrm{H}_2\mathrm{O}) \\ & 252.1 & 68.1 & 463.3 & 429.3 \\ & & + 4\,\mathrm{NH}_4\mathrm{NO}_3 \\ & 2\,\mathrm{Cu}(\mathrm{OH})\mathrm{NH}_4\mathrm{Cr}\mathrm{O}_4 = \mathrm{Cu}\mathrm{O} + \mathrm{Cu}\mathrm{Cr}_2\mathrm{O}_4 + 5\,\mathrm{H}_2\mathrm{O} + \mathrm{N}_2 \\ & & 429.3 & 79.6 & 231.0 \end{array}$

A solution of 126 g. of $(NH_4)_3Cr_3O_7$ A.R. in 600 ml. of water is prepared, and 150 ml. of 28% aqueous animonia is added to it. This solution is poured in a thin stream into a warm (50-60°C) solution of 242 g. of $Cu(NO_3)_2 \cdot 3 H_2O$ in 800 ml. of water while stirring manually. The reddish-brown precipitate of $Cu(OH)NH_4CrO_4$ [3] is stirred for an additional few minutes and then filtered on a Bickner funnel. The moisture is pressed out and the filter cake dried in an oven at 110°C. The mass is then broken up into coarse pieces and heated in a covered nickel or porcelain dish in a muffle

1672

furnace (350-450 °C, one hour). The product $(CuO + CuCr_{i}O)$ [10, 11] is ground in a mortar and suspended three times in 105 acetic acid (1.2 liters each time); the product is settled and the liquid decanted after each washing. This removes the CuO. The residue is washed four times with water in the same manner, filtered with suction, dried at 110°C and ground. After the last washing the precipitate sometimes settles only with difficulty due to partial peptization [8].

After this treatment, the catalyst may still contain an excess of CuO; the latter may convert during use to Cu₂O [9], which decreases the catalytic activity. The deactivation of the catalyst is much less likely if 24 g. of the Cu(NO₃)₂ · 3 H₂O in the initial charge is replaced by 26 g. of Ba(NO₃)₂. The Ba appears in the product catalyst as BaCrO₄ [11]. Equivalent quantities of Mg, Ca, Mn (II) or Zn nitrates may be used instead of the Ba(NO₃)₂.

PROPERTIES:

Fine black powder; completely stable in atmospheric oxygen and moisture. Active catalyst for the hydrogenation of organic hetero compounds containing multiple bonds [1, 5].

GENERAL:

Even the simple ammonium chromates can undergo thermal decomposition [4, 6, 7, 12] which yields very active Cr (III) oxides on decomposition in the air. Partial formation of higher chromium oxides is observed at reduced pressures [6]. Since these decomposition reactions release a considerable quantity of heat, they must be carried out in thin layers (flat dishes); the mildest conditions are obtained if only one spot in the dish is heated at a time and that spot is pushed onto a cold surface as soon as the material starts to react. The thermal decomposition of NH₄MnO₄ in air leads to explosions; vacuum decomposition yields, apart from NH₄NO₃, manganese oxides [Mn (III)-Mn (IV)], which are pseudomorphous to the starting crystals [2].

The above method is also useful for the production of other mixed oxides where chromium oxide is a constituent, e.g., Mn-Cr. oxide, Zn-Cr oxide [13].

. a. .

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Hopkalite (Hopcalite)

HOPKALITE I

Hopkalite I is a mixture of 50% MnO, 30% CuO, 15% Co₂O₃ and 5% Ag_O [9]. Its constituents are prepared as follows:

a) Manganese dioxide [2, 5]

$$2 \text{ KMnO}_{4} + 5 \text{ H}_{2}\text{SO}_{4} = \text{ K}_{2}\text{SO}_{4} + 2 \text{ Mn}(\text{SO}_{4})_{2} + 5 \text{ H}_{2}\text{O}_{4} + 1^{1}/_{2}\text{O}_{2}$$

316.1

$$2 \operatorname{Mn}(\mathrm{SO}_4)_2 + 4 \operatorname{H}_2 O = 2 \operatorname{MnO}_2 + 4 \operatorname{H}_2 \operatorname{SO}_4$$

173.9

Cold 75% sulfuric acid (650 g.) is poured over 100 g. of fine KMnO4 powder; the mixture is left standing for several days. During this time, the initially separating HMnO4 decomposes with evolution of oxygen, leaving a dark yellow Mn (IV) solution. This is added to a large excess of water; a very fine powder of hydrated MnO₂ separates out. This powder is washed several times by decantation with water. The washing is continued on a funnel until the filtrate is free of sulfate.

Allemate method: Reduction of permanganate by Mn (II) salts (1, 4, 13).

b) Copper oxide [9] (see also [6]):

A solution of 103.5 g. of CuSO4 · 5 HaO in 300 ml. of water is poured with efficient stirring into 430 ml. of 2N NaOH preheated to about \$0°C. The mixture is stirred for a few minutes; during this time, $2N H_2SO_4$ is added until the solution, which contains the CuO in suspension, becomes neutral (about 15 ml. of the acid is required). The mixture is allowed to settle and washed in the same way as the MnO₂ (see above).

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c) Cobalt (III) oxide [8]
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 $2 \text{ CosO}_4 + 4 \text{ NaOH} + \text{NaOCl} = \text{Co}_2\text{O}_3 + 2 \text{ Na}_2\text{SO}_4 + \text{NaCl}$ (7 H₂O) 562.2 160.0 165.9

A solution of 56.2 g. of $CoSO_4 \cdot 7$ H₂O in 200 ml, of water is mixed at room temperature with a slight excess of strongly alkaline hypochlorite solution. As soon as gas evolution comes to a virtual stop, the solution is decanted from the immediately appearing dense black precipitate, which catalyzes the decomposition of excess hypochlorite. The washing procedure is the same as for MnO₂.

The oxides prepared as in (a), (b) and (c) are suspended in about 1.5 liters of water. This suspension is then mixed with a solution of 8.07 g. of $AgNO_3$ in the minimum amount of water, and the Ag_2O is precipitated by addition of 23.8 ml. of 2N NaOH (intensive stirring). Further treatment is given under Hopkalite II.

HOPKALITE JI

Hopkalite II consists of 60% MnO₂ and 40% CuO (the MnO₂:CuO molar ratio is 1.375). The catalyst may be prepared by mixing the separately prepared components [10] or by mixed precipitation ([13]; see also [11]).

| a) | $MnSO_{4} + 2 NaOH + \frac{1}{2}O_{2} = MnO_{2} + Na_{2}SO_{4} +$ | | | | H _r O | | [4] | |
|----|---|----------|------------------------------------|---|------------------|---|-----|--|
| | (4 H _t O) 223.1 | 80.0 | 86.9 | • | · :: • | | • | |
| b) | • | + 2 NaOH | $= C_{U}O + Na_{2}SO_{4} + H_{4}O$ | | | ĥ | | |
| | (5 H ₂ O) 249.1 | 80.0 | 79.6 | | * | _ | 1 | |

The reactor is a three-liter Erlenmeyer flask, in which 155 g. of $MnSO_4 \cdot 4 H_3O$ and 125 g. of $CuSO_4 \cdot 5 H_3O$ are dissolved in 1.5 liters of hot (70-80 °C) water. A fast stream of air is then bubbled through the hot solution and 400 ml. of 25% NaOH is added (vigorous shaking) from a dropping funnel. The passage of air is continued for another 10 minutes. The precipitate is then washed several times by decantation with hot water. Then washing is continued on a filter until the wash liquor is neutral. The precipitate is suction-dried (the water should be removed as completely is possible by repeated pressing). After the by-product fine powder has been sieved out, the product is granulated by heating for 3 hours at 200°C.

PROPERTIES:

Brownish-black granules, which must be stored under anhydrous conditions. Catalyzes the combustion of CO at room temperature; used in gas-mask cartridges.

GENERAL:

The methods of preparation described above consist of precipitation immediately followed by a reaction of the precipitated product (dehydration, oxidation). The oxidation is a topochemical reaction yielding products with defect structures. The full activity of such a multiple-compound catalyst can frequently be developed only after an aging process called forming. To strengthen the structure of the catalyst granules (which at the same time increases the accessibility of their internal surfaces to gases), rather large amounts (up to 50% and more) of kieselgur may be added to the catalyst (as, for instance, in the Fischer-Tropsch catalysts).

Some other oxidation catalysts based on metal oxides have been described in the literature: Ag_2O-Cu_2O [7]; $Ag_2O-Cr_2O_3$ [12] and $MnO_2-CuO-Co_XO_Y$ [3].

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SECTION 2 Hydroxo Salts R. SCHOLDER

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General

"Hydroxo salt" is the term used for a group of complexes where the central atom of the complex anion is a metal to which hydroxyi ions are bound as ligands. The number of these ions depends on the normal coordination number of the metal. The cation of a hydroxo salt is usually an alkali metal, particularly sodium, or the alkaline earth metals barium, strontium and, in some cases, calcium. Heavy-metal salts can be prepared from a few hydroxo anions via a double decomposition reaction.

Hydroxo salts correspond closely to the well-known halo salts in their formula type and structure. Accordingly, mixed halohydroxo salts of a number of metals can be prepared. At elevated temperature, hydroxo salts can be converted into oxo salts, provided it is feasible to prepare the latter from a metal hydroxide (the central atom) and an alkali or alkaline earth metal hydroxide. In numerous systems, however, such oxometalates can be obtained only from oxides. In some cases, oxohydroxo salts are also formed as intermediates.

Complex hydroxometal anions are formed in solution via the following equilibrium reaction:

$$\{M(OH)_x \rightleftharpoons M^{n(+)} + x OH^-\}$$
$$M^{n(+)} + y OH^- \rightrightarrows \{M(OH)_y\}^{(y-x)} (\cdots)$$

The reagents are strong bases and poorly soluble metal hydroxides: In the above equations, the metal hydroxides function as "acids" in agreement with the modern theory of their amphoteric he havior. As far as is presently known, the following metals (arranged in order of increasing valence) form hydroxo salts:

> M(II): Be, Mg, Sn, Pb, Mn, Fe, Co, Ni, Cu, Zn, Cd M(II): Al, Ga, In, Bi, Cr, Mn, Fe M(IV): Sn, Pb, Pt M(V): Sb

The equilibrium distribution is of controlling importance in the preparation of crystalline alkali hydroxometalates. Most hydroxo salts, alkali salts in particular, rapidly decompose into their components in the presence of H_2O or dilute alkali hydroxide. Only the hexahydroxo salts of Sn (IV), Pt (IV) and Sb (V) dissolve in H_2O at room temperature without decomposition, whereas the other alkali hydroxometalates are stable only when they constitute the solid phase in the presence of (usually very concentrated) alkali hydroxide solution. The alkaline earth hydroxometalates are relatively sparingly soluble and hence are stable in dilute hydroxide; the compound $Ca[Zn(OH)_3]_3 \cdot 2 H_3O$ is stable even in water. The equilibrium shifts toward the reagents with temperature.

Metal oxide-sodium oxide-water systems at constant temperature exhibit the same general behavior regardless of the particular compounds involved (see Fig. 341). Thus, with increasing alkali hydroxide concentration, the solubility at first increases to a maximum and then decreases sharply. The rising branch of the curve corresponds to solid $M(OH)_m$ or MO_n while the decreasing branch corresponds to sodium hydroxometalate, whose solubility is sharply reduced as the NaOH concentration increases.

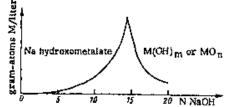


Fig. 341. Solubility of the system metal oxide-sodium oxide-water as a function of sodium hydroxide concentration.

The experimental fact that the sodium hydroxide concentration at the solubility maximum is usually over 30% indicates that highly concentrated (usually 45-50%) NaOH is required for the preparation of most alkali hydroxo salts. This is also necessary to ensure good yields. However, most alkaline earth hydroxometalates can be prepared from more dilute NaOH solutions.

Spreading the microcrystalline solid phase on a clay dish does not afford complete separation from the residual mother liquor. It has recently been established that alkali hydroxometalates can be separated from the mother liquor much more efficiently by brief shaking with pure isoamyl alcohol, and the alkaline earth saits by treatment with anhydrous methanol, possibly containing a small amount of NaOH. Several types of hydroxo salts of some di- and trivalent metal can be prepared just as in the case of halo salts. These diffet in the number of coordinated OH⁻ ions. The number of OH⁻ ligands depends on the concentration and temperature of the alkali hydroxide!

Among the less stable alkali hydroxometalates, it is often only the Na salt, but not the K salt, that can be prepared. This is due to the unusually high solubility of the corresponding K salts. It fact, the precipitation of the latter even from highly concentrated hydroxide solutions is often impossible without simultaneous crystallization of KOH. The rather sparingly soluble Ba and Sr salts can be precipitated from the metal hydroxide or oxide solutions by addition of Ba^{2+} or Sr^{2+} . The alkaline earth saits can be obtained more conveniently by simultaneous dropwise addition, in proper ratios, of concentrated solutions of the perchlorates of the central metal atom and of the alkaline earth metal to hot, moderately concentrated sodium hydroxide (sodium perchlorate is much more readily soluble in strong sodium hydroxide than is NaCl). The free hydroxo acids, which should exist as well-defined higher hydrates of the metal oxides, are not known, the exception being hexahydroxoplatinic (IV) acid, $H_2[Pt(OH)_{e}]$.

In some cases the fact that the hydroxometalates are chemical complexes is indicated by the color of the salts and of their solutions. The proof of structure is based on their thermal dehydration curve, their ability to form mixed halo-hydroxo salts, data on isomorphic relations, and some powder pattern studies.

Handling of Concentrated Alkali Hydroxides

STARTING MATERIALS

Very pure or reagent grade (97-98%) NaOH pellets and a similar grade of potassium hydroxide (containing an average of 85% of KOH, the remainder being H₂O) are used.

CONTAINER MATERIALS

Chemical glassware is sufficiently resistant to concentrated alkali hydroxide solutions at room temperature that it can be used without adversely affecting the purity of the products. However, hot, concentrated alkali hydroxide solutions attack any glass so strongly that the latter can be used at high temperatures only for short periods of time, if at all. Such experiments must therefore be run in refined silver containers, which resist even concentrated boiling alkali hydroxide solutions. While pure motion containers are also suitable, they are not cheaper than silver.

1660

FILTERS

Fritted Pyrex glass of medium and high porosity is suitable. However, its life may be limited in repeated use for filtering hot alkali hydroxide solutions. When filtering very hot and concentrated alkali hydroxide solutions, the glass suction funnel should be wrapped with a strong cloth so as to reduce as much as possible the ever-present danger of sudden breakage (this danger is real even with infrequently used filters). To prevent solidification of solutions containing more than 50% NaOH during filtration, the glass suction funnel is surrounded with a sheet metal jacket containing hot glycerol. When such solutions are boiled in a flask, the rubber stopper must be protected with an asbestos liner.

Even though filter plates made of certain plastics resist hot concentrated alkali hydroxide solutions, we have not yet tested them sufficiently to recommend them for laboratory use.

CARBONATE-FREE SODIUM HYDROXIDE

A 50% sodium hydroxide solution is prepared from the calculated amount of commercial NaOH in a silver flask. To prevent the occasional nuisance of the NaOH sticking to the bottom, the flask is vigorously shaken; solution is promoted by the strong, spontaneous heat evolution. However, external heating should be avoided because of the danger that the hot caustic solution will bump and spill out of the flask, a danger not obviated by the presence of a reflux condenser on the flask. The 50% hydroxide solution is allowed to cool slowly and, if possible, to stand at room temperature for 2-3 days. The precipitated Na₂CO₃ is then filtered off on glass frit of small pore size (rigorous exclusion of air). The completely clear filtrate is virtually carbonate-free. To avoid waiting for precipitation of the carbonate, one can add 1-2 g. of Ba(OH); per 100 ml. of hot, 50% sodium hydroxide; the mixture may then be filtered immediately after cooling to room temperature.

Sodium hydroxide solutions of lower concentration can be prepared by dilution of the 50% solution with boiled $H_{2}O$. Removal of $Na_{2}CO_{3}$ from a solution containing more than 50% NaOH must be carried out at 40-60°C to prevent crystallization of NaOH. Such solutions may also be prepared by distilling the calculated amount of water from carbonate-free 50% sodium bydroxide into a graduated cylinder. For obvious reasons, CO_{2} must be rigorously excluded. All equipment, including the reflux condenser and the glass suction filter, is protected with **Peligot tubes** (containing 50% KOH) held in place by rubber Handling alkali hydroxide solutions is often facilitated by a knowledge of their boiling points. For this reason, the boiling points of 20-70% NaOH and KOH solutions, taken from Gerlach [2], are tabulated below.

| | 25 | 42.8 | 53.8 | 66.7 | 81,8 | 100 | 122,2 | 150 | 233.3 | g. NaOH (KOH)/ 100 g. H2O |
|-------|-----|------|-------|-------|-------|-------|-------|-------|-------|------------------------------|
| | 20 | 30 | 95 | 40 | 45 | 50 | 55 | 60 | 70 | % NaOH (KOH) |
| NaOII | 108 | 116 | 121.5 | 128 | 134.5 | 142.5 | 150,5 | 160 | 180,5 | B.p., °C |
| кон | 106 | 113 | 118 | 124,5 | 133 | 145 | 160,5 | 177.5 | 228 | B.p., °C |

SAFETY RULES

The destructive action of caustic alkali solutions begins immediately. Therefore, the eyes must always be protected by goggles which fit tightly on all sides. Any caustic solution under the fingernails should immediately be washed off with a large amount of water followed by dilute acetic acid. Silver being a much better heat conductor than glass, one should remember that silver equipment will get hot much more rapidly than glass.

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Sodium Hydroxozincates

The system $2nO-Na_2O-H_2O$ contains the following four solid hydroxozincates, whose existence depends on the NaOH concernation:

Na{Zn(OH)₃] • 3 H₂O; Na[Zn(OH)₃]; Na₂[Zn(OH)₄] • 2 H₂O; Na₂[Zn(OH)₄].

SODIUM TRIHY DROXOZINCATE, Na [Zn(OH)3]

 $ZnO + NaOH + H_2O = Na[Zn(OH)_3]$ 81.4 40.0 18.0 139.4

PREPARATION OF CRUDE MATERIAL

A hot solution of 185 g. of NaOH in 100 ml. of H_2O is prepared, and ZnO (105 g.) is added. The mixture is refluxed 0.5 hours and cooled to 100°C. Water (85 ml.) is then gradually added through the condenser (use a funnel). The solution is filtered hot to remove residual ZnO and the filtrate is immediately cooled to about 15°C. If crystallization does not set in within a day, some NaOH pellets are dissolved in a few milliliters of the boiling zincate solution, the solution is cooled in a freezing mixture, and the resulting tetrahydroxozincate, which precipitates readily at this higher NaOH concentration, is used to seed an additional 5ml. portion of the original zincate solution (moderate cooling). Rubbing with a glass rod initiates crystallization of the trihydroxozincate. The entire zincate solution is then seeded with this material. The precipitate obtained is filtered off after a few hours, washed with 50% sodium hydroxide, and dried on a clay plate in an empty desiccator. Yield: 50-60 g.

B. PREPARATION OF THE PURE COMPOUND.

A solution (prepared at the boil) of 60 g. of ZnO and 250 ml. of pure, 51% sodium hydroxide is filtered at about 40°C, cooled to 15°C, and seeded with zincate prepared as described under (A). After 12 hours the mixture is filtered and worked up as under (A). Yield 40 g.

The moist product (10 g.) is shaken for two hours with 150 ml. of alkaline methanol solution (100 ml. of CH_3OH plus 15 g. of NaOH), filtered, washed first with the same methanol solution and then repeatedly with acetone, and dried over silica gel. This method removes the last traces of NaOH, and the analysis shows the calculated percentages of ZnO, Na₂O and H₃O.

PROPERTIES:

Colorless, microcrystalline powder (small rods). Decomposes immediately in water; decomposes after a few hours in 10%methanolic NaOH; stable in 15% methanolic NaOH (18° C). When prepared by method (A), contains about 0.1 moles of NaOH per mole of zincate.

SODIUM TETRAHYDROXOZINCATE, Na2 [Zo(OH)4]

A carbonate-free, clear solution of 195 g. of NaOH in 140 ml. of H_2O is prepared, and 2nO (56 g.) is dissolved in it at the boil; the mixture is filtered at 90°C. The crystals that separate out after a few hours are washed with 50% NaOH and spread in as thin a

1682

layer as possible on a clay dish. They are dried in an empty desiccator. Yield: about 100 g.

1.4

PROPERTIES:

Formula weight 179.42. Microcrystalline, thin platelets. The NaOH traces (about 0.2 moles per mole of zincate) cannot be removed.

REFERENCES:

R. Scholder and H. Weber, Z. anorg. allg. Chem. <u>215</u>, 355 (1933); R. Scholder and G. Hendrich, Ibid. <u>241</u>, 76 (1939); R. Scholder and K. Osterloh, Unpublished data.

Sodium Tetrahydroxomagnesate

Na_t[Mg(OH)_t]

 $Mg(OH)_{2} + 2 NaOH = Na_{2}[Mg(OH)_{4}]$ 58.3 80.0 138.3

An approximately 65% NaOH solution is prepared in a silver flask by distilling 180 ml. of H2O from 500 ml. of 50% sodium hydroxide. The solution is cooled to about 100°C and 6 g. of Mg(OH)2, prepared by slaking MgO (calcined at 500°C) with hot H_2O , is added to it. The mixture is agitated with a silver stirrer and refluxed for 20 hours at 100°C in the absence of CO₂. Without interrupting the heating, the flask contents are transferred . by suction (use silver tubing interconnected with polyethylene sleeves) onto a glycerol-heated, medium-pore-size fritted-glass filter, which is maintained at 100°C. The filter cake is dried by st. suction and immediately spread on a clay dish heated to 190°C. The dish is then kept for about five hours in a vacuum desicoator heated to 100°C, to promote absorption of the surface sodium bydroxide by the clay plate. This procedure yields 8-10 guot relatively dry sodium hydroxomagnesate which is strongly con-taminated with NaOH. To remove the NaOH, 3 g. of the crute product is pulverized in the absence of CO_2 and H_2O_2 and H_2O_2 shaken for 30-45 min. with freshly distilled iscemyl alcohol (b.p. 127-129°C). The mixture is suction-filtered (again in the absence of CO₂) through a medium-pore-size iritted-glass filter, and rinsed with 50 ml. each of isoamyl alcohol and ether. product is then dried for a few hours over silica gel while show - + × taneously removing the ether in vacuum. Ter 18 2

1684

PROPERTIES:

Microcrystalline hexagonal platelets. Yields crystalline Mg(OH)2 (brucite) on treatment with H₂O. Decomposed by strongly alkaline methanol or ethanol even below 0°C; isoamyl alcohol gradually splits off NaOH, but only on prolonged reaction.

REFERENCE:

R. Scholder and C. Keller. Unpublished data.

Sodium Tetrahydroxocuprate (II)

Nat[Cu(OH)4]

 $CuO + H_tO + 2 NaOH = Na_t[Cu(OH)_t]$ 177.6 80.0 79.5 18.0

4. CRUDE MATERIAL

Very pure CuO (15 g.) is dissolved in a clear, carbonate-free solution of 500 g. of NaOH in 330 ml. of H2O (brief refluxing). The dark-blue solution is cooled to 110°C and carefully diluted by adding 140 ml. of H_aO through the reflux condenser (use a funnel). The small quantity of unreacted CuO is then filtered off, collecting the filtrate in a preheated Erlenmeyer flask of refined silver. The Erlenmeyer flask is protected by a Peligot tube (filled with 50%) KOH) and kept in an electric drying oven for six days at 75°C to allow the filtrate to crystallize. The mixture is then filtered; the crystals are washed with some 50% and 45% sodium hydroxide (once each) at room temperature and dried on a clay plate over H₂SO₄. Yield: 13 g.

B. PURIFICATION

The considerable amount of NaOH still present in the product is removed immediately following the washing with the 50% NaOH. Thus the dark-blue crystals are shaken for one hour with 150 ml. of 40% NaOH at room temperature and filtered.

The crystals are then shaken for one minute with the following solutions (in the order given): 150 ml. CH₃OH + 22.5 g. NaOH (18°C); 150 ml. CH3OH + 15 g. NaOH (0°C); 150 ml. CH3OH + 1.5 € NaOH (---10°C).

After decantation, the solid is finally digested twice with pure methanol (-10°C), filtered and washed with methanol at --15°C. The crystals are placed on a clay plate and dried over silica gel is a minimum size desicoator.

When the cuprate solution remaining after filtering off the Cut is quickly cooled to room temperature in a freezing mixture, the salt precipitates as very thin, light-blue platelets. These, however, cannot be completely freed of the excess NaOH. Yield: 20 g.

PROPERTIES:

Firm, dark-blue crystals. The very pure salt obtained by method (B) is extremely sensitive to moisture and rapidly turns dark brown on exposure to air.

REFERENCES:

R. Scholder, R. Felsenstein and A. Apel. Z. anorg. alig. Chem. <u>216</u>, 138 (1934); R. Scholder and K. Osterloh. Unpublished data.

Barium Hexahydroxocuprate (II)

Ba₂[Cu(OH)₄]

 $Na_{2}[Cu(OH)_{4}] + 2 Ba(OH)_{2} = Ba_{2}[Cu(OH)_{6}] + 2 NaOH$ 177.6 342.8 440.3 60.0

A solution of 10 g. of $CuBr_2$ in 25 ml. of H_2O is added to 200 ml. of carbonate-free 50% sodium hydroxide at +5°C. The resulting mixture is heated to 70°C (water bath) and the small amount of CuO filtered off. The filtrate is refluxed 130°C and a hot solution of 30 g. of $Ba(OH)_3 \cdot 8 H_3O$ in 50 ml. of H_2O is added to it through a fluted filter (shaking). The salt that separates is immediately filtered off, cooled to 0°C in an Erlenmeyer flask, shaken for 5 min, with 100 ml. of methanol at -10°C, and filtered off. It is washed with methanol at 0°C and then thoroughly with acetone and anhydrous ether. The residual ether is removed by prolonged vacuum treatment in a desiccator. The product is completely pure. Yield: 13 g.

PROPERTIES:

Light-blue powder (rhombic crystal aggregates), Decomp by H_2O .

REFERENCES:

R. Scholder, R. Felsenstein and A. Apel. Z: anorg. alls. Chem. 216, 138 (1934); R. Scholder and V. Voelskow. Unpublished of the

1686

Sodium Tetrahydroxoferrate (II)

Na₁[Fe(OH)₄]

 $Fe + 2 NaOH + 2 H_tO = Na_t[Fe(OH)_t] + H_t$ 55.9 80.0 36.0 169.9

The reactor is a round-bottom, refined-silver flask, carrying a rubber stopper holding a reflux condenser protected by a Peligot tube (filled with an alkaline pyrogallol solution) and a silver tube serving as inlet for pure nitrogen. The flask is charged with 8 g. of reduced iron and 350 ml. of a 50% solution of pure NaOH. The air is displaced with N_2 and the mixture is refluxed for 2.5 hours in a steady N_2 stream. The blue solution is cooled to 120°C and suction-filtered (in the absence of air) through a glass frit covered with a layer of reduced iron. The filtrate is collected in a Pyrex suction flask containing 100 ml. of 50% sodium hydroxide, through which a nitrogen stream may be passed. The filtrate is allowed to cool for about 12 hours under N_2 ; the gray-green precipitate is then filtered off under N_2 , washed with 50% sodium hydroxide, and dried on a clay dish in a nitrogen-filled desiccator. Yield: 4 g.

PROPERTIES:

Gray-green microcrystalline powder (polyhedral crystals); very sensitive to moisture and O₂. Besides the polyhedra, microscopic examination also reveals colorless platelets with oblique sides of Na₄[Fe(OH)₇] \cdot 2 H₂O (see p. 1689).

REFERENCE:

R. Scholder. Angew. Chem. 49, 255 (1936).

Strontium Hexahydroxonickelate (II)

Sr.[Ni(OH).]

 $\frac{\text{Ni}(\text{CIO}_4)_2}{257.6} + 2 \operatorname{Sr}(\text{CIO}_4)_2 + 6 \operatorname{NaOH} = \operatorname{Sr}_2[\operatorname{Ni}(\text{OH})_6] + 6 \operatorname{NaCIO}_4 \\ 336.0 \\ 784.7$

A mixture of 250 g, of NaOH and about 8 g. of $Sr(OH)_2 \cdot 8 H_2O$ is dissolved in 455 ml. of H_2O contained in a silver flask. The solution is briefly refluxed and allowed to stand for 24 hours; the $SrCO_2$ precipitate is then filtered off. The solution is then brought to a boll, and 35 ml. of a Ni(ClO_4)₂ : $Sr(ClO_4)_2$ solution (molar ratio~1:4) is added. The latter solution is prepared by adding 25 ml. of H_2O to 6.5 g. of NiCl₃ · 6 H_2O and 16 g. of SrCOund then gradually adding 25 ml. of 70% HClO4. To remove HClother solution is concentrated until dense HClO4 fumes are evolved then diluted with H_2O to 35 ml. After addition of the perchievant solution, the reactor mixture is refluxed in the absence of CO2 The Sr₂[Ni(OH)₆] precipitate is filtered off with suction while the mother liquor is still hot (use small-pore-size glass frit). While thorough exclusion of CO₂; it is washed with 35% NaOH at norm temperature, and then with absolute methanol. The precipitate is shaken for eight hours with absolute methanol, filtered, and washed with methanol and ether. The product is dried and freed of ether by keeping it for several hours in vacuum in a desiccator containt ing silica gel.

PROPERTIES:

Gray-green, very fine crystalline powder of unidentifiable crystalline habit; not attacked by half-saturated aqueous $Sr(OH)_{P}$ solution (0.35 g. SrO/100 ml. H₂O); gradually decomposed by H₂O.

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REFERENCE:

R. Scholder and E. Giesler, Unpublished data.

Sodium Trihydroxostannate (II)

Na[Sn(OH)₁]

| SnCl ₂ + 2 | 2 NaOH == | Sn(OH) ₂ + | 2 NaCl |
|-----------------------|-----------|-----------------------|--------|
| 189.6 | 80.0 | 152.7 | 116.9 |
| Sn(OH) | , + NaOH | = Na{Sn(C | |
| 152.7 | 40.0 | 192.3 | |

Tin (II) hydroxide is prepared by treating a milky solution of 25 g. of $SnCl_2 \cdot 2 H_2O$ in 1.5 liters of H_2O with a small excess of approximately 10% ammonia (room temperature), diluting to two liters, allowing the solid to settle, removing the slightly happenear by aspiration, adding two liters of H_2O , again removing the supernatant, and then repeating this process 2-3 times. It is cipitated $Sn(OH)_2$ is filtered off on a large Pyres glasses in a medium pore size, at first without suction, then by slowly explain vacuum; it is then washed until essentially chloride-free. The pass is thoroughly dried by suction, calcined to SnO_2 , and analyzed to $Sn(OH)_2$ content. Yield of $Sn(OH)_2 : 85\%$; $Sn(OH)_2$ contents about 50%.

Reagent grade NaOH (35 g.) is dissolved and 3 mb on the tained in a wide-mouth 150-ml. Erlenmeyen glass that

R. SCHOLDER

solution is cooled to 50-60 °C and the entire $Sn{OH}_{3}$ paste is added to it, even though some crystalline NaOH may be present. The container is immediately closed off with a rubber stopper carrying a Peligot tube filled with an alkaline pyrogallol solution. The Sn{OH}_{3} after brief shaking dissolves while a small amount of dark SnO separates from the sodium hydroxide solution (the concentration of which is now 50%). The mixture is filtered warm through small-pore-size glass frit. The clear filtrate is protected from air and kept at 0°C; after a few hours, crystallization of the salt is complete. The mixture is carefully warmed to 8°C and filtered through large-pore-size glass frit. To remove the mother liquor still on the crystals, the latter are spread on a clay dish precooled to 0°C, and the dish is kept for 12 hours at 0-3°C in an evacuated desiccator. Yield: 6 g.

PROPERTIES:

Colorless, partly clustered small rods, pointed at the ends. When stored for some time in a closed container (even at $\theta^{\circ}C$) turns dark because of decomposition; very sensitive to moisture and O_2 . After removal from the clay dish, the product is still contaminated with 0.1-0.2 moles of NaOH per mole. During separation and drying, a small percentage of the Sn (II) is converted to Sn (IV).

REFERENCES:

R. Scholder and R. Pätsch, Z. anorg. allg. Chem. <u>216</u>, 176 (1933); R. Scholder and K. Krauss. Unpublished data.

Sodium Hexahydroxochromate ()())

Na₁[Cr(OH)₆]

 $\frac{Cr(CiO_4)_2}{350.4} + \frac{6}{240.0} NaOH = Na_5[Cr(OH)_6] + \frac{3}{387.4} NaClO_4$

Since commercial chromic hydroxide always contains an appreciable percentage of carbonate, sodium bexabydroxochromate (U3) is best prepared from an aqueous $Cr(ClO_4)_3$ solution obtained from Cr_5O_3 -aq.; the NaClO₄ formed by reaction with NaOH is sufficiently soluble even in highly concentrated NaOH.

A sample of commercial $Cr_3O_3 \cdot aq$. of known Cr_3O_3 content corresponding to 3 g. of Cr_3O_3 is dissolved in the stoichiometric quantity of 20-25% HClO₄. The solution is concentrated to 25 ml. and filtered; the filtrate is then added to 300 ml. of carbonate-free SME MACH. The mixture is refluxed for about 0.5 hours, cooled to

1690

about 120°C, and filtered into a suction flask preheated to **HERA**. The dark-green filtrate is transferred to a silver flask preioded by a Peligot tube (filled with 50% KOH) and allowed to stand for about four hours in an electric drying oven at 85°C. The precipitated hexahydroxochromate is washed twice with some 46%. NaOH (18°C), shaken for 0.5 hours with 80 ml. of 5% methanolic NaOH (18°C), washed several times with the same alkaline methanol solution, and, finally, thoroughly washed with acctomes the acetone is then removed by prolonged vacuum evaporation in a desiccator containing silica gel. The product is very pure (Cr: Na = 1:2.99-3.02). Yield: 5-6 g.

On cooling, the Na₃[Cr(OH)₈] mother liquor deposits tightly clustered platelets of mixed crystals of hepta- and octahydroxochromate (III).

PROPERTIES:

Microcrystalline green powder (well-formed polyhedra). At first soluble in cold H_aO, affording a clear solution, which after a long time gradually yields a flocculent precipitate of $Cr_2O_3 \cdot ag$.

REFERENCE:

R. Scholder and R. Pätsch. Z. anorg. allg. Chem. 220, 411 (1934).

Sodium Hydroxoferrates (III)

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These products are obtained by the oxidation of a solution of Na₂[Fe(OH)₄] in 50% NaOH with O₂. Under otherwise identical conditions, sodium octahydroxoferrate (III) is formed at 20-25 °C, heptahydroxoferrate (III) at 50-60°C, and olive-green oxoferrate (III) at 100-130°C. Boiling 55-60% NaOH yields the red oxoferrate (III), NaFeO₂.

SODRUM HEPTAHYDROXOFERRATE (III), Na4[Fe(OH)7] · 2H2O

L $2 \operatorname{Na}_{2}[\operatorname{Fe}(OH)_{4}] + 4 \operatorname{Na}OH + \frac{1}{2}O_{2} + H_{2}O = 2 \operatorname{Na}_{4}[\operatorname{Fe}(OH)_{4}]$

339.8 160.0

A solution of $Na_2[Fe(OH)_4]$ in 50% NaOH, prepared as described on p. 1686 and cooled to 120 °C, is filtered into an Erlenney of flask containing 100 ml. of 50% NaOH. This flask is connected to two wash bottles each containing 50% KOH, and a fast O_3 site is passed through the solution (kept at 60 °C) for about 12 to the This causes a gradual discoloration of the graduate but to the

18.0

and simultaneous crystallization. The crystals are filtered off, rapidly washed with 50% NaOH, and dried as a thin layer on a olay dish in an empty desiccator containing silica gel.

The oxidation with Br₂ is more elegant. The flask containing Na₃[FefOH]₄] solution is closed off with a rubber stopper carrying a Peligot tube and a dropping funnel. Then a solution of 2-3 ml. of Br₃ in 10 ml. of CCl₄ is added dropwise at 50-60°C with vigorous agitation until the iron solution just turns colorless. An excess of Br₂ must be avoided. The mixture is allowed to stand for two hours at the same temperature and filtered.

II. Freshly precipitated, thoroughly washed $Fe_2O_3 \cdot aq$. is added to carbonate-free 50% NaOH. An amount of NaOH equal in weight to the water contained in the Fe_2O_3 paste is then added and the latter is dissolved with moderate heating (not to exceed 60°C). The mixture, in a silver Erlenmeyer flask protected with a Peiigot tube (filled with 50% KOH), is allowed to stand for several days in an electric drying oven at 70°C. In this manner, the $Fe_2O_3 \cdot aq$. is completely converted into the nearly colorless, microcrystalline Na₄[Fe(OH)₇] · 2 H₂O, which is sparingly soluble in concentrated NaOH.

PROPERTIES:

Nearly colorless crystalline powder (beveled, partly clustered platelets); very sensitive to moisture. Instantly decomposed by $H_{0}O$ and $CH_{0}OH$, affording $Fe_{2}O_{0} \cdot aq$. Unstable even in 30% NaOH (18°C).

SODIUM OCTAHYDROXOFERRATE (III), Na5 [Fe(OH)8] · 5 H2O

Oxidation of $Na_{2}[Fe(OH)_{4}]$ with O_{2} in a strongly alkaline solution (see method I above) at 20°C yields fine needles of octahydroxoferrate (III), which is also nearly colorless. When allowed to stand at room temperature for a few days, freshly prepared $Fe_{2}O_{3}$ -aq. (see method II above) is converted to a large extent, but never completely, to the same salt,

REFERENCES:

B. Scholder. Angew. Chem. <u>49</u>, 255 (1936); R. Scholder and K. Krause. Unpublished data.

Barium Hydroxoferrates (11)

Barium hydroxoferrates (III) are prepared by dropwise addition of an $Pe(ClO_4)_3$ -Ba $(ClO_4)_3$ solution to hot NaOH. If the initial NaOH concentration is 25-39%, a precipitate of the hexabydrone salt, $Ba_3[Fe(OH)_6]_3$, is obtained; however, if this NaOH concentration exceeds 42%, the heptahydroxo salt, $Ba_3[Fe(OH)_7] \cdot \frac{1}{3}$ Fe(OH) precipitates.

The starting $Fe(ClO_4)_3$ -Ba(ClO_4)_2 solution (1:3 molar ratio) is obtained by dissolving 3.5 g. of Fe_3O_3 (analytical grade) in a mixture of 35 ml. of 70% HClO_4 and 25 ml. of conc. HCl. To eliminate the HCl, the solution is concentrated until dense fumes of HClO_4 are given off. The resulting solution is added, with agitation, to a slurry of 26 g. of BaCO_3 in 125 ml. of H_3O; the mixture is then filtered.

BARIUM HEXAHYDROXOFERRATE (III), Ba3[Fe(OH)6]2

The starting 33% NaOH is prepared by diluting 189 ml. of carbonate-free 50% NaOH with 140 ml. of CO_2 -free H₂O in a refined silver flask. The mixture is heated to reflux with exclusion of CO_2 , and 75 ml. of the above $Fe(ClO_4)_3$ -Ba(ClO₄)₃ solution is added dropwise. A white precipitate of Ba₃[Fe(OH)e]₃ forms immediately. The mixture is allowed to reflux for one hour, after which it is cooled to room temperature, suction-filtered through a medium-pore-size glass frit, and washed with a small amount of 33% NaOH. The precipitate is vigorously shaken for a few minutes with 200 ml. of absolute methanol, filtered through a small-pore-size glass frit, and washed with absolute methanol and anhydrous ether. It is then dried for one hour in a vacuum desiccator over silica gel.

PROPERTIES:

White to slightly yellowish hexagonal platelets. Decomposed by H_2O , affording $Fe_2O_3 \cdot aq_2$; stable in absolute methanolasis afford

BARIUM HEPTAHYDROXOFERRATE (III), Ba2 [Fe(OH)2] · ½ H2O

The preparation of this compound is analogous to the $Ba_{3}[Fe(OH)_{6}]_{2}$. However, instead of 33% sodium hydroxider 400 ml. of 50% NaOH is used.

PROPERTIES:

White to slightly yellowish hexagonal platelets. Decomposed by H_3O , affording $Fe_3O_3 \cdot aq$. Prolonged contact with absolute methanol yields a brown solution.

Strontium hexabydroxoferrate (III), Srs[Fe(OH)s]s, can be used pared in a similar way, using 5% NaOH, while strontium to the hydroxoferrate (III), Srs[Fe(OH)7] · 3 H2O requires 20% NaOH REFERENCE:

R. Scholder. W. Zeiss and M. Kreutz. Unpublished data.

Alkali Aluminates

Depending on the temperature, the following three sodium aluminates crystallize from a solution containing NaOH and Al_2O_3 in equal concentrations:

tetrasodium heptahydroxoaluminate Na₄[Al(OH)₇] · 3 H₂O monosodium oxohydroxoaluminate I Na₂O · Al₂O₃ · 2.67 H₂O = Na₆[Al₆O₄(OH)₁₆]

 $\begin{array}{l} \text{Nae}[\text{A1eO4}(\text{OB}/18)]\\ \text{monosodium oxohydroxoaluminate }\Pi \text{ NaeO - AleO3 - 2.5 HeO} =\\ \text{Nae}[\text{A1eO3}(\text{OH})_{10}] \end{array}$

Only monopotassium oxohydroxoaluminate, $K_2O \cdot Al_2O_3 \cdot 3H_2O = K_2[Al_2O(OH)_6]$, is obtained from a potassium aluminate solution.

TETRASODIUM HEPTABYDROXOALUMINATE, Na4 [AI(OH)7] + 3 H2O

 $Al(OH)_{4} + 4 NaOH = Na_{4}[Al(OH)_{7}]$ 78.0 160.0 292.1

Aluminum hydroxide (45 g.) is dissolved in a solution of 130 g. of NaOH in 100 ml, of H_3O by refluxing one half hour. The solution is slowly cooled to room temperature, allowed to stand for six hours, and only then filtered through a small-pore-size glass frit to remove the considerable amount of Na₃CO₃ precipitate [commercial Al(OH)₃ often contains a large percentage of carbonate]. The crystallization of sodium aluminate, which usually takes a long time to develop, does not start during this period. The clear filtrate is transferred to a round-bottom glass flask closed off with rubber stoppers carrying an air-tight agitator and a Peligot tube. The flask is immersed in 18 °C water and its contents are vigorously stirred for 10-14 hours. A thick crystal slurry is formed; this is dried by suction, spread out in a thin layer on a clay dish, and finally dried in an empty desiccator.

PROPERTIES:

Microcrystalline powder; strongly birefringent oblong prisms with bevelod end faces. Soluble in H_2O . Contains (as impurity) 0.2-0.3 moles of NaOH per mole of aluminate.

1692

MONOSODIUM OXOHYDROXOALUMINATE I, Na6 [A1604(OH)16]

A clear aluminate solution is prepared in the manner described above and stirred for 8-10 hours at 40-45°C. The crystal sivery is washed with 50% NaOH, covered with methanol, and shaken for 0.5 hours with 150 ml. of methanol. The mixture is filtered, thoroughly washed with a large quantity of methanol followed by acetone, and vacuum-dried over silica gel. Yield: 24 g. Analysis shows Al: Na = 1:1.02-1.04.

PROPERTIES:

Formula weight 636.15. Microcrystalline powder (square plates with beveled edges). Transient solubility in H_0O .

MONOSODIUM OXOHYDROXOALUMINATE II, Na4 [AI4O3(OH)10]

The aluminate solution (see above) is stirred for about sir hours at 100-105 °C. Otherwise, the preparation, isolation, purification and drying are the same as described above. Very pure product is obtained.

PROPERTIES:

Formula weight 417.98. Microcrystalline powder (thin polygonal platelets).

MONOPOTASSIUM OXOHYDROXOALUMINATE, K2 (AI2O(OH)6]

A solution prepared at the boil from 126 g. of KOH, 30 g. of $Al(OH)_3$, and 100 ml. of H_2O is allowed to stand for several hours at room temperature, filtered, seeded with the salt (see below), and shaken for 24 hours. The microcrystalline solid deposit is washed with a small amount of 50% KOH, then with 150 ml of methanol containing 5% KOH, and finally with acetone; it is then vacuum-dried over silica gel. Yield: 5 g.

Without seeding, the crystallization is delayed for several days. The seeding crystals are obtained by preparing a solution containing 20 g. of KOH, 5 g. of Al(OH)₃, and 10 ml. of H₂O, filtering, at room temperature, and shaking for 12 hours. This produces an abundant crop (about 6.5 g.) of monopotassium aluminate crystals. These crystals, however, are very small and are difficult to free from the adhering KOH, particularly if the latter is very concentrated.

PROPERTIES:

Formula weight 250.20. Microcrystalline powder (polyhedre).

H5H

REFERENCES:

 R. Fricke and P. Jucaitis. Z. anorg. allg. Chem. <u>191</u>, 129 (1930);
 R. Scholder, W. Kleeberg and M. Schröder. Naturforschung und Medizin in Deutschland, 1939-1946 (FIAT Review), Vol. 25, Inorg. Chem., part III, p. 141.

Sodium Hexahydroxostannate (IV)

Na₁[Sn(OH)₆]

 $Sn(OH)_{*} + 2 N_{B}OH = Na_{2}[Sn(OH)_{0}]$ 188.7 S0.0 266.8

A solution of SnCl, in very dilute hydrochloric acid is neutralized to methyl orange with carbonate-free NaOH. The SnO₂aq. precipitate is filtered off, washed until chloride-free with H_2O , and added in portions to an excess of concentrated, 100 °C NaOH, in which it dissolves rapidly, affording a clear solution. The crystalline hexahydroxostannate precipitates after a short time. The crystal slurry is filtered in the absence of CO₂ and washed with 30% NaOH and then several times with ethanol and ether.

PROPERTIES:

Coloriess crystalline powder (thin hexagonal leaflets). Readily soluble in H_2O ; the solubility decreases markedly with temperature (see Reiff and Toussaint). Always contains small amounts of adsorbed NaOH. Very sensitive to CO_2 .

REFERENCES:

H. Zocher. Z. anorg. allg. Chem. <u>112</u>, 1 (1920); R. Reiff and S. M. Toussaint. Ibid. <u>241</u>, 372 (1939).

Sodium Hexahydroxoplumbate (IV)

Na₂[Pb(OH)₆]

1. ELECTROCHEMICAL METHOD

 $\frac{Na[Pb(OH)_{3}] + NaOH + 2OH - 2e}{281.2} = \frac{Na_{2}[Pb(OH)_{6}]}{40.0}$

Yellow PbO (analytical grade, 18.5 g.) is dissolved in 300 ml. of boiling 13N NaOH; the solution is suction-filtered through a small-pore-size glass frit and allowed to cool in a CO₃-free atmosphere. This hydroxoplumbate (II) solution is unstable and on prolonged standing gradually deposits crystalline lead oxide. Hence it should be electrolyzed as soon as it has cooled to room temperature. Sometimes it may be necessary to separate the solution from the precipitated PbO by decantation right after cooling.

A rectangular 300-ml, glass jar covered with a rubber plate forming an air-tight seal is used as the electrolysis cell. Through appropriate openings in the lid the tank is provided with a gas outlet tube, a thermometer, an air-tight stirrer, an anode lead-in wire cemented into a glass tube, and a porous clay cell serving as the cathode space. The entire system must be gas-tight. Smooth platinum electrodes (5 × 5 cm.) are used. The electrolysis is carried out at ambient temperature with a current density of 0.12~0.18 amp./in.", while vigorously stirring the strongly alkaline hydroxoplumbate (II) solution in the anode space. The cathode space contains concentrated NaOH. The plumbate (IV) separates in the form of a white crystalline precipitate. The precipitate is allowed to settle, the clear solution is siphoned off, and the crystal slurry is covered with absolute ethanol. The crystals and liquid are then transferred to a smaller container and repeatedly digested with absolute ethanol until the latter no longer shows an alkaline reaction. The pure white crystals become slightly yellowish on vacuum drying in a desiccator.

II. CHEMICAL METHOD

 $Pb(CH_3COO)_4 + 6 NaOH = Na_2[Pb(OH)_0] + 4 CH_3COONa$ 443.4 240.1 355.3 328.2

A one-liter, round-bottom glass flask equipped with an airtight stirrer, a dropping funnel and a Peligot tube (filled with 30% KOH), all inserted through rubber stoppers, is charged with 200 ml. of carbonate-free 30% NaOH. The tip of the dropping funnel is inserted into a short glass tube (15 mm. I.D.) to protect it from the splashing NaOH solution. A solution (usually yellowish) of 50 g. of Pb(CH3COO)4 in 200 ml. of K2CO3-dried chloroform containing 1 ml. of glacial acetic acid (filtered, if necessary) is added drop-by-drop with vigorous stirring. The brown PbOs, formed at the site of contact between the drops of the chloroform solution and the NaOH in the flask, dissolves rapidly; after a while, Na₂[Pb(OH)₆] begins to precipitate. Following the addition of the chloroform solution, the mixture is stirred until the crystalline suspension is pure white. The precipitate is allowed to settle for several hours; it is then filtered officed washed twice with 30% NaOH and at least five times with methanol containing 1%

alkali. During this procedure, atmospheric moisture and CO₂ must be absent. The precipitate is then dried on a clay dish placed in an evacuated desicoator over silica gel. A pure white product is obtained provided processing is rapid. Yield: 33 g.

product is obtained provided processing to hapter take of g. **Should the salt be** yellowish, it can be purified as follows. The **moist product** is added in small portions to 500 ml. of 15% NaOH **at 75°C (agitation)**, making sure that each portion is completely **at 75°C (agitation)**, making sure that each portion is completely **dissolved before** adding the next. The small residue is filtered **off, 150 g.** NaOH is added to the filtrate while it is still hot, and **off, 150 g.** NaOH is added to the filtrate while it is still hot, and **the mixture** is vigorously shaken to complete dissolution. After **cooling**, the pure white crystalline powder is filtered off and washed **and dried as described** above. Yield: 26 g.

PROPERTIES:

Colorless crystalline powder (hexagonal polyhedra); stable in 2% NaOH at 18°C; very sensitive to moisture. Discolors after absorbing H_2O . Always contains some excess NaOH.

REFERENCES:

- L G. Grube. Z. Electrochem. <u>28</u>, 273 (1922); A. Simon, Z. anorg. allg. Chem. <u>177</u>, 109 (1929).
- II. R. Scholder. Unpublished data.

Barium Oxohydroxostannate (II)

Ba[Sa₄O(OH)₄]

| 2 Na[Sn(OH) ₁] | + Ba(OH); | = Ba[Sn ₂ O(OH) ₄] | + 2 NaOH | + H₂O |
|----------------------------|-----------|---|----------|-------|
| 385.5 | 171.4 | 458.8 | 80.0 | 18.0 |

The entire $Sn(OH)_3$ paste obtained from 25 g. of $SnCl_2 \cdot 2 H_3O$ (preparation as for $Na[Sn(OH)_3]$, p. 1687) is added to a 50°C solution of 60 g. of NaOH in 50 ml, of H_3O . The mixture is cooled to 30°C and a hot solution of 1 g. of $Ba(OH)_3 \cdot 8 H_3O$ in 2 ml, of H_2O is added. The mixture is allowed to stand at this temperature for about one hour (air must be absent) and is then filtered to remove the dark SnO and the precipitated carbonate. The clear filtrate is heated to 65°C and treated with a hot solution of 9 g. of $Ba(OH)_2 \cdot 8 H_3O$ in 20 ml. of H_3O (95°C). The greenish-yellow baring oxohydroxostannate precipitates within a few minutes. The supermatant is decanted; the solid is filtered off and covered with 50% NaOH. The salt is then washed with 50 ml. of 2% $Ba(OH)_2 \cdot 8 H_2O$ solution in methanol, followed by pure, 0°C methanof; it is dried on a clay dish over silica gel. Yield: 5 g.

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PROPERTIES:

Yellowish microcrystalline powder (plates beveled at ender). Decomposed by H_2O .

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REFERENCES:

R. Scholder and R. Pätsch. Z. anorg. alig. Chem. 216, 176 (1933); R. Scholder and K. Krauss. Unpublished data.

SECTION 3

Iso- and Heteropoly Acids and Their Salts B. GRÜTTNER AND G. JANDER

Introduction

ISOPOLY COMPOUNDS

Compounds with higher aggregated anions, in which the anionforming element occurs at least twice, are termed isopoly compounds. Usually it is the alkali or ammonium salts of the isopolyacids that are synthesized. Compounds with isopolyanions are formed, among others, by boron, silicon, phosphorus, arsenic, sulfur, vanadium, molybdenum and tungsten. They may be prepared in a number of ways, e.g., by fusion of an acid anhydride with an alkali hydroxide, dehydration of acid salts, or treatment of a normal salt with its acid anhydride.

Derivatives of the weaker, oxygen-containing metallic acids, such as those of tungstic, molybdic or vanadic acids, exhibit a quite characteristic behavior, and may therefore be considered as the "classical" isopoly compounds. One property characteristic of these metallic acids is the more or less sharply pronounced hydrolysis of their salts in aqueous solution, particularly in the presence of H⁺ lons. The hydrolysis products then undergo, over a period of time, a secondary reaction, combining to more highly aggregated ions, that is, the isopolyanions. For example:

 $\begin{array}{l} 6 \left(WO_{4} \cdot aq. \right)^{\pm -} + 6 H^{+} \rightleftharpoons 8 \left(HWO_{4} \cdot aq. \right)^{\pm -} \\ 8 \left(HWO_{4} \cdot aq. \right)^{\pm -} + H^{+} \rightleftharpoons \left(HW_{b}O_{21} \cdot aq. \right)^{a -} + 3 H_{2}O. \end{array}$

In addition, the following rules apply to the isopoly compounds of vanadium, molybdenum and tungsten,

Specific isopolyanions of definite degrees of condensation and epecific chemical properties predominate in the solution; their existence is a function of the H⁺ concentration and their crystalline salts may be isolated if certain conditions are observed. When solid, almost all salts of these isopolyacids contain water of crystallization. In keeping with their structure, these compounds are very sensitive to OH, which rapidly degrades most of them to simple molecular compounds. The free acids cannot be isolated since the presence of excess H⁺ causes progressive aggregation until insoluble high-molecular-weight hydrated oxides precipitate. "Metatungstic acid" (dodecatungstic acid) is an exception; its overall chemical and crystallographic behavior places it among the heteropoly compounds; thus, it will be discussed in that section.

The preparation of polyphosphates, polysilicates and polyborates is discussed in sections on the respective elements, e.g., on pages 546 ff., 697 ff., 793 ff., and 704 ff. of this handbook.

HETEROPOLY COMPOUNDS

Heteropoly compounds are composed not only of the weak, oxygen-containing metallic acids (tungatic, molybdic and vanadic), but also of moderately strong to weak acids of nonmetals, e.g., boric, silicic, phosphoric, arsenic, telluric, etc., acids. Stable heteropoly compounds very frequently show nonmetallic to metallic acid ratios of 1:12, 1:6 or 1:9. Since the heteropoly compounds form under conditions similar to those in which isopoly compounds are obtained, that is, only in solutions containing H^+ ions, it is assumed that the building blocks of the heteropolyanions are isopolyanions [1].

In keeping with their constitution, all compounds of this class are quite unstable in the presence of OH ions and are degraded to the simple metallic and nonmetallic acids. The careful degradation of very complex heteropolyanions by agents such as KaCO3. which act as weak sources of hydroxyl ions, permits the isolation of several intermediates, but nothing further is yet known concerning the mechanism. The heteropolyacids are somewhat more stable to H+ ions, so that partial isolation of the free acide is possible. Further characteristic properties of numerous heteropoly compounds include their good crystallizability and their relatively high water content per mole of the solid. No heteropoly compounds lacking water in the anion complex are known. Another peculiarity of this class of compounds is that many of the free acids, as well as their salts, crystallize isomorphously [2]. The free acids are rather basic and the formation of neutral salts occurs only as an exception; generally, only acid salts can be isolated. The free acids are specifically capable of forming heavy, oily addition compounds with ether, even when the latter is in the vapor form; these have only a limited miscibility with water and excess ether and easily decompose [3]. This property is commonly used in the preparation of the crystalline acids (see below).

In general the heteropoly compounds of tungstic acid are more complexed and more resistant to hydrolysis than those of molytike or even vanadic acid. The stability within the same class of compounds varies depending on the nonmetallic acid, so that compounds with phosphoric and silicic acids are more stable than those containing arsenic acid.

than chose containing arsenic acta. Several recently described compounds of molybdic and tungstic acids with phosphoric acid, where the ratio of Mo (or W)/P is below 3:1 (e.g., 2 MoO₃ · P₂O₈ or Na₂O · 2 WO₃ · P₂O₅), are not heteropoly compounds; rather, the Mo or W is bound as a cation [4]. We shall omit their discussion.

REFERENCES:

- 1. G. Jander and K. F. Jahr. Kolloid-Beiheite 41, 297 (1935).
- See, e.g., A. Rosenheim and J. Jaenicke. Z. anorg, Chem. <u>77</u>, 239 (1912); <u>101</u>, 235 (1917); H. Copaux. Ann. Chim. Phys. [8] <u>17</u>, 207 (1909); R. Abegg. Handbuch d. anorg. Chem. [Handbook of Inorganic Chemistry], Vol. IV., part 1, 2nd half, p. 993.
- E. Drechsel, Ber. dtsch. chem. Ges. 20, 1452 (1887); A. Rosenheim and J. Jaenicke. Z. anorg. alig. Chem. 101, 224, 250 (1917).
- 4. I. Schulz. Ibid. 281, 99 (1955); 284, 31 (1956).

General Methods

1. FREE HETEROPOLYACIDS BY THE METHOD OF DRECHSEL

A solution of the sodium salt of a heteropoly acid is concentrated as far as possible (even to the sirupy state), placed in a separatory funnel, and covered with about 1/3 its volume of ether. The funnel is shaken vigorously to saturate the solution with the ether. Ice-cold, conc. (37%) iron-free HCl is now added in small portions, with vigorous shaking after each addition. The liquid must not be allowed to heat up during this step; if necessary, the separatory funnel should be externally cooled with water, The liberated acid immediately forms an adduct with the ether and sinks to the bottom as heavy, oily drops which form a third layer. When this layer clarifies, it is drained into a flask. The reaction is complete when addition of hydrochloric acid does not produce further oily droplets at the ether-solution interface. The oil is treated with about an equal volume of H₂O, and the ether is driven off by drawing a stream of clean, dry air through the mixture. The residual clear aqueous solution of the acid is placed, until incipient crystallization, in a vacuum desiccator over conc. H₃SO, and then over solid KOH to absorb the still present HCi. Only the 12-tungstic-1-boric acid should be crystailized in desiccator over P2Os, in which case this is done to

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prevent decomposition of the heteropolyacid by volatilization of the boric acid. Only hydrochloric acid should be used for extraction since the ether adduct is always capable of absorbing this acid, and the latter can then be removed more readily than either sulfuric or nitric acids.

2. FREE BETEROPOLYACIDS VIA ION EXCHANGE

The advantage of this method lies in the high purity of the final product. The starting materials-heteropoly saits prepurified by many recrystallizations and extremely soluble in water-are best prepared by the method given below (see 3). In view of the very pronounced acidity of the heteropolyacids and their frequent sensitivity to reducing agents, it is desirable to use cation exchange resins carrying sulfonic acid groups (e.g., Permutit RS), which exhibit only a strong acid function and have almost no reducing power. The operating conditions depend on the sensitivity, quality and quantity of the heteropolyacid to be prepared, and can easily be optimized in preliminary experiments. The following rules of thumb should be observed: The exchange capacity of the resin normally amounts to about 2 meq./cm³ (bulk volume); it is desirable to work with starting solutions which are as concentrated as possible; the throughput of the solution through the column should be low (approx, 2-5 cm³/min.). The free heteropolyacid solutions should be concentrated on a steam bath or in a desiccator and, if needed, crystallized.

The method fails with heteropolysalts whose aqueous solutions exhibit a strong acid reaction. Additional complications arise if salt impurities (NaCl, NaNO₃, etc.) are present in the solution; since these salts produce HCl, HNO₃, etc., during passage through the column. A too strongly acid medium hinders the formation of free, crystalline heteropolyacids during concentration of the eluate.

The one advantage of this method has already been mentioned: The disadvantages are that one must begin with pure, crystalline alkali salts (which in some cases can only be obtained by the roundabout route of first preparing the free acid by Drechsel's method), and, in addition, the heteropolyacid solutions obtained by ion exchange are often relatively dilute so that their concentration is time-consuming.

3. HETEROPOLYSALTS

If the saits cannot be synthesized from their components or cannot be isolated in pure form, they may be conveniently of tained from moderately concentrated solutions of their acids by supersaturation with metal chlorides, or in better yield and purer form by addition of stolchiometric quantities of the metal carbonate. The carbonate should be added carefully, since an excess will induce decomposition of the heteropolyanion.

REFERENCES:

- E. Drechsel. Ber. dtsch. chem. Ges. 20, 1452 (1887); A. Rosenbeim and J. Jaenicke. Z. anorg. allg. Chem. <u>101</u>, 224 (1917).
- Based on unpublished experiments of G. Jander and D. Ertel;
 L. C. W. Baker, B. Loev and Th. P. McCutcheon. J. Amer. Chem. Soc. <u>72</u>, 2374 (1950); R. Klement. Z. anorg. Chem. <u>260</u>, 267 (1949); F. Hein and H. Lilie, Z. anorg. alig. Chem. <u>270</u>, 45 (1952).
- A. Rosenheim and J. Jaenicke. Ibid. <u>101</u>, 224 (1917); H. Copaux. Ann. Chim. Phys. [8] <u>17</u>, 217 (1909).

ISOPOLY COMPOUNDS

Isopolyvanadates

1. The Sodium Salt 2Na20 · V205 · aq.

 $\begin{array}{rl} 2 \ Na_{3} VO_{4} \ (aq.) + 2 \ HClO_{4} \ \simeq \ 2 \ Na_{2} O \cdot V_{2} O_{5} \ (aq.) + 2 \ NaClO_{4} \\ 367.9 \ & 200.9 \ & 305.9 \ \ast \ & 244.9 \end{array}$

A 1.1M Na₃VO₄ solution is prepared by dissolving V_2O_5 in the stoichiometric quantity of carbonate-free NaOH solution, so that 3 moles of Na are present per mole of V; this corresponds to 100.0 g. of V_2O_5 and 132.0 g. of NaOH per liter. Then, 160 ml. of this solution is acidified by dropwise addition of 24.9 ml. of 4.44N HCIO₄ (vigorous mechanical stirring). The solution is briefly heated on a steam bath to achieve equilibrium, whereupon the orange liquid becomes colorless. This is then concentrated in vacuum at 25-30°C. The resulting crystals are filtered and washed with some water.

SYNONYM:

Sodium pyrovanadate.

PROPERTIES:

Colorless, water-soluble crystals. Water content: 15 moles of $H_2O/mole$. In keeping with its molecular weight, should be considered a salt of a divanadic acid $H_4(V_2O_7 \cdot aq_2)$.

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[&]quot;The formula weights given here and subsequently refer to the

REFERENCES:

G. Jander and K. F. Jahr. Z. anorg. allg. Chem. <u>211</u>, 53 (1933); Kolloid-Beihefte <u>41</u>, 35 (1935).

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2. The Sodium Salt Na20 · V205 · aq.

A 0.812M solution of Na₃VO₄ is prepared as in (1) but using 73.9 g. of V_2O_5 and 97.5 g. of NaOH per liter. Then, 100 ml, of this solution is treated with 57.5 ml. of 2.54N HCIO₄ (dropwise addition with stirring) and briefly heated on a steam bath until colorless. The mixture is then concentrated in vacuum at 25-30°C. After filtration the crystals are washed with some water.

SYNONYM:

Sodium metavanadate.

PROPERTIES:

Colorless, water-soluble crystals. Water content: 3 moles of $H_2O/mole$. In keeping with its molecular weight, should be considered a salt of a tetravanadic acid $H_6(V_4O_{13} \cdot aq.)$. Many authors also consider it as the derivative of a trivanadic acid $H_3(V_3O_8 \cdot aq.)$.

REFERENCES:

- G. Jander and K. F. Jahr. Z. anorg. allg. Chem. <u>211</u>, 53 (1933); Kolloid-Beihefte <u>41</u>, 35 (1935).
- 3. The Sodium Sait 3 Na20 5 V205 aq.

 $\begin{array}{c} 10 \text{ Na}_{5} \text{VO}_{4} \ (\text{aq.}) \ + \ 24 \text{ HClO}_{4} \ = \ 3 \text{ Na}_{2} \text{O} \cdot 5 \text{ V}_{4} \text{O}_{5} \ (\text{aq.}) \ + \ 24 \text{ Na}_{3} \text{ClO}_{7} \text{ Base} \\ 1839.4 \ 2411.3 \ 1095.5 \ 2886.6 \ 3000 \text{ ClO}_{7} \text{ Base} \\ 1000 \text{ ClO}_{7} \text{ Base} \ - \ 3000 \text$

The 0.812M Na₃VO₄ solution (150 ml.) is prepared as in the and 381 ml. of 0.8M HClO₄ is added dropwise with stirring. The mixture is then allowed to stand for about 14 days in a closed flask. At first it becomes dark red, changing to a permanent brighter orange-red in the course of time. It is concentrated in vacuum at 25-30°C. The crystals which form are washed with some water. PROPERTIES:

Small, hexagonal orange-red platelets with beveled edges, or thin rhombohedra. Grinding changes the crystals into a bright yellow powder. Soluble in H₃O. Water content: 22 moles of H₃O/mole. In keeping with the molecular weight, should be considered as a salt of a pentavanadic acid H₇(V₅O₁₆·aq.) [G. Jander and K. F. Jahr, Kolloid-Beihefte <u>41</u>, 35 (1935)]. Regarded by many authors as a mixture of salts of different basicity, all of them derivatives of hexavanadic acid H₄(V₅O₁₇ · aq.) [see P. Souchay and G. Carpeni, Bull. Soc. Chim. France (5) <u>13</u>, 160 (1946); A. Rosenheim, Z. anorg. allg. Chem. <u>96</u>, 139 (1916)].

REFERENCE:

G. Jander and K. F. Jahr. Z. anorg. allg. Chem. 211, 53 (1933).

4. The Polassium Salt K20 · 3 V205

This salt is obtained from solutions of commercial potassium "metavanadate" $(1.04 K_2 O \cdot V_2 O_3 \cdot 0.78 H_2 O)$ by addition of 1.4 moles of acetic acid per mole of vanadate.

Commercial potassium "metavanadate" (7 g.) is dissolved in 25 ml. of water in a beaker placed in a large heating bath (75°C). The hot solution, which is about 2M in vanadium, is then treated with 70 ml. of 1M acetic acid added from a burette whose tip is immersed in the vanadate solution (vigorous mechanical stirring). The acetic acid is introduced at the rate of 1 ml./minute. The red solution is allowed to remain in the heating bath until the latter cools to room temperature (about 15 hours). The clear solution is then cooled to 0°C to induce crystallization. The crystals are filtered off and washed with some ice-cold water, then with acetone.

PROPERTIES:

Formula weight 545.7. Orange-red rhombic crystals or hexagonal platelets, sometimes rather large double pyramids. In view of its chemical behavior and molecular weight, this salt also should be regarded as the salt of pentavanadic acid $H_5(V_8O_{15} \cdot aq.)$. A part of the vanadium is said to be bound cationically, the salt thus having the formula $K_3(VO)[V_8O_{18}]$.

REFERENCE:

K. F. Jahr and G. Jander, Z. anorg. allg. Chem. 220, 204 (1934).

Isopolyniobates

Three types of anions exist in aqueous solutions of alkali niobates; these are in reversible equilibria with each other and their ranges of stability depend on the pH of the solution. All alkali isopolyniobates are salts of the hypothetical hexaniobic acid HeNb Ole. The general method of preparation of those sakes in which six to eight H+ are replaced by M+ consists of fusion of Nb₂O₅ with alkali hydroxide or carbonate, solution of the fused cake in H₂O, and concentration to obtain crystals. The orthoniobate MaNbO4 (M = alkali cation) formed in the melt is irreversibly converted to an isopolyniobate by treatment with water. The solubility of the alkali isopolyniobates in water is strongly dependent on the size of the cation. Thus, Li and Na salts invariably dissolve with difficulty (especially in the presence of excess Li+ or Na+), while K, Rb and Cs salts are readily to very readily soluble. The solutions are strongly alkaline. All alkali niobate solutions are very sensitive to acids; even small amounts of mineral acids produce irreversible clouding of the solutions or precipitates of Nb 205 aq. On heating to over 300°C, all alkali isopolyniobates lose water irreversibly to give the anhydrous, insoluble alkali metaniobates MNbO3.

Mg[Nb6019 + aq.] or 4M20 - 3Nb205 + aq. (8:6 type)

 $8 \text{ MOH} + 3 \text{ Nb}_2 O_6 = 6 \text{ M}_3 \text{ Nb} O_4 + 9 \text{ H}_2 O$ (fusion) $6 \text{ M}_3 \text{ Nb} O_4 + 5 \text{ H}_2 O = M_8 [\text{Nb}_6 O_{16} \cdot \text{aq}] + 10 \text{ MOH}$

To prepare the K salt, Nb₂O₅ and KOH (mole ratio ~1:20, weight ratio ~4:17) are heated in a silver or alumina crucible until a clear melt is obtained. The melt is cooled, ground and dissolved in H₂O. The solution is decanted to remove any in-soluble matter which may be present, then concentrated in vacuum over conc. H₂SO₄ until formation of crystals. These are washed with some water and dried on filter paper.

The corresponding Na salt is obtained from aqueous solutions of the K salt by treatment with NaOH (stirring). The fine, crystal? line, white precipitate is filtered off, washed with water, algohol and ether, and dried.

PROPERTIES:

Well-crystallized salts; the water content varies somewhat depending on the method of preparation. The large, transperent crystals of the K salt effloresce when stored under sharply desiccating conditions; they then become cloudy, but retain their good solubility in water.

n Arstan Seite Depending on the conditions of precipitation (hot or ice-cold solutions). the 8:6 sodium salt gives differing crystalline forms (meedies or leaflets), which also differ in their water content.

In aqueous solutions, salts of the type $M_{e}[Nb_{e}O_{16} \cdot aq_{e}]$ are stable only at pH > 13.

M7[HNb6019 + aq.] or 7M20 + 6Nb205 - aq. (7:6 type)

 $M_{a}[Nb_{s}O_{1s} \cdot aq] + H_{z}O = M_{r}[HNb_{s}O_{1s} \cdot aq] + MOH$

Two recrystallizations of the 8:6 sodium salt from H_2O afford $Na_7[HNb_6O_{18} \cdot aq.]$.

Another method of preparation starts with the fusion of Nb₃O₅ with Na₂CO₃ (mole ratio ~ 1:4, weight ratio ~ 5:8); the cooled melt is ground, treated with a large amount of H₂O, and stirred for several hours. Since the solubility of sodium niobate is poor, only the excess Na₂CO₃ dissolves in this operation. The residue is recrystallized from H₂O to give pure 7:6 sodium niobate.

The corresponding K salt is best prepared by addition of alcohol to solutions which contain 10 weight percent or more of pure 8:6 potassium niobate.

PROPERTIES:

The 7:6 sodium niobate forms long crystalline needles; water content: 32 moles of $H_2O/mole$.

The 7:6 potassium niobate precipitated with alcohol readily loses its water of crystallization and forms lower hydrates; e.g., at 100°C, it gives the penta- or tetrahydrate, and at 150°C, the dihydrate.

In aqueous solutions, salts of the type M_7 [HNb₆O₁₆ · aq.] are stable only in the pH range of 9 to 13.

(M.[Nb(O10 · 2q.]), or (6 M10 · 6 Nb(O6 · aq.), (6:6 type)

$$n M_{1}[HNb_{6}O_{19} \cdot aq] + n H_{2}O = (M_{6}[Nb_{6}O_{18} \cdot aq])_{a} + n MOH$$

A 2-4% aqueous solution of 8:6 potassium niobate (or a concentrated solution of 7:6 potassium niobate) is treated by dropwise addition of an equal volume of methyl alcohol (cooling in ice, vigorous mechanical stirring). The product is an amorphous, flocculent hydrated potassium niobate.

It is filtered, washed with 50% methyl alcohol, and dried under mild conditions.

PROPERTIES:

Pure white powder. Readily soluble in water. The water content varies depending on the conditions of preparation. The hydrated

metaniobate is stable only in aqueous solutions of pH < 8 (probably as far as the region of the isoelectric point, which occurs et al. ~4.5). At higher pH values, changes first to the 7:6 type (pH 8-13), and then to the 8:6 type (pH > 13). Based on diffusion measurements, the anion ($[Nb_6O_{16} \cdot aq.]^6$), has an ionic weight ~3000 (n = 3-4), so that the designation in the heading of this section is preferred to the formulas $M_2O \cdot Nb_2O_8 \cdot aq$. or $MNbO_3 \cdot aq$, which are sometimes encountered.

REFERENCES:

G. Jander and D. Ertel, J. Inorg. Nuclear Chem. <u>14</u>, 71, 77, 85 (1960); A. V. Lapitskiy and V. I. Spitsyn. Zh. Prikl. Khim. <u>26</u>, 101 (1953); F. Windmaisser, Österr. Chemiker-Ztg. <u>45</u>, 201 (1942); P. Sue. Ann. Chimie [11] <u>7</u>, 493 (1937).

Isopolytantalates

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As far as the general method of preparation of alkali isopolytantalates, their water solubility and their thermal behavior are concerned, the introductory remarks made in the section on isopolyniobates apply here as well. However, the composition of the alkali isopolytantalates, i.e., the base:acid ratio, is not yet completely clear. While some authors find hexatantalates (8:6) exclusively, others have established that only pentatantalates (7:5) exist, and still others insist that both types of compounds occur together, and are possibly related to each other via a region in which only one exists.

For this reason, we have given here several procedures taken from the original references.

 K_7 [Ta₅O₁₆ · aq.] or 7 K₂O · 5 Ta₂O₅ · aq. (pentatantalate, 7:5 type) Kg [Ta₆O₁₉ · aq.] or 4 K₂O · 3 Ta₂O₅ · aq. (hexatantalate, 8:6 type)

Either Ta_2O_5 and KOH (mole ratio ~1:20, weight ratio ~2:5) or Ta_2O_5 and K_2CO_3 (mole ratio ~1:4) are heated in a silver or alumina crucible (or a platinum vessel) until a clear melt is 'ob-tained. The melt is cooled, ground and dissolved in H₂O. The solution is decanted from any insoluble matter and concentrated in vacuum over conc. H₂SO₄ until crystallization occursication crystals are rinsed with H₂O and dried on filter paper. The crystal size increases with the excess alkali hydroxide or carbonate present in the mother liquor.

PROPERTIES;

Hexagonal prismatic columns up to 1 cm. long, with the

Readily soluble in water, giving a strong alkaline reaction. The contant of water of crystallization varies.

REFERENCES:

G. Jander and H. Schulz, Z. anorg. alig. Chem. <u>144</u>, 233 (1925);
 G. Jander and D. Ertel, J. Inorg. Nuclear Chem. 3, 139 (1956);
 F. Windmaisser, Z. anorg. alig. Chem. <u>248</u>, 283 (1941).

Nay [Ta5016 + aq.] or 7Na20 + 5Ta205 + aq. (pentatostalute)

A mixture of Ta_2O_5 and NaOH (mole ratio 1:5, weight ratio 11:5) is melted. The melt is cooled, ground, dissolved in H_2O and treated in the cold (stirring) with 0.1N NaOH. Pure white Na pentatantalate precipitates. It is washed with H_2O , alcohol and ether, and dried. Sodium pentatantalate also forms when the aqueous solution of the melt is evaporated at 85°C.

Alternate method: The same salt is obtained by treatment of a hot potassium tantalate solution with hot aqueous NaOH.

PROPERTIES:

Small prismatic needles; d^{30} 3.78. Water content: 22 moles of H₂O/mole; moderately soluble in water. The pH of a 1% solution is 8.48.

REFERENCES:

V. I. Spitsyn and N. N. Shavrova, Zh. Obshch. Khim, 26, 1258 (1956); G. Jander and D. Ertel, J. Inorg. Nuclear Chem. <u>3</u>, 139 (1956).

Nag[Ta6 019 · aq.] or 4Na2 0 · 3 Ta2 05 · aq. (hexatantalate)

The melt obtained by fusion of Ta_2O_5 and NaOH (mole ratio 1:5. weight ratio 11:5) is cooled, ground and treated with ten times its weight of cold H_2O to remove excess alkali. The residue is dissolved in H_2O at 80°C and concentrated at 50°C.

PROPERTIES:

Small leaflets; d^{90} 3.58. Water content: 33 moles of H₃O/mole; moderately soluble in water; pH of a 1% solution = 8.58. Goniometric measurements indicate that this Na hexatantalate belongs to the hexagonal system.

REFERENCES:

V. I. Spitsyn and N. N. Shavrova. Zh. Obshch. Khim. 26, 1256, 1262 (1956).

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Constant and

Isopolyarsenates

Sodium Hydrogen Trintsenate Na3H2As3O10

 $3 \text{ NaH}_2\text{AsO}_1 \cdot \text{H}_2\text{O} \rightarrow \text{Na}_3\text{H}_2\text{As}_3\text{O}_{10} + 5 \text{H}_2\text{O}$ 545.8 (incl. H_2O) 455.7 90.1

This sait is formed on dehydration of $NaH_2AsO_4 \cdot H_2O$. Very, slow heating of the starting material yields several intermediate products (NaH_2AsO_4 and $Na_2H_2As_2O_7$), which transform above 135°C to the triarsenate $Na_3H_2As_3O_{10}$. The last is stable up to 230°C. Rapid heating of the starting $NaH_2AsO_4 \cdot H_2O$ to temperatures above 96°C yields the triarsenate directly.

The best method of preparation is to place about 10 g. of $NaH_2AsO_4 \cdot H_2O$ (see p. 602) in a weighing bottle and heat it to constant weight (about 25 hours) in an electric furnace at 135°C.

PROPERTIES:

Absorbs H_2O from air at room temperature; after several intermediate stages, $NaH_2AsO_4 \cdot H_2O$ is finally regenerated. Immediately hydrated to the orthoarsenate upon solution in water. Considered by Thilo and Plaetschke to be the doubly acid salt of the pentabasic triarsenic acid $H_5As_2O_{10} = As_2O_5 \cdot \frac{5}{3} H_2O_2$. For the preparation of $As_2O_5 \cdot \frac{5}{3} H_2O_3$, see this handbook, p. 601.2 and

REFERENCE:

E. Thilo and I. Plaetschke. Z. anorg. Chem. 260, 315 (1949).

Isopolych romates

Potassium Trichromate K20 - 3 CrO3

This salt is formed on careful evaporation of an equeous solution of $K_2Cr_2O_7$ and excess CrO_3 .

A solution of 11.0 g. of $K_3Cr_2O_7$ and 17.4 g. of CrO₃ (molecularity of K_2O:CrO₃ = 1:6.66) in 22.0 ml, of water is prepared at 60002 a temperature at which the solution is saturated. Expose the 60°C yields deep red crystals. The liquid is exponented to 1000 ml.

13 ml. and then decanted rapidly while still warm. The crystals are dried by pressing on filter paper. Yield: about 7.8 g.

PROPERTIES:

Formula weight 394.2. Deep red prisms, containing no water of crystallization; decomposes on solution in water. Stable in solutions only in the presence of excess CrO_3 or conc. HNO_3 .

Potassium Tetrachromate $K_2 0 + 4 C_2 0_3$

This salt is obtained from aqueous solutions of $K_2Cr_2O_7$ in the presence of a large excess of CrO_3 . The evaporation should not be carried too far.

A saturated solution of 15.67 g, of $K_2Cr_2O_7$ and 43.43 g, of CrO_3 (mole ratio $K_2:CrO_3 = 1:10.15$) in 40.9 ml, of water is prepared at 60°C and concentrated at this temperature to about 10 ml. The nascent crystals are separated and dried as described in the case of the trichromate. Yield: about 13 g.

PROPERTIES:

Formula weight 494.2. Brownish red tablets, containing no water of crystallization; decomposes on solution in water. Stable in solutions only in the presence of excess CrO_3 or conc. HNO_3 .

REFERENCES:

 E. Jäger and G. Krüss. Ber. dtsch. chem. Ges. <u>22</u>, 2040 (1889);
 F. A. H. Schreinemakers. Z. phys. Chem. <u>55</u>, 71 (1906). Checked by the present authors.

Isopolymolybdates

The compounds described below should be considered derivatives of a hexamolybdic acid $H_{e}(Mo_{e}O_{a1}, aq.)$ [see G. Jander and K. F. Jahr, Kolloid-Beibefts <u>41</u>, 27 (1935)].

The Sodiam Sale 5Na2Q - 12Mo O3 - ag.

Sodium hydroxide (8 g.) is dissolved in 160 ml. of hot H_2O , and 29 g. of MoO_3 is added. The pH of the cooled, clear solution (filtered, if necessary) is about 5. It is evaporated in a vacuum

desiccator over H_2SO_4 to 3/4 to 2/3 of its original volume. The compound precipitates in the form of a slurry, which is filtered and washed with some H_2O_2 .

SYNONYM:

Sodium paramolybdate.

PROPERTIES:

According to Rosenheim, large, lustrous monoclinic prisms which effloresce easily. Water content: 38 moles of $H_2O/mole$. Soluble in H_2O . In our own experiments, evaporation in vacuum or on a steam bath gave a granular white mass, which was not significantly soluble in water either after drying or when freshly prepared and moist.

REFERENCE:

A. Rosenheim. Z. anorg. allg. Chem. <u>96</u>, 143 (1916). Checked by the present authors.

The Ammonium Salt 5(NH4)20 · 12MoO3 · ag.

The reaction vessel is a porcelain dish. It contains 20 g. of MoO_3 , covered with 230 ml, of conc. ammonia. The solution is gently evaporated on a steam bath (solution temperature 60-70°C) until the excess NH₃ is removed and the first crystals form (this occurs upon concentration to about 1/5 of the original volume). The concentrate is cooled and the crystals are filtered off. Yield: about 20 g.

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PROPERTIES:

Formula weight 1987.8. According to Rosenheim, large, clear, colorless hexagonal prisms, moderately soluble in H_2O . Water content: 7 moles of H_2O /mole. This product is the ammonium molybdate of commerce. Its aqueous solution gives an acid reaction and the compound undergoes hydrolytic cleavage on prolonged boiling. Our own experiments yielded small, white crystals, soluble in hot H_2O .

REFERENCE:

A. Rosenheim. Z. anorg. allg. Chem. 96, 141 (1916). Checker in the present authors. The Sodium Salt NagO + 4Mo Og + nq-

$$4 \operatorname{Na_2MoO_4}(aq.) + 6 \operatorname{HCl} = \operatorname{Na_2O} \cdot 4 \operatorname{MoO_8}(aq.) + 6 \operatorname{NaCl}_{359.8} \\ \begin{array}{r} 218.8 \\ 350.7 \end{array}$$

A solution of 9.3 g. of $Na_2MoO_4 - 2 H_2O$ in about 8 ml. of hot H_2O is treated, while still hot, with 11 ml. of 5.5N HCl added dropwise from a burette. The initial precipitate redissolves, giving a yellowish solution. The liquid, in a stoppered Erlenmeyer flask, is left in a cool place to crystallize. A crystalline crust appears after 24 hours and its thickness increases in the course of the next few days. The crystals are filtered off, washed three times with cold water, and dried by drawing air through the crystal layer. Yield: 6 g.

SYNONYM:

Sodium metamolybdate.

PROPERTIES:

Relatively long needles, partially pulverized when touched. Moderately soluble in cold H_2O , very soluble in hot. Water content: 6 moles of $H_2O/mole$.

REFERENCE;

G. Wempe, Z. anorg. Chem. <u>78</u>, 302 (1912). Checked by the present authors.

Isopolytungstates

The compounds described below are derivatives of a hexatungstic acid $H_{B}(W_{6}O_{21} \cdot aq.)$ [see G. Jander and K. F. Jahr, Kolloid-Beihefte <u>41</u>, 18 (1935)].

The Sodiam Salt 5Na20 · 12WO3 · aq.

$$\begin{array}{rl} 12 \operatorname{Na_{r}WO_{4}}\left(\mathrm{aq.}\right) \ + \ 14 \ \mathrm{HCl} \ = \ 5 \ \operatorname{Na_{r}O} \cdot 12 \ \mathrm{WO_{8}}\left(\mathrm{aq.}\right) \ + \ 14 \ \mathrm{NaCl} \\ 3526.9 & 510.6 & 3093.0 & 818.3 \end{array}$$

A solution of 20 g. of $Na_3WO_4 \cdot 2 H_3O$ in 40 ml. of hot H_2O is neutralized to litmus with 2N HCl. About 23.5 ml. of HCl is reof the solution is then 6.8. The salt is allowed to crystallize in a vacuum desiccator at room temperature over H_2SO_4 .

SYNONYM:

Sodium paratungstate.

PROPERTIES:

Large transparent or milky-white trichlinic crystals. Water content: 28 moles of $H_2O/mole$. Readily soluble in water. Other hydrates exist at higher temperatures. The recent views on the complex processes involved in the formation of paratungstates are given by Jander and Kruerke.

REFERENCES:

A. Rosenheim. Z. anorg. allg. Chem. <u>96</u>, 160 (1916); C. Scheibler,
 J. prakt. Chem. <u>83</u>, 284 (1861). Checked by the present authors.
 G. Jander and U. Krüerke, Z. anorg. allg. Chem. <u>265</u>, 244 (1951).

The Ammonium Salt 5(NH₄)₂O · 12WO₃ · eq.

Hydrated tungstic acid is dissolved in excess ammonia, and the solution is concentrated on a steam bath or at room temperature, whereby the excess ammonia evaporates.

SYNONYM:

Ammonium paratungstate.

PROPERTIES:

Formula weight 3042.72. Microscopically small, rectangular tablets when the solution is evaporated at high temperatures. Water content: 7 moles of $H_2O/mole$. A different hydrate exists at room temperature and below. Rather sparingly soluble; in H_2O . On prolonged boiling in aqueous solution, the salt is hydres. lytically decomposed and loses NH_3 .

REFERENCE:

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A. Rosenheim. Z. anorg. allg. Chem. 96, 158 (1916).

The Zine Sait 5Zn 0 + 12W03 - sq.

 $5 \operatorname{Na}_{e}O \cdot 12 \operatorname{WO}_{s}(\operatorname{aq.}) + 5 \operatorname{ZnSO}_{e} = 5 \operatorname{ZnO} \cdot 12 \operatorname{WO}_{s}(\operatorname{aq.}) + 5 \operatorname{Na}_{s}SO_{e}$ 3093.01 807.2 3189.94 (2.1) (710.3) (71.0.3)

A solution is prepared by heating a mixture of 7.8 g. of sodiul paratungstate (prepared as above) and 70mml. of waters find mixture is then reacted with a warm, saturated solution of 2000

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EnSO₄ • 7 H₂O in 15 ml. of water. A white precipitate forms, partially redissolves, and then settles out. It is suction-filtered and dried over conc. H₂SO₄.

SYNONYM:

Zinc paratungstate.

PROPERTIES:

White needles or fine, crystalline precipitate; poor solubility in H_2O . Water content: 35 moles of H_2O /mole.

REFERENCE:

I.

A. Rosenheim, Z. anorg. allg. Chem. <u>96</u>, 162 (1916). Checked by the present authors.

Isopolysulfates

Potessium Trisulfate X253010

 $K_{3}SO_{4} + 2SO_{3} = K_{3}S_{3}O_{10}$ 174.3 160.1 334.4

According to Baumgarten and Thilo, $K_2S_3O_{10}$ may be prepared from K_2SO_4 by treatment with SO₂. The apparatus used is shown in Fig. 342.

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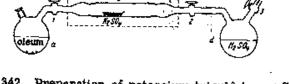


Fig. 342. Preparation of potassium trisulfate. a flask with oleum; b reactor tube, here shown surrounded by an electric tubular furnace; d flask with conc. H₂SO₄;
I-3 stopcocks. The reactor tube c is longer in relation to other parts of the apparatus than shown.

All parts of the glass apparatus are connected by ground joints. The joints are sealed with a paste made from 10 g. of powdered tale (preboiled several times in HCl) and 14 g. of anhydrous phosphoric acid. Stopcock plugs 1 and 2 should be of as large a

diameter as possible; stopcock 3 may be of normal size. After thorough drying of all parts of the apparatus a boat of quarter glazed porcelain, or platinum containing finely powdered, ignited K₂SO₄ is inserted into reaction tube b; following this, adapter 3 and flask d (containing 96.5% H2SO4) are attached. Stopcock 145 closed, and the section b-d is evacuated with an aspirator. Stopeople 3 is then closed, and the apparatus is left to dry for a while, Flask a is then filled with 70% oleum, a few glass beads are added, stopcock 1 is reopened, and the entire apparatus is rapidly evacuated with the aspirator, so that the oleum evolves, Stopcocks 2 and 3 are then closed. The flask containing the oleum is heated to about 110°C in a sulfuric acid bath until enough SOs distills and condenses in tube b to entirely surround the boat with the liquid. Flask a is then allowed to cool somewhat and stopcock 1 is closed. Tube b (between 1 and 2) is heated externally to 59-53°C, using a sheet iron heating trough lined with asbestos, and covering the top with asbestos. The trough is heated with a row burner. while the stopcocks and flasks are insulated with aspestos to prevent heating. The 50-53°C temperature desired is measured in the space between the reactor tube and the trough. Alternatively, an electric furnace may be used, as shown in the figure.

In the next two hours, the $K_{2}SO_{4}$ will sinter, become a slurry and finally convert to a clear liquid. If the quantity of SO_{3} present is insufficient, the melt may resolidify. At the end of the reaction, stopcock 2 is reopened, flask d is cooled in ice, and the excess SO_{3} is distilled onto the cooled $H_{2}SO_{4}$, first at room temperature and finally by heating the reaction tube two hours at 100°C. The apparatus is allowed to cool and stopcock 3 is opened; little or no fuming should then occur.

п.

 $2 \text{ KClO}_4 + 3 \text{ SO}_3 = \text{K}_8\text{S}_3\text{O}_{10} + \text{Cl}_2\text{O}_7$ 277.1 240.2 334.4 182.9

According to Lehmann and Krüger, the reaction of SOs with KClO₄ produces potassium trisulfate and Cl₂O₇; the latter distribution of the excess SO₃. The residue obtained on vacuum evapeoration of the excess SO₃ and the Cl₂O₇ is chlorine-free, stoichlog metric K₂S₃O₁₀.

Extremely dry, fine KClO₄ powder, free of reducing impurities: is placed in the apparatus of Baumgarten and Thilo shown in file: 342 and treated with SO_2 -free SO_3 at 25-30°C until the contents of the boat become completely liquid. Excess SO_3 and Cl_2O_7 are then absorbed in conc. H_2SO_4 at room temperature, while vacuum is applied at 3.

PROPERTIES:

According to recent studies, K₂S₃O₁₀ is thermisly stable upto 110°C. Above this temperature the vapor pressure of SOs being t

to increase and the compound decomposes into potassium pyrosulfate and SO₃. The $K_{a}S_{3}O_{10}$ prepared by the method of Baumgarten and Thilo is a cake which can readily be ground to a fine powder. It absorbs water from the air and converts to an adduct of sulfuric it absorbs water from the air and converts to an adduct of sulfuric acid and pyrosulfate or bydrogen sulfate. It decomposes immediacid and pyrosulfate or bydrogen sulfate. It decomposes immediacid and pyrosulfate or bydrogen sulfate of decomposition, ataly (with fixing) in cold water; in the first stage of decomposition, only 1 mole of SO₃ is evolved and a pyrosulfate of relatively poor solubility is formed.

REFERENCES:

P. Baumgarten and E. Thilo. Ber. dtsch. chem. Ges. <u>71</u>, 2596 (1938); H. A. Lehmann and G. Kruger. Z. anorg. allg. Chem. <u>274</u>, 141 (1973); H. A. Lehmann and A. Kluge. Ibid. <u>264</u>, 120 (1951).

HETERPOLY COMPOUNDS

12-Tungstic Acid-1-Borates

In keeping with their constitution and molecular weight, these compounds should be regarded as salts of 12-tungstic-1-boric acid H₂[BO₄(W₃O₂)₄ · aq.) [R. Signer and H. Gross, Helv. Chim. Acta 17, 1076 (1934)].

The Free Acid B203 · 24 W03 · aq.

The first step involves the preparation of a solution of $5 \operatorname{Na_2O} \cdot \operatorname{B_2O_3} \cdot 24 \operatorname{WO_3} \cdot \operatorname{aq}$, from $\operatorname{Na_2WO_4} \cdot \operatorname{aq}$. and $\operatorname{H_3BO_3}$. A large excess of boric acid is used to bind the alkali of the $\operatorname{Na_2WO_4}$ and to ensure that the solution remains acidic. The acid can be isolated from the solution of the sodium salt by addition of ether and sulfuric acid according to the method of Drechsel (see p. 1760 f.).

A solution of 100 g. of $Na_2WO_4 \cdot 2 H_2O$ and 150 g. of H_3BO_3 is prepared in 400-500 ml. of boiling H_2O . The solution is boiled until a sample deposits no tungstic acid when dil. HCl is added. The solution is cooled, suction-filtered to remove the boric acid and sodium polyborate crystals, reacted again with 70 g. of H_3BO_3 , and concentrated over a free flame. The crystalline mass which separates on cooling is again filtered off and washed with some 23% H₂SO₄. The mother liquor, which contains 5 Na₂O · B₃O₃ · 24 WO₃ · aq., is extracted with 2-3 volumes of 33% H₂SO₄ and enter according to the method of Drechsel. For further workup new p. 1761.

PROPERTIES:

Formula weight 5634.3. Two forms:

a) Perfectly clear octahedral crystals, initially bright but acquiring a greasy luster and a yellowish cast on storage; otherwise, can be stored for a long time. Water content: 65 or 66 moles of $H_2O/mole$. M.p. 45-51°C. Soluble in water.

b) Hexagonal needles, less stable, more apt to become yellow and cloudy. Water content: 53 moles of $H_2O/mole$. Soluble in H_2O . The m.p. cannot be determined, since heating causes decomposition. These crystals were formerly thought to be those of an isoborotungstic acid.

REFERENCE:

A. Rosenheim and J. Jaenicke. Z. anorg. Chem. <u>77</u>, 244 (1912); 101, 236 (1917).

The Sodium Salt 5Na20 · B2O3 · 24WO3 · aq.

The crystalline sodium salt is best prepared from the free acid by addition of the stoichiometric quantity of Na_sCO_3 .

 $\begin{array}{rl} B_{2}O_{3} \cdot 24 \ WO_{3} \ (aq.) \ + \ 5 \ Na_{2}CO_{3} \ = \ 5 \ Na_{2}O \cdot B_{2}O_{3} \cdot 24 \ WO_{3} \ (aq.) \ + \ 5 \ CO_{2} \ \\ 5635.7 \ 530.0 \ 5945.7 \end{array}$

A solution containing 34.4 g, of free 12-tungstic-1-boric acid (equivalent to about 41.6 g, of the hydrated acid) is reacted with 3.1 g, of anhydrous Na_2CO_3 , and concentrated first on a steam bath and then in a desiccator over conc. H_2SO_4 .

PROPERTIES:

White, well-formed octahedra. Soluble in H_2O . Water contents 58 moles of $H_2O/mole$.

REFERENCE:

A. Rosenheim and H. Schwer. Z. anorg. Chem. 89, 236 (1914): 1 📉

12-Tungstic Acid-I-Silicates

In view of their structure and molecular weight, all compounds of this type should be considered as salts of 12-tungstic-1-silicite acid $H_4[SiO_4(W_3O_2)_4 - aq_.]$ [R. Signer and H. Gross, Helv. China Acta 17, 1076 (1934)].

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The Free Acid SiOg - 12WO3 . aq.

$$13 N_{32} WO_{4} (aq) + SiO_{7} + 20 HC] = 2 Na_{2}O \cdot SiO_{2} \cdot 12 WO_{3} (aq.) + 20 NaClSiSS6.9 60.06 729.4 2967.1 1)69.0$$

The free acid is isolated from a solution of $2 \operatorname{Na}_2 O \cdot \operatorname{Si}O_2 \cdot$ 12 WO₃ • aq. by the method of Drechsel, that is, extraction with ether and conc. HCl.

A solution of 50 g. of $Na_2WO_4 \cdot 2 H_2O$ in 400 ml. of cold H_2O is prepared. It is then treated by dropwise addition of about 27 ml. of 6N HCl, until neutral to litmus. The white precipitate formed during the addition redissolves on swirling the flask. An excess of freshly precipitated silicic acid hydrate is now added to the solution. (The silicic acid is prepared as follows. Commercial sodium silicate is dissolved in a minimum of cold H_2O and made neutral to litmus by dropwise addition of conc. HCl. After 15 minutes a small excess of acid is added. The solution is decanted and the precipitate is washed once or twice with cold water, which is likewise decanted.)

The mixture of tungstate and silicic acid is boiled for about two hours (the liquid being kept acidic by periodic addition of small amounts of HCl) until a filtered sample of the solution no longer precipitates tungstic acid hydrate on addition of dil. HCl. The solution is filtered to remove undissolved SiO_2 and shaken with ether and conc. HCl. For further workup, see p. 1701. If the free acid is to be used only as starting material for preparation of a salt, the oily adduct may be decomposed at about 40°C, the ether removed by long heating, and the excess hydrochloric acid removed by drawing air through the slowly solidifying residue. The yield is 27 g.; the product is not completely pure.

PROPERTIES:

Formula weight 2842.4. The acid crystallizes at room temperature in coloriess, lustrous octahedra; m.p. 53°C. Water content: 32 moles of $H_2O/mole$. Readily soluble in H_2O . Several different crystalline hydrates exist, one of which is denoted the "iso acid."

REFERENCE:

A. Rosenheim and J. Jaenicke. Z. anorg, allg. Chem. <u>101</u>, 240 (1917). Checked by the present authors.

The Potassium Salt 2K20 · SiO2 · 12WO3 · aq.

 $\begin{array}{c} \textbf{SiO}_{s} \cdot 12 \, \textbf{WO}_{s}(\textbf{aq.}) \, + \, 2 \, \textbf{K}_{s} \textbf{CO}_{r} \, = \, 2 \, \textbf{K}_{s} \textbf{O} \cdot \textbf{S} i \textbf{O}_{s} \cdot 12 \, \textbf{WO}_{s}(\textbf{aq.}) \, + \, 2 \, \textbf{CO}_{s} \\ \textbf{2843.1} \quad 276.4 \quad 3091.5 \end{array}$

As agreeus solution of the free acid (about one part by weight of acid to three or four parts of H_2O), whose content is determined

by evaporation and ignition of an aliquot, is treated by slow addition of the stoichiometric quantity of solid K_2CO_3 (two moles of K_3CO_3 per mole of acid) while applying heat. The clear solution, which must retain an acidic reaction, is evaporated on a steam bath to 1/2 to 1/4 its volume. Cooling precipitates $2K_3O \cdot SiO_2 \cdot 12WO_3 \cdot$ aq., first in hexagonal prisms and then also as rhombic crystals. The product is recrystallized from hot H_3O_3 .

PROPERTIES:

The hexagonal, colorless prisms efficience easily. Water content: 18 moles of $H_2O/mole$. Readily soluble in hot H_2O , somewhat less so in cold. The rhombic crystals are said to be the sait of the so-called "iso acid"; they do not efficience so rapidly. Water content: 9 moles of $H_2O/mole$.

REFERENCE:

A. Rosenbeim and J. Jaenicke, Z. enorg. allg. Chem. <u>101</u>, 243 (1917). Checked by the present authors.

10-Tungstic Acid-1-Silicates

The Potassium Salt 7K20 · 2SiO2 · 20WO3 · aq.

This salt is obtained by careful decomposition of a 12-tungetic acid-1-silicate with K_2CO_3 .

A solution of 8 g. of 2 K₂O·SiO₂. 12 WO₃ aq. in a minimum of H_2O is prepared at room temperature and treated carefully (no heating) with a fairly conc. solution of K₂CO₃ in H_2O (2 moles of $K_2CO_3 = 276.4$ g. per mole of 2 K₂O·SiO₃. 12 WO₃; one mole of the compounds containing 18 or 9 moles of H_2O /mole weight 3355.8 or 3193.6 g., respectively). At this point, the solution gives a neutral reaction, and the desired potassium salt crystallizes out immediately with no need for further concentration. The salt is washed with some cold water. Yield: 4.5 g.

PROPERTIES:

Formula weight 5416.78. Sparkling crystals. Water contents 23 moles of $H_2O/mole$.

REFERENCE:

F. Kehrmann. Z. anorg. Chem. 39, 103 (1904). Checked by the present authors.

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12-Tungstic Acid-1-Phosphates

In theoring with their molecular weight and constitution, these compounds should be regarded as derivatives of a 12-tungstic-1-phosphoric acid $H_{3}[PO_{4}(W_{3}O_{2})_{4} \cdot aq_{2}]$ [J. F. Keggin, Proc. Roy. Sec. A 144, 75 (1934)].

A solution of 50 g, of $Na_2WO_4 \cdot 2 H_2O$ and 25 g, of $Na_2HPO_4 \cdot 12 H_2O$ in 80 ml. of H_2O is evaporated until a surface skin of crystals forms; then 75 ml. of 24% HCl (d 1.12) is added with stirring. A precipitate forms momentarily, but then redissolves completely. The solution is reevaporated on a steam bath until a crystal skin begins to form. The product is recrystallized from H_2O .

PROPERTIES:

Large colorless (sometimes slightly greenish) columnar crystals. Water content: 30 moles of $H_2O/mole$. Another hydrate also exists. Soluble in H_2O .

REFERENCE:

A. Rosenheim and J. Jaenicke. Z. anorg. allg. Chem. <u>191</u>, 251 (1917). Checked by the present author.

The Free Acid P2O5 · 24WO3 · aq.

This salt is obtained by Drechsel's method (p. 1700), that is, by entracting a solution of $3 \operatorname{Na}_{3}O \cdot P_{3}O_{6} \cdot 24 \operatorname{WO}_{3} \cdot aq$, with ether and conc. HCl. Light yellow or greenish crystals precipitate. However, if the starting sodium salt is first recrystallized once or twice, the product consists of transparent, colorless orystals.

This acid is also prepared very readily by ion exchange (see p. 1701). The starting solution contains 20 g. of 3 Na₃O \cdot P₃O₅ · 24 WO₃ · aq. in 100 ml. of H₂O. The colorless eluate is concentrated in a vacuum desiccator. Yield: 11 g.

PROFESSION:

Formula weight 5706.59. The colored crystals disintegrate,

crystals may often be kept for months. Large, lustrous octahedra. soluble in H2O. Water content; 63 moles of H2O/mole. This hydrate readily converts to a hydrate with 51 moles of H₂O/mole. which forms trigonal crystals and begins to melt at 89°C. It loses its water of crystallization in a vacuum desiccator over HaSO4.

REFERENCES:

A. Rosenheim and J. Jaenicke, Z. anorg. allg. Chem. 101, 251 (1917); G. Jander and D. Ertel, unpublished experiments.

The Potassium Salt 3K20 · P205 · 24W03 · ac.

The Ammonium Salt 3(NH4)20 - P205 - 24WO3 - aq.

 $3 \text{ Na}_{2}\text{O} \cdot P_{2}\text{O}_{5} \cdot 24 \text{ WO}_{5} (\text{aq.}) + 6 \text{ KCl} [6 \text{ NH}_{4}\text{Cl}]$ 447.3 5894.0 321.0

= $3 K_2 O \cdot P_2 O_3 \cdot 24 WO_3 (aq.) [3 (NH_4)_2 O \cdot P_2 O_3 \cdot 24 WO_3 (aq.)] + 6 NaCl$ 5864.3 350.7 5990.8

A solution of the free acid $P_2O_8 \cdot 24 WO_3 \cdot aq$, or the sodium sait 3 Na₂O · P₂O₅ · 24 WO₃ · aq, is treated with KCl or NH Cla A thick white precipitate forms, even if the solutions are very dilute and contain free mineral acids. 5. 8. Šr

PROPERTIES:

Microcrystalline white precipitates, which filter with difficulty. 1.5 1020 Very poor solubility in H₂O. . . . પક્ષે

REFERENCE:

F. Kehrmann and M. Freinkel. Ber. dtsch. chem. Ges. 24, 2326 (1891). Checked by the present authors.

The Barium Sair 3BaO · P2O5 · 24WO3 · aq.

| 3 Na2O • P2O5 • 24 WO3 (aq 5894.0 | 1.) + 3 BaCl ₂ = 3 ! | BaO · P3O5 · 24 WO3 | (aq.) + 6 NaCl 4 |
|--------------------------------------|---------------------------------|---------------------|---|
| 5894.0 | 624.8 | 61 68. 1 | 850.7 . 14 |
| | | | 1. A |

A saturated solution of 14 g. of 3 Na₂O · P₂O₅ · 24 WO3 * au is mixed, while hot, with 60 ml. of hot, saturated BaCla solutions The liquid becomes cloudy, and a heavy, white orystalline prescipitate forms on cooling. Concentration of the mother liques (not too far) gives a second fraction of the desired barium and Yield: about 7 g.

44

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PROPERTIES:

Well-formed, regular, colorless octahedra, which effloresce in air. Water content: 58 moles of $H_2O/mole$. Moderately soluble in H_2O .

REFERENCE:

F. Kehrmann and M. Freinkel, Ber. dtsch. chem. Ges. <u>24</u>, 2326 (1891). Checked by the present authors.

22-Tungstic Acid-2-Phosphotes

The Potassium Salt $7K_20 + P_20_5 + 22W0_3 + aq$.

Produced by careful decomposition of a 12-tungstic acid-1phosphate with K_2CO_3 .

An approximately 30% suspension of $3 K_3 O \cdot P_2 O_5 \cdot 24 WO_3 \cdot aq$. aq. in water is heated to boiling and treated with about 10% $K_2 CO_3$ solution until solution is complete. Excess $K_2 CO_3$ should be avoided. The solution, which then has a neutral reaction, is evaporated on the steam bath. On cooling, $7 K_3 O \cdot P_2 O_5 \cdot 22 WO_3 \cdot aq$. separates out. It may be recrystallized from $H_2 O$ which contains some acetic acid.

PROPERTIES:

Formula weight 5902.3. Large, octahedral crystals, partially present as spearlike aggregates, accompanied by a fine powder. Soluble in hot water, less so in cold. Decomposes in the presence of free mineral acid (see next preparation).

REFERENCES:

F. Kehrmann, Z. anorg. Chem. 1, 435 (1892); P. Souchay. Ann. Chimie [12] 2, 204 (1947). Checked by the present authors.

The Potansian Salt 3K20 · P205 · 21 W03 · aq.

Produced from $7 K_{2}O \cdot P_{2}O_{5} \cdot 22 WO_{3} \cdot aq$. by treatment with **BC1.** In addition to the desired compound, the potassium salt of **12-tangetic-1-phosphoric** acid, $3 K_{2}O \cdot P_{3}O_{5} \cdot 24 WO_{3} \cdot aq$., is also formed.

A conc. solution of $7 K_2O \cdot P_2O_6 \cdot 22 WO_3 \cdot aq$, is prepared at the boiling point, and dilute (about 7%) HCl is added dropwise until the solution becomes acidic. An insoluble white precipitate of $3 K_2O \cdot P_2O_5 \cdot 24 WO_3 \cdot aq$. appears. This is filtered off, and the filtrate is treated with KCl powder to salt out the desired compound. The latter is recrystallized from H_2O containing two drops of HCl.

PROPERTIES:

Formula weight 5293.6. Relatively large, lustrous, hexagonal columns, partly intergrown. Readily soluble in H_2O . The aqueous solution is unstable on boiling, depositing a white precipitate.

REFERENCES:

F. Kehrmann. Z. anorg. Chem. <u>1</u>, 436 (1892); P. Souchay. Ann. Chimie [12] 2, 204 (1947). Checked by the present authors.

18-Tungstic Acid-2-Phosphates

Based on molecular weight determinations, these compounds should be regarded as saits of an 18-tungstic-2-phosphoric acid $H_{cl}(PO_4)_2(W_3O_9)_8 \cdot aq.$] [G. Jander and F. Exner, Z. phys. Chem. (A) <u>190</u>, 195 (1942)].

The Ammonium Salt 3(NH4)20 · P205 · 18 WOg · aq.

A solution of $Na_2WO_4 \cdot aq$. is bolied for a long time with a large excess of phosphoric acid. This involves an apparently slow condensation reaction. The resulting solution of the sodium salt of 18-tungstic-1-phosphoric acid is treated with solid NH_4CI to salt out the ammontum salt.

One mole of $Na_3WO_4 \cdot 2 H_2O$ is dissolved in hot H_3O and treated with four moles of phosphoric acid (in the form of a conc. solution, d 1.17) and about 100 ml, of additional H_2O . The yellow solution is boiled for 3-5 hours while stirring and replacing the water lost by evaporation; the boiling point is 108°C. To remove any reduction products which may have formed, a few drops of nitric acid are added at the end. As the solution cools, solid NH₄Cl is added until the desired ammonium salt 3 (NH₄)₂O · P₂O₅ · 18 WO₃ is completely precipitated and the solution becomes coloriess. The salt is filtered out, redissolved in hot H_2O , and reprecipitated with conc. NH₄Cl solution. It is then filtered out again, washed and recrystallized twice from water; the first crystal fraction is discarded each time. An analytically purp preparation is thus obtained. STRONTN:

Ammonium luteophosphotungstate.

PROPERTIES:

Formula weight 4471.7. Lemon-yellow or pale yellow-green triclinic crystals. Water content: 14 moles of H₂O/mole. Soluble in H₂O.

REFERENCES:

F. Kehrmann. Z. anorg. Chem. <u>1</u>, 432 (1892); Ber. dtsch. chem. Ges. <u>20</u>, 1808 (1887); G. Jander and H. Banthien. Z. anorg. allg. Chem. <u>229</u>, 142 (1936).

The Free Acid P2O5 · 18 WO3 · aq.

Obtained by the method of Drechsel (see p. 1700 f.) from the solution of the sodium salt described in the previous preparation.

It can also be prepared by ion exchange (cf. p. 1701), using a solution of 10 g. of 3 $(NH_4)_2 \circ P_2 \circ P_3 \circ 18 \circ W \circ O_3 \circ aq$. in 50 ml. of H₂O. The eluate is clear and pale yellow-green. It is concentrated in a vacuum desiccator. Yield: 9 g.

SYNONYM:

Luteophosphotungstic acid.

PROPERTIES:

Formula weight 4315.4. M.p. 28°C. Lemon-yellow hexagonal tablets. Water content: 42 moles of H_2O /mole. Readily soluble in H_2O .

BEFERENCES:

A. Rosenheim and J. Jaenicke. Z. anorg. allg. Chem. <u>101</u>, 261 (1917); G. Jander and F. Exner. Z. phys. Chem. (A) <u>190</u>, 195 (1942); G. Jander and D. Ertel. Unpublished experiments.

12-Tungstic Acid-1-Arsenates

By analogy with the 12-tungstic acid-1~phosphates, compounds of this class should be regarded as salts of a 12-tungstic-1treenie acid $H_3[AsO_4(W_3O_9)_4 \cdot aq.]$ [J. W. Illingworth and J. F. Keggin, J. Chem. Soc. (London) <u>1935</u>, 575].

All tungstic acid arsenates resemble closely the tungstic acid phosphates in their manner of preparation and their behavior. They are only a little less stable.

The Ammonium Salt 3(NH4)20 · As205 · 24 WO3 · aq.

Obtained by addition of NH₄Cl to a solution of the corresponding sodium salt $3 \text{ Na}_2\text{O} \cdot \text{As}_2\text{O}_5 \cdot 24 \text{ WO}_3 \cdot \text{aq.}$, which is not known to exist as a solid.

$$3 \operatorname{Na_2O} \cdot \operatorname{As_2O_5} \cdot 24 \operatorname{WO_5}(\operatorname{aq.}) + 6 \operatorname{NH_4C}$$

$$5981.9 \qquad 321.0$$

$$= 3 (\operatorname{NH_4}_2O \cdot \operatorname{As_2O_5} \cdot 24 \operatorname{WO_5}(\operatorname{aq.}) + 6 \operatorname{NaCl}$$

$$5952.1 \qquad 350.7$$

A solution of 52.8 g. of $Na_3WO_4 \cdot 2 H_3O$ is prepared by heating a mixture of the salt and sufficient water to make the final volume 90 ml. A second solution is prepared from 2.3 g. of As_2O_5 and 15 ml. of very concentrated aqueous NaOH, and is then diluted with water to a final volume of 70 ml. After cooling, both solutions are combined and treated with conc. HCl until the mixture is strongly acid (pH paper). This requires 15-20 ml. of conc. HCl: The resulting mixture is unstable; on long standing, a white sediment is formed. Therefore 21 g. of solid NH4Cl is added immediately; the mixture is heated once to boiling and allowed to stand for two hours on a steam bath. The white precipitate is filtered out, washed first with NH4Cl solution acidified with HCl and then with some cold H_3O , and dried in a desiccator.

PROPERTIES:

Fine white, crystalline precipitate. Water content: 12 moles of $H_2O/mole$. Relatively sparingly soluble in H_2O .

REFERENCES:

F. Kehrmann, Z. anorg. Chem. 22, 286 (1960); A. Rosenheim and J. Jaenicke. Z. anorg. allg. Chem. <u>161</u>, 268 (1917). Checked by the present authors.

18-Tungstic Acid-2-Arsenates

These compounds are exactly the same in appearance and water content as the 18-tungstic acid-2-phosphates. The ammonium salt and the free acid are obtained by methods used for those compounds (see p. 1723), using arsenic acid instant of phosphoric.

1723

1. 21 M.O.C.

2 C 2

Formula weights: As₂O₅ · 18 WO₃ · aq.: 4404.4; 3 (NH₄)₂O · As₃O₅ · 18 WO₃ · aq.: 4560.6.

REFERENCES:

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F. Kehrmann, Z. anorg. Chem. <u>22</u>, 290 (1900); A. Rosenheim and J. Jaenicke, Z. anorg. allg. Chem. <u>101</u>, 270 (1917).

6-Tungstic Acid_1-Tellurates

In keeping with their molecular weight, these compounds should be considered 6-tangstic acid-1-tellurates (salts of a 6tangstic-1-telluric acid $H_{g}[TeO_{g} \cdot 6 WO_{3} \cdot aq.]$) [G. Jander and K. F. Jahr, Kolloid-Beihefte <u>41</u>, 308 (1935)].

The Gaussidiana Solt $3(CN_3H_6)_2O + TeO_3 + 6WO_3 + aq.$

Tungsten (VI) oxide is dissolved in guanidinium carbonate, HCl is added to ensure the level of acidity required for the formation of a heteropoly compound, and the required quantity of telluric acid is introduced.

 $\begin{array}{rcl} 6\,({\rm CN_3H_4})_2{\rm CO_3} &+ {\rm H_sTeO_s} &+ 6\,{\rm WO_3} &+ 6\,{\rm HCl} \\ 1061.0 && 229.6 && 1391.5 && 218.8 \\ &= 3\,({\rm CN_3H_s})_2{\rm O}\cdot{\rm TeO_3}\cdot 6\,{\rm WO_3}\,({\rm aq.}) &+ 6\,({\rm CN_sH_0}){\rm Cl} &+ 6\,{\rm CO_2} \\ && 1975.6 && {\rm S13.1} \end{array}$

A boiling aqueous solution of 0.06 moles of guanidinium carboate is gradually treated (stirring) with 0.06 moles of fine yellow tangstic acid powder (not too strongly ignited). The tungstic acid dissolves. The solution is filtered, and 0.06 moles of HCl is added to the clear filtrate. The nascent precipitate is redissolved by addition of hot $H_{2}O$. Then, 0.01 moles of telluric acid is added. On cooling, the desired salt crystallizes out. It is recrystallized from hot $H_{2}O$.

PROPERTIES:

Pure white, well-formed platelike crystals. Relatively poor solubility in H_2O . Water content: 3 moles of H_2O /mole.

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STERENCE:

B. Haberle, Thesis, Univ. of Berlin, 1911.

Metatungstates, Dodecatungstates

In keeping with their molecular weight and structure, these compounds should be considered salts of a dodecatungstic acid $H_8[H_2O_4(W_3O_9)4^*aq.]$ [see, for example, G. Jander, Z. phys. Chem. (A) <u>187</u>, 149 (1940); R. Signer and H. Gross, Helv, Chim. Acta <u>17</u>, 1976 (1934); G. Schott and C. Harzdorf, Z. anorg, alig. Chem. <u>288</u>, 15 (1956)]. P. Souchay [Ann. Chim. (11) <u>18</u>, 1; 169 (1943)] terms the product obtained by acidification of a monotungstate a ψ -metatungstate. These compounds are hexatungstates, and also differ chemically from the "true" metatungstates, but they are not identical with the "paratungstates." [See G. Jander and U. Krüerke, Z. anorg, alig. Chem. <u>265</u>, 244 (1951).]

The Sodium Salt Na20 - 4803 - aq.

I.
$$5 \operatorname{Na_2O} \cdot 12 \operatorname{WO_3}(\operatorname{ag.}) + 8 \operatorname{WO_3} = 5 \left[\operatorname{Na_4O} \cdot 4 \operatorname{WO_3}(\operatorname{ag.})\right]$$

3092.2 1854.9 4947.1

A dilute solution of "sodium paratungstate" $5 \text{ Na}_{2}O \cdot 12 \text{ WO}_3$ aq, is boiled with an excess of yellow tungstic acid hydrate until a filtered sample no longer gives a precipitate of tungstic acid when treated with dil. HCI. The solution is then filtered to remove the excess tungstic acid and the insoluble white products formed during boiling. The filtrate is concentrated somewhat on a steam bath and allowed to crystallize in a desiccator over H₂SO₄.

II. The salt may be prepared more simply as follows:

$$Na_{2}WO_{4}(aq.) + 3WO_{3} = Na_{2}O \cdot 4WO_{3}(aq.)$$

293.3 695.6 989.4

A solution of 20 g. of $Na_3WO_4 \cdot 2 H_3O$ in 200 ml, of H_3O is prepared and an excess of yellow tungstic acid is added to it in portions. The suspension is boiled for about 1.5 hours, which produces white insoluble precipitates, settling out together with the excess tungstic acid. The pH of the solution after boiling and filtration is about 3. It is concentrated as described above.

SYNONYM:

Sodium metatungstate.

PROPERTIES:

Colorless tetragonal bipyramids. Water content: 10 moles of $H_2O/mole$. The crystals effloresce easily, and lose almost all their water over H_2O_4 . Readily soluble in H_2O_4 .

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MERENCES:

- 1. C. Scheibler. J. prakt. Chem. 83, 301 (1861).
- I. Authors' experiments.

The Silver Salt Agg 0 - 4 #03 + #4

Na₂O \cdot 4 WO₃ (aq.) + 2 AgNO₃ = Ag₂O \cdot 4 WO₃ (aq.) + 2 NaNO₃ 989.4 389.8 1159.2 170.0

A solution of "sodium metatungstate" Na₃O \cdot 4 WO₃ \cdot aq. is allowed to react with a solution containing the equivalent quantity of AgNOs. A white precipitate slowly crystallizes out.

PROPERTIES:

Small white scales. Water content: 3 moles of $H_2O/mole$. Quite insoluble in H_2O .

REFERENCE:

A. Rosenheim and F. Kohn, Z. anorg. Chem. 69, 250 (1911).

The Free Acid H20 · 4803 · aq.

The free acid may be isolated from a solution of $Na_2O \cdot 4 WO_3 \cdot$ aq. (see above for preparation) by Drechsel's method (see p. 1700 f.). The oily ether addition product is best distributed onto several watch glasses, which are then placed in a fast stream of dry air. The product is then rapidly dried by pressing on clay plates. This affords a relatively stable preparation, which is soluble in H₂O, forming a clear solution. Some preparations convert to yellow tungstic acid in only a few days.

Better results are obtained if the acid is prepared by ion exchange (see p. 1701) from crystalline "sodium metatungstate." A solution of 20 g. of the sodium salt $Na_2O \cdot 4 WO_3 \cdot aq$. in 50 ml. of H_2O is used. The clear eluate does not hydrolyze when concentrated in a vacuum desiccator. White crystals. Yield: 18 g.

PROPERTIES:

Formula weight 945.5. Large octahedra; according to some methors, also rhombohedra or bipyramids; readily effloresce in air. Water content: 8 moles of H_2O /mole; some authors report deviation from this value. Readily soluble in H_2O . Dilute solutions may be kept in the cold for extended periods of time, but coagulation occurs on heating. Concentrated solutions often coagulate

even at moderately high temperatures. Because of its constitution and chemical behavior, this acid should be considered a heteropoly compound.

REFERENCES

A. Rosenheim and F. Kohn, Z. anorg. Chem. <u>69</u>, 253 (1911); G. Jander and D. Ertel. Unpublished experiments.

12-Molybdic Acid-1-Silicates

In keeping with their constitution, all compounds of this composition are salts of a 12-molybdic-1-silicic acid H₄[SiO₄ (Mo₃O₉)₄ · aq.] [J. W. Illingworth and J. F. Keggin, J. Chem. Soc. (London) <u>1935</u>, 575].

The Sodium Salt 2Na20 · SiO2 · 12MoO3 · aq.

The procedure given below affords a nitric acid-soluble solution of the sodium salt, which is the starting material for the preparation of the rubidium or cesium salts. Since this solution of the sodium salt also contains a very large quantity of NaNO₃, it cannot be used directly for the preparation of the crystalline sodium salt or the free acid (by Drechsel's method).

Solid NaOH (60 g.) is dissolved in 400 ml. of boiling H_2O and a total of 172 g. of MoO_3 (free of ammonium salt) is added in portions during the course of 10-15 min. When this is completely dissolved, boiling is interrupted and 500 ml. of cold H_2O is poured in. Then 250 ml. of HNO_3 (d 1.39) is made up to 350 ml. with water, and portions of this are rapidly added to the molybdate with constant stirring. No appreciable amount of precipitate should form. The sodium silicate solution described below is added immediately for a thin stream and with constant stirring.

The sodium silicate solution is made by dissolving 28 g; of \approx commercial crystalline Na₂SiO₃ • 9 H₂O in 125 ml, of 2N NaOH and boiling 10-15 minutes to effect conversion to the monosilicate.

The solution of 2 Na₂O \cdot SiO₂ \cdot 12 MoO₃ is intensely yellow and is not as stable as solutions of other heteropolysalts. It is therefore advisable to maintain the conditions specified above; particularly as far as the H⁺ concentration is concersed. A solution of the sodium salt is used in the potassium industry for recovering rubidium and cesium from carnallite. Formula weight 1911.5.

REFERENCE:

G. Jander and F. Busch. Z. anorg. allg. Chem. 187, 173 (1930).

The Rubidium Soli 2Rb20 · SiO2 · 12MoO3 · aq.

The Cesium Salt 2Cs20 - SiO2 - 12MoO3 - aq.

$$\begin{array}{rl} 2 \operatorname{Na_{2}O} \cdot \operatorname{SiO_{2}} \cdot 12 \operatorname{MoO_{3}}\left(\operatorname{aq.}\right) &+ 4 \operatorname{RbCl} \left[4 \operatorname{CsCl} \right] \\ & 1911.5 & 483.8 & 673.5 \\ &= 2 \operatorname{Rb_{2}O} \cdot \operatorname{SiO_{2}} \cdot 12 \operatorname{MoO_{3}}\left(\operatorname{aq.}\right) & \left[2 \operatorname{Cs_{2}O} \cdot \operatorname{SiO_{2}} \cdot 12 \operatorname{MoO_{3}}\left(\operatorname{aq.}\right) \right] &+ 4 \operatorname{NaCl} \\ & 2161.4 & 2351.1 & 233.8 \end{array}$$

A mitric acid solution of the sodium salt described above is treated at about 65°C with a solution of RbCl or CsCl. Cooling to 40-50°C gives a fine yellow crystalline precipitate of the rubidium or cesium salt.

PROPERTIES:

Fine yellow powder. Relatively poor solubility in cold H_2O_3 , better in hot.

REFERENCE:

G. Jander and H. Faber. Z. anorg. alig. Chem, 179, 323 (1929).

12-Malybdic Acid-1-Phosphates

In keeping with their structure, compounds of this class should be classified as salts of 12-molybdic-1-phosphoric acid $H_0[PO_4(Mo_3O_9)_4 \cdot aq.]$ [J. W. Illingworth and J. F. Keggin, J. Chem. Soc. (London) <u>1935</u>, 575).

The Amagnium Salt 3(NH4)20 · P205 · 24MoO3 · aq.

$$2 [5 (NH_4)_7O \cdot 12 MoO_3 (aq.)] + 2 Na_4 HPO_4 + 18 HNO_3$$
3675.6 284.0 1134.4
$$= 3 (NH_4)_7O \cdot P_2O_4 \cdot 24 MoO_3 (aq.) + 14 NH_4NO_3 + 4 NaNO_3$$
3758.0 1120.7 340.0

A solution of 50 g. of Na₂HPO₄ in a mixture of 300 ml, of mixture acid (d 1.48) and 300 ml, of H_2O is prepared, cooled and

mixed with a clear, cold solution of 200 g. of commercial animonium molybdate [this generally is $5 (NH_4)_2 O \cdot 12 MOO_3 \cdot aq.;$ see p. 1711] in the minimum of H_2O ; the last solution is added in a thin stream and with stirring. A precipitate forms immediately. It is washed with hot H_2O to which a few drops of conc. HNO₃ have been added.

The ammonium salt is of value in analytical chemistry, where it is used for the determination and separation of phosphoric acid.

PROPERTIES:

Deep yellow, microcrystalline salt, soluble with great difficulty.

REFERENCE:

F. Kehrmann. Z. anorg. Chem. 7, 417 (1894).

The Free Acid P2O5 · 24MoO3 · aq.

 $2 H_{5}PO_{4} + 24 M_{0}O_{5} \approx P_{2}O_{5} \cdot 24 M_{0}O_{4}$ (ag.) 196.0 3454.8 3596.6

About 35 g. of MoO_3 is added in portions to a boiling solution of 6.3 g. of 25% phosphoric acid in 100 ml. of H₂O, and the boiling is continued for another 2-2.5 hours. The insolubles are removed by filtration and the yellow solution is shaken with ether to purify the crude product. It is unnecessary to add acid here. Further workup is the same as on p. 1701. Yield: about 20 g. The crystals thus obtained may be recrystallized from a small amount of hot water to which some HNO₃ has been added.

The success of the preparation depends on the availability of ammonium-free MoO_3 . Commerical MoO_3 frequently contains some ammonium ions. To purify this material, the proper quantity is dissolved in an excess of pure aqueous NaOH and the solution is boiled until NH₃ can no longer be detected. The molybdic acid is reprecipitated by careful addition of conc. HNO₃. It is freed of HNO₃ and NaNO₃ by several decantantions with water and filtered out.

PROPERTIES:

Well-formed orange-yellow octahedra. Very readily soluble in H_2O . Water content: 63 moles of H_2O /mole. Melting range 78 to 98°C. Other hydrates also exist. NEFERENCE:

A. Rosenbeim and J. Jaenicke, Z. anorg. allg. Chem. 101, 248 (1917). Checked by the present authors.

The Barium Salt 3 BaO + P2O5 + 24 MoO3 + #4-

This salt is obtained by treatment of the free acid with BaCl₂ solution.

 $\begin{array}{rl} P_{y}O_{x} \cdot 24 \ \text{MoO}_{3} \ (\text{aq.}) \ \stackrel{2}{\rightarrow} \ 3 \ \text{BaCl}_{2} \ \ + \ 3 \ \text{H}_{4}O \\ & & & & & \\ & & & & 54.0 \\ & & & & & & 3 \ \text{BaO} \cdot P_{z}O_{3} \cdot 24 \ \text{MoO}_{3} \ (\text{aq.}) \ \ + \ \ 6 \ \text{HCi} \\ & & & & & \\ & & & & & 4056.8 \end{array}$

A clear conc. solution of the free acid is mixed with excess hot, saturated BaCl₂ solution. The barium salt separates at once as coarse crystals. These are filtered out and washed with small amounts of cold H_2O , then recrystallized twice from hot H_2O to which some HNO₃ has been added.

PROPERTIES:

Lemon-yellow octahedra; appreciably soluble in H₂O,

REFERENCE:

F. Kehrmann, Z. anorg. Chem. 7, 417 (1894). Checked by the present authors.

18-Molybdic Acid-2-Phosphates

By analogy with the 18-tungstic acid-2-phosphates, compounds of this class should be classified as salts of an 18-molybdic-2**phosphoric** acid $H_5[(PO_4)_2(Mo_3O_9)_5 \cdot aq.].$

The Free Acid P205 + 18 MoO3 + aq.

The sodium salt of 18-molybdic-2-phosphoric acid is prepared first.

 $\begin{array}{rcl} 2 \operatorname{Na_{s}PO_{4}} &+& 18 \operatorname{MoO_{3}} &=& 3 \operatorname{Na_{t}O} \cdot \operatorname{P_{t}O_{5}} \cdot 18 \operatorname{MoO_{3}} (\operatorname{aq.}) \\ 327.9 & & 2591.1 & & 2919.0 \end{array}$

The free acid is then obtained by Drechsel's method. Since the resulting product is still contaminated with 12-molybdic-1-phosphoric acid, the pure 12-molybdic-1-phosphoric acid is pre-

A boiling solution of Na₃PO₄ is treated with portions of MoO₃ $(Na_3PO_4:MoO_3 mole ratio = 1:9)$. The solution is filtered and concentrated to a small volume. Any reduction products present are oxidized by means of some bromine water. The free acid is obtained from the solution by extraction with ether and HCI (see p. 1700 f.). The 18-molybdic-2-phosphoric acid thus prepared is never pure, but still contains rather large amounts of 12molybdic-1-phosphoric acid. Therefore the aqueous solution of the acid is treated with sirupy phosphoric acid, the latter being added in a quantity corresponding to the amount missing in the formula. (Roughly, it may be assumed that about 1/3 of the heteropolyacid product is still in the form of 12-molybdic-1phosphoric acid. To convert this, two moles of HaPO4 are required for three moles of P2O5.24 McO3.aq.) The aqueous solution is allowed to stand until NH4 or K salts cause no further precipitation. The free 18-molybdic-2-phosphoric acid then separates out in a vacuum desiccator over conc. H_SO4.

SYNONYM:

Luteophosphomolybdic acid,

PROPERTIES:

Formula weight 2733.06. Orange-colored prisms, readily soluble in H_2O . Several hydrates exist; various water contents are reported by individual authors. Quite unstable; an equeous solution soon reverts to 12-molybdic-1-phosphoric acid.

REFERENCE:

G. Jander and E. Drews. Z. phys. Chem. (A) 190, 228 (1942).

The Potassium Salt 3K20 - P205 - 18MoO3 - aq.

May be obtained from a solution of the free acid by salting gut with solid KCl.

A solution of 18-molybdic-2-phosphoric acid, as concentrated as possible, is treated in the cold with KCl powder until the desired potassium salt separates as a yellow precipitate.

PROPERTIES:

Formula weight 3015.64. Orange yellow, prismatic crystals, weight water content: 14 moles of H₂O/mole. Soluble in H₂O.

REFERENCE:

F. Kebrmann, Z. anorg. Chem. 7, 147 (1894). Checked by the present authors.

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12-Molybdic Acid-1-Arsenates

By analogy to the 12-molybdic acid-1-phosphates, which they very closely resemble, all compounds of this class should be classified as salts of a 12-molybdic-1-arsenic acid $H_5[AsO_4(Mo_3O_5)_4 \cdot aq.].$

The Potassian Salt 3K20 . As205 . 24MoO3 . aq.

Commercial ammonium molybdate $5 (NH_4)_2 O \cdot 12 MoO_3 \cdot aq.$ (see p. 1711) is heated with an excess of aqueous KOH, forming a solution of K₂MoO₄ · aq. Addition of HNO₃ and As₂O₃ yields the desired salt.

 $\begin{array}{rcl} \underline{34 \ K_{3}MoO_{4}(aq.) & \top & As_{4}O_{5} & \neg & 42 \, HNO_{5} \\ & & & \\ & & 5715.4 & 229.82 & 2646.8 \\ & & & = & 8 \, K_{2}O \cdot As_{2}O_{5} \cdot 24 \, MoO_{5}(aq.) \, + \, 42 \, KNO_{3} \\ & & & & \\ & & & 3967.2 & 4248.2 \end{array}$

Commercial ammonium molybdate (39 g.) is heated in a porcelain dish with an aqueous solution of KOH (one part of KOH by weight to two parts of H_2O) until all NH_2 has been driven off. (An excess of KOH should be avoided, since excessive quantities of KNO₃ are then formed during the reaction; this can crystallize out under some circumstances and contaminate the product.) After cooling, the solution is diluted with 50 ml. of H_2O and slowly poured into an excess of conc. HNO_3 ; external cooling may be used if required. The solution remains clear. It becomes deep yellow on addition of the stoichiometric quantity of As_2O_5 in 50 ml. of H_2O . It is briefly heated to $60-70^{\circ}C$ to produce a yellow precipitate, more of which appears on cooling. Yield: about 8 g.

PROPERTIES:

Fine, yellow crystalline powder. Water content: 12 moles of $H_2O/mole$. Not particularly soluble in cold water, somewhat more soluble in bot.

REFERENCE:

O. Pufahl. Thesis, Univ. of Leipzig, 1888. Checked by the present authors.

18-Molybdic Acid-2-Arsenates

By analogy with the 18-molybdic acid-2-phosphates, these compounds should probably be classified as saits of an 18-molybdic-2-arsenic acid $H_{6}[(AsO_{4})_{2}(Mo_{3}O_{9})_{6} \circ aq_{*}]_{*}$.

The Sodium Sail 3Na20 · As205 · 18MoO3 · aq.

Since the 18-molybdic acid-2-arsenates are more stable than the 12-molybdic acid-1-arsenates, $3 \text{ Na}_2\text{O} \cdot \text{As}_2\text{O}_5 \cdot 18 \text{ MoO}_3 \cdot \text{ag}_3$ is produced when a sodium arsenate solution is treated with excess MoO₃.

 $\frac{2 \operatorname{Na_3AsO_4} + 18 \operatorname{MoO_3} = 3 \operatorname{Na_2O} \cdot \operatorname{As_1O_5} \cdot 18 \operatorname{MoO_3} (\operatorname{aq.})}{415.8}$ $\frac{2591.1}{3006.9}$

A solution of Na_3AsO_4 is saturated with MoO₅ at the boil, and boiling is continued for some time. The deep-yellow solution is then filtered and concentrated. The desired sodium salt precipitates as yellow crystals.

PROPERTIES:

Yellow monoclinic crystals. Water content: 23 or 24 moles of $H_2O/mole$. Soluble in H_2O .

REFERENCE:

A. Rosenheim and A. Traube. Z. anorg. allg. Chem. 91, 92 (1915).

The Free Acid As205 + 18Mo Og + aq.

I. Drechsel's method (see p. 1700) (that is, extraction of a solution of the sodium salt with HCl and ether) is used.

II. $18 \operatorname{BaMoO_4} + \operatorname{As_{gO_5}} + 18 \operatorname{H_{sSO_4}} = \operatorname{As_{s_2O_5}} \cdot 18 \operatorname{MoO_3}(aq) + 18 \operatorname{BaSO_4}$ 5351.6 229.8 1763.4 2820.9 4201.6

Preparation of BaMoO₄: About 50 g. of commercial ammonium molybdate is dissolved in about 300 ml. of boiling H₂ (some ammonia is added). This solution is introduced gradually into a solution of 100 g. of Ba(OH)₂ · 8 H₂O in 300 ml. of H₂O heated on a steam bath. The mixture is heated and stirred for 2-3, hours longer. The white precipitate is washed several times with hot H₂O, then heated once more with baryta water [aqueous Ba(OH)₂] and thoroughly washed.

The BaMoO₄ is suspended in a solution of arsenic acid so that one g.-atom of As is present per nine moles of MoO₃. Then the Ba is precipitated by addition of the stoichiometric quantity of H₂SO₄ (mechanical stirring). The filtered yellow solution is concentrated in vacuum at about 40°C and crystallized over conc. H₂SO₄.

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PROPERTIES:

Deep-red triclinic crystals; decompose readily when stored the triclinic crystals; decompose readily when stored the tricline to the tricline tricline to the tricline trine tricline tricline trise trine tric

REFERENCES:

A. Rosenbeim and A. Traube. Z. anorg. allg. Chem <u>91</u>, 91 (1915); O. Pufahl. Thesis, Univ. of Leipzig, 1888.

6-Molybdic Acid-2-Arsenates

According to molecular weight studies, the compounds of this class are salts of a 6-molybdic-2-arsenic acid $H_6[(AsO_4)_2(Mo_3O_9)_2 \cdot aq.]$ [G. Jander and E. Drews, Z. phys. Chem. (A) <u>190</u>, 219 (1942)].

The Free Acid As20s - 6MoO3 - Aq.

 $\begin{array}{rrrr} 6 \text{ BaMoO}_4 + \text{ As}_2 \text{O}_5 + 6 \text{ H}_2 \text{SO}_4 = \text{ As}_2 \text{O}_5 \cdot 6 \text{ MoO}_5 (\text{aq}.) + 6 \text{ BaSO}_4 \\ 1783.9 & 229.8 & 588.5 & 1093.5 & 1400.5 \end{array}$

A solution of 2.6 g. of As_2O_5 in 200 ml. of boiling H_2O is prepared; the hot solution is poured onto 20 g. of $BaMoO_4$ (one g.-atom of As per three moles of MoO_3). A solution of 6.6 g. of conc. H_2SO_4 in about 20 ml. of H_2O is added, and the mixture is heated for one hour on a steam bath (stirring). The $BaSO_4$ precipitate is filtered off, and the clear (sometimes greenish) solution is concentrated in a vacuum desiccator until crystallization.

PROPERTIES:

Large, fragile, coloriess crystalline scales. Water content: 18 moles of $H_2O/mole$. Soluble in H_2O . The compound is a strongly held, very stable complex.

REFERENCE:

O. Pufahl, Thesis, Univ. of Leipzig, 1888, Checked by the present authors.

The Sodium Salt NagO - AngOs - 6 Mo Og - aq.

A solution of sodium paramolybdate $5 \text{ Na}_3 \text{O} \cdot 12 \text{ MoO}_3 \cdot \text{aq}$. Is treated with the stoichiometric quantity of $\text{As}_3 \text{O}_5$, and the salt

is synthesized by addition of HCl. However, only half of the theoretical quantity of HCl is used, since otherwise the sait decomposes.

A solution of "sodium paramolybdate" is prepared by dissolving three moles (431.9 g.) of MoO_3 in three moles (120.0 g.) of NaOH. One mole of H_3AsO_4 is added, and the clear solution is gradually treated with one mole of HCl. The desired salt crystallizes out on concentrating the solution.

PROPERTIES:

Formula weight 1155.5. Transparent, lustrous prisms. Water content: 12 moles of $H_2O/mole$. Readily soluble in H_2O .

REFERENCE:

A. Rosenheim and A. Traube. Z. anorg. allg. Chem. 91, 88 (1915).

12-Molybdic Acid-2-Chromites

The Ammonium Salt $3(NH_4)_2 O \cdot Cr_2 O_3 \cdot 12M_0 O_3 \cdot aq.$

 $5 (NH_4)_2 O \cdot 12 MoO_3 (aq.) + 2 KCr(SO_4)_2 (aq.) + H_3O$ 1987.8 586.5 18.0 $= 3 (NH_4)_2 O \cdot Cr_2O_3 \cdot 12 MoO_3 (aq.) + 2 KHSO_4 + 2 (NH_4)_3 SO_4$ 2035.7 272.3 284.3

A solution of 2 g, of $KCr(SO_4)_2 \cdot 12 H_3O$ in 20 ml. of H_3O is heated to boiling and a solution of 30 g, of ammonium paramolybdate 5 $(NH_4)_2O \cdot 12 MOO_3 \cdot aq$, in 110 ml, of H_2O is slowly added. During this operation the color of the solution changes from green to brownish and then bluish-rose. The pH of the solution should be about 5. On cooling, the desired rose-colored salt crystallizes out, although it sometimes takes 24 hours for this to occur. Yield: about 6 g.

PROPERTIES:

Relatively large, rose-colored rectangular platelets or scales. Water content: 20 moles of $H_2O/mole$. Quite soluble in hot H_2O , somewhat poorer solubility in cold H_2O . A relatively weak complex.

100.49

REFERENCE:

A. Rosenheim and H. Schwer. Z. anorg. allg. Chem. <u>89</u>, 226 (19) 4. Checked by the present authors. 6-Molybdic Acid-1-Periodates

These compounds are salts of a 6-molybdic-1-periodic acid H=[10. • 6 MoO3 • aq.] [G. Jander and K. F. Jahr, Kolloid-Beihefte 41, 305 (1935)].

The Solium Salt 5Na2O - 12O7 - 12MoO3 - aq.

 $\frac{2 \operatorname{Na_{z}H_{3}|O_{s}} + 12 \operatorname{MoO_{s}} + 3 \operatorname{Na_{z}CO_{s}}}{543.9} = 5 \operatorname{Na_{z}O} \cdot I_{2}O_{7} \cdot 12 \operatorname{MoO_{s}}(aq.) + 3 \operatorname{CO}_{2}}{2393.6}$

It has been found advisable to use two moles of Na₂CO₃ rather than the three moles called for by the equation.

A mixture of 10 parts by weight of $Na_2H_3IO_6$ and almost 32 parts of MoO_3 in about 120 parts of H_2O is heated. After a short time Na_2CO_3 (four parts) is added. When solution is complete, the liquid is concentrated to a small volume. Well-formed white, rhombohedral crystals appear, together with many-faceted, somewhat yellowish prisms.

PROPERTIES-

The rhombohedral crystals effloresce easily in air, becoming pure white and opaque. Water content: 34 moles of $H_2O/mole$. Readily soluble in H_2O .

The asymmetric, lustrous yellowish prisms do not effloresce in air. Water content: 26 moles of $H_2O/mole$. Soluble in H_2O .

The Free Acid 1207 · 12MoO3 · ag.

The free acid can be prepared by ion exchange (see p. 1701). Thus, 25 g, of $5 \operatorname{Na_2O} \cdot 1_2 \operatorname{O_7} \cdot 12 \operatorname{MoO_3} \cdot \operatorname{aq}$. is dissolved in 100 ml. of H₂O. After passage through the column, the eluate is clear and colorless. Gas evolves during concentration in a vacuum desiccator. A bright-yellow crystalline compound is obtained. Yield: 22 g.

PROPERTIES:

Bright-yellow crystals; moderately soluble in cold H₂O, readily soluble in bot.

SEPERENCES:

C. W. Blomstrand. Z. anorg. Chem. <u>1</u>, 10 (1892); G. Jander and D. Ertel. Unpublished experiments.

48-Vanadic Acid-2-Phosphates and

24-Vanadic Acid-2-Phosphates

It was concluded from chemical and physicochemical studies that the anions of these heteropolyacid compounds consist of phosphate ions and ions of octavanadic acid $H_{10}(V_8O_{25} \cdot aq.)$ in varying molecular ratios [G. Jander and K. F. Jahr, Kolloid-Beihefte <u>41</u>, 324 (1935)]. Other authors obtained compounds which they classify as salts of a 12-vanadic-1-phosphoric acid $H_7[PV_{12}O_{36} \cdot aq.]$ [A. Rosenheim and M. Pieck, Z. anorg. allg. Chem. <u>98</u>, 223 (1916); P. Souchay and S. Dubois, Ann. Chimie (12) <u>3</u>, 88 (1948)].

In addition to the compounds described here, there exists an immense number of salts of other compositions. The composition of the crystalline salt depends essentially on the molar ratio of phosphoric and vanadic acids in the starting solution, and also on the R⁺ concentration, the nature of the cation, and the absolute concentration.

The brownish-red heteropolyacid compounds of this class, rich in vanadic acid, are designated in the older literature as "purpureophosphovanadates."

The Sodium Salt 10 Na20 - P205 - 24 V205 - eq.

Prepared by combining solutions of NaVO₃. Na₂HPO₄ and HNO₃. Thus, the solution used is 0.75M in sodium metavanadate (NaVO₃ · aq.), 0.315M in Na₂HPO₄, and 1.125M in HNO₃ (these quantities do not take the reaction into account); it therefore contains 2.38 moles of vanadic acid per mole of phosphoric acid. This deep-red solution is treated with 1/5 its volume of acetone and allowed to stand in the cold. After a while, the desired salt crystallizes out.

PROPERTIES:

Formula weight 5128.5. Small, dark-red octahedral crystals. Soluble in H_2O . Like all "purpureophosphovanadates," it is quite susceptible to hydrolysis; excessive heating of the solution must be avoided.

REFERENCE:

G. Jander and K. F. Jahr. Kolloid-Belhefte 41, 332 (1935).

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The Barium Salu 10 BaO - P2O5 - 24 V2O5 - aq.

$$\begin{array}{rl} 10 \ N_{a_2}O \cdot P_aO_s \cdot 24 \ V_aO_s \ (aq.) \ + \ 10 \ Ba(NO_s)_s \\ & 5136.5 \\ & = \ 10 \ BaO \cdot P_aO_s \cdot 24 \ V_aO_s \ (aq.) \ + \ 20 \ NaNO_s \\ & 6041.2 \end{array}$$

A solution prepared in the same way as described for the sodium sait (50 ml.) is treated with 100 ml. of 0.375N Ba(NO₃)₂ solution and about 1/5 its volume of acetone. After standing for some time, the barium salt crystallizes out.

PROPERTIES:

Deep-red cubic crystals; poor solubility in H₂O.

REFERENCE:

G. Jander and K. F. Jahr. Kolloid-Beihefte 41, 332 (1935).

The Potassium Salt 17K20 · 2P205 · 24V205 · aq.

The Ammonium Salt 5(NH4)20 · 2P205 · 24 V205 · aq.

These are obtained from solutions of the sodium salt 10 Na₂O \cdot P_{2O5} \cdot 24 V_{2O5} \cdot aq. by means of KNO₃ or NH₄NO₃.

The same solution as described above in the case of the sodium salt (50 ml.) is treated with 100 ml. of $0.375N \text{ KNO}_3$ solution or $0.375N \text{ NH}_4\text{NO}_3$ solution and 1/5 its volume of acetone. After standing for some time, the desired salt crystallizes out.

PBOPERTTES:

Formula weight of 11 $K_2O \cdot 2 P_2O_5 \cdot 24 V_2O_5 : 5685.5$; formula weight of 5 (NH₄)₂O $\cdot 2 P_2O_5 \cdot 24 V_2O_5 : 4909.9$. The potassium salt crystallizes in deep red rhombohedra, the ammonium salt in six-sided columns. Both are soluble in H₂O,

REFERENCE:

G. Jander and K. F. Jahr. Kolloid-Beihefte 41, 332 (1935).

: **P** SECTIO . **4** 4 Carbonyl and Nitrosyl Compounds 3.05 F. SEEL

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General Introduction

The classical method for the preparation of Mo, Fe, Co and Ni carbonyls consists of a direct reaction of CO with the respective metal at high pressures (150-200 atm.) and temperatures (100-200°C). Under these conditions steel is generally attacked by CO with formation of $Fe(CO)_5$, so that pressure vessels fully lined with a CO-resistant material (e.g., copper-silver alloy) must be used. Since such special autoclaves are not normally found in general-purpose chemical laboratories, this compilation of carbonyl syntheses will be restricted to preparative methods which are compatible with the usual laboratory apparatus, i.e., atmospheric-pressure syntheses or those requiring simple steel autoclaves.

With this goal in mind, several completely new methods were worked out (i.e., for Ni(CO)₄, [Co(CO)₄]₂Hg, Co(CO)₃NO), while in the case of others [Fe(CO)₄H₂, Co(CO)₄H] the apparatus used was improved. All methods were rechecked. For this we thank especially W, Hieber and his co-workers.

Descriptions of specific autoclaves for preparation of carbonyl compounds may be found in L. Mond, Z. anorg. Chem. <u>58</u>, 207 (1910) and W. Hieber, H. Schulten and R. Martin, Z. anorg. allgo Chem. <u>240</u>, 261 (1939).

Chromium, Molybdenum, Tungsten Carbonyls

Cr(CO), Mo(CO), W(CO).

The hexacarbonyls of the chromium group are formed via reaction of CO with a suspension of anhydrous halides of Cr. Mo or W in a Grignard solution, followed by hydrolysis. The reaction mechanism has not yet been elucidated.

The reactor vessel *j* in Fig. 343 is a one-liter flask fitter with a two-hole rubber stopper. The dropping funnel what a

considerably enlarged tip to prevent plugging during the reaction. **R** is used for the addition of the Grignard solution (via a), as well as that of CO (at b). Stopcock h is a gas vent which remains **cornally closed** during the reaction but which is occasionally opened to allow flushing the reactor with CO. Flask f is fitted exactly into the ice bath c, and the whole apparatus is vigorously shakes on a machine. To monitor the CO consumption, a standardised gasometer is connected to b via a drying train (whose last tube is filled with P_2O_5).

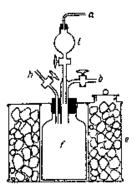


Fig. 343. Preparation of hexacarbonyls of the chromium group. *a* and *b* inlet tubes; *e* ice bath; *f* reactor vessel; *t* dropping funnel. Note that the tip of funnel *t* should be enlarged.

The reactor flask f is filled with nitrogen. The metal chloride (10 g. of fine anhydrous CrCl₃ powder; 17 g. of sublimed MoCl₅; or 20 g. of WCl₆ (0.05 moles)) is introduced, and the vessel is evacuated and filled with CO. A mixture of 50 ml. of anhydrous ether and 50 ml. of anhydrous benzene is added through the dropping funnel and the apparatus is then connected to the CO line.

The Grignard reagent is prepared from 12 g. (0.5 moles) of Mg. 54 g. of C_2H_BBr and approximately 300 ml. of anhydrous ether. This solution is added to the metal chloride suspension first in portions of about 5 ml. each, later dropwise. The initiation of the CO reaction as well as its progress may be observed via a wash bottle containing some conc. H_2SO_4 provided the stopcock of t is closed. The absorption of CO, which for reasons unknown occasionally slows down and then accelerates, is continued for about 4-6 hours after the addition of all of the Grignard reagent. The reaction absorbs on the average 7 liters and occasionally up to 9 Mers of CO.

The reddish-brown reaction product is hydrolyzed by cautisite addition to a mixture of ice and dilute H_3SO_4 , and the mixture in then steam-distilled without prior removal of ether and benzene) The steam distillation is continued for 3-4 hours or as long as white needles of the carbonyl product are observed in the (descending) condenser. The organic layer (benzene-ether) in the distillate is separated and the aqueous phase extracted 3-4 times with fresh ether. The combined ether extracts are concentrated by distillation, keeping the temperature below 60°C, and the residue is allowed to crystallize in a refrigerator.

The yields of crude carbonyls are quite variable: in the case of $Cr(CO)_6$ they are 2 g. maximum, while up to 3-4 g. of $W(CO)_6$ may be isolated. Higher yields of $Cr(CO)_6$ (up to 67%) are obtained in an autoclave under high CO pressure (35-70 atm.). To remove strongly adhering, odorous organic impurities, an immediate vacuum sublimation of the hexacarbonyls is recommended.

. 84

PROPERTIES:

Formula weight of $Cr(CO)_5$: 220.1; of $Mo(CO)_5$: 264.0; of $W(CO)_5$: 352.0. Colorless, strongly refractive orthorhombic crystals which are isomorphic among themselves; well soluble in inert organic solvents and sublimable. $Cr(CO)_5$ melts at 149-50°C in a sealed tube. The hexacarbonyls are remarkably stable in comparison to all other metal carbonyls. Their vapors decompose above 120°C in a combustion tube, depositing the metals as mirrors.

REFERENCES:

W. Hieber and E. Romberg. Z. anorg. alig. Chem. <u>221</u>, 321 (1935);
 B. B. Owen, J. English, Jr., H. C. Cassidy and A. V. Dundon.
 J. Amer. Chem. Soc. <u>69</u>, 1723 (1947).

iron Pentacarbonyl

Fe(CO)₆

Iron carbonyl is an industrial product which is prepared by classical carbonyl synthesis from CO and finely divided iron:

 $F_6 + 5 CO = Fe(CO)_5$ 55.9 112.0 l, 195.9

This material serves as the starting substance for work in the field of iron carbonyls; laboratory preparation is not worthwhile since it requires the special autoclaves mentioned on page 1748 There is, however, a method for the preparation of small quantities of $Fe(CO)_6$ in which a regular laboratory autoclave may be used; it starts with $Fe(CO)_4I_2$ (see p. 1751):

 $3 \operatorname{Fe}(\operatorname{CO})_{1} + 10 \operatorname{Cu} = 10 \operatorname{Cul} + 4 \operatorname{Fe}(\operatorname{CO})_{8} + \operatorname{Fe}_{2108,5} = 636 = 783.6$

An intimate mixture of equal weights of $Fe(CO)_4I_3$ and copper dust is heated in a CO stream. The initial temperature is 40°C. It is then increased to 55°C and the $Fe(CO)_5$ (30% yield) is condensed in a U tube at -50°C.

If an autoclave at about 10 atm. pressure is used, the yield becomes nearly quantitative since the decomposition reaction

$$Fe(CO)_{J_{*}} = FeI_{*} + 4CO$$

which occurs at atmospheric pressure, becomes impossible. Iron pentacarbonyl can then be distilled directly from the reaction vessel.

PROPERTIES:

At room temperature yellow, oily liquid, d^{20} 1.46. Vapor pressure equation in the range of 0 to 102.7°C.: log p = 7.349--1681/T. At -25°C, solidifies to monoclinic needles; distills without decomposition at 102.6°C and 760 mm.; crit. temp. 265-288°C. Produces a metallic iron mirror on passage through a hot glass tube (200-350°C). Not altered in the dark; decomposed in light to Fe₂(CO)₉ and CO (must be stored in dark bottles). Pyrophoric in air (caution!); burns to Fe₂O₃. Nearly insoluble in water; readily soluble in many organic solvents, especially benzene, petroleum ether, ether, glacial acetic acid and acetone.

REFERENCE:

W. Hieber and H. Lagally. Z. anorg, allg. Chem. 245, 295 (1940).

Diiron Nonacarbonyl

Fe₂(CO),

Formed during decomposition of Fe(CO)₅ by light:

 $\frac{2 \operatorname{Fe}(\operatorname{CO})_{s}}{391.8} = \frac{\operatorname{Fe}_{2}(\operatorname{CO})_{9}}{363.8} + \frac{\operatorname{CO}}{22.4 l_{*}}$

A solution of 20 g. of Fe(CO)₆ in 40 ml. of glacial acetic acid for acetic anhydride) is prepared and exposed to direct sunlight

in an atmosphere of hydrogen or under vacuum. Very soon, turbidity and crystallization of $Fe_2(CO)_9$ are observed. The nascent CO is removed by flushing with H_2 or by reconcustion of the vessel. After several hours of illumination, the crystals are collected by filtration and washed with ethanol and ether. Minimum yield: 30% (5 g.). Further illumination of the mother liquors vields more $Fe_2(CO)_9$.

PROPERTIES:

Shiny, orange hexagonal platelets; d^{19} 2.085. Nearly insoluble in ether, petroleum ether and benzene; somewhat soluble in methanol, ethanol, and acetone; more readily soluble in pyridine. Stable at room temperature in dry air; on heating to 100-120°C, decomposes according to:

$$2 \operatorname{Fe}_{\underline{s}}(\operatorname{CO})_{\underline{s}} = 2 \operatorname{Fe}(\operatorname{CO})_{\underline{s}} + 2 \operatorname{Fe} + 3 \operatorname{CO}$$

SYNONYM:

Diiron enneacarbonyl.

REFERENCE:

E. Speyer and H. Wolf. Ber. dtsch. chem. Ges. 60, 1424 (1927).

Triiron Dodecacarbonyl

[Fe(CO)4]3 or Fe3(CO)12

Oxidation of $Fe(CO)_4H_2$ gives $Fe(CO)_4$. The former may be prepared and oxidized in one consecutive process.

A) PREPARATION OF Fe(CO)₄H₂ SOLUTION:

 $Fe(CO)_s + 2 NaOH = Fe(CO)_sH_e + Na_sCO_s$ 195.9 80.0 Halo Halo

A two-liter flask is filled with N_2 . Then, 14 mil. (= 20 g.) of $Pe(CO)_5$ and 60 ml. of methanol are added and againsted with a complete mixture of both liquids has been obtained. At this point, 30 ml. of 50% sodium hydroxide is added and, to avoid decompatition of the product, the mixture is cooled to 0°C. The reaction of the base with the pentacarbonyl occurs at room temperature and in completed after several minutes of shaking. Insucclinitly effort the addition of the base, the solution shows a milly tenticilly the to the formation of sodium methyl carbonate, which is only slightly soluble. Exposure to air (it is not necessary to exclude the latter completely to obtain the product) scon leads to a deep reddishbrown color.

B) OXIDATION WITH MnO2

 $3 Fe(CO)_{4}H_{4} + 3 MnO_{4} = {Fe(CO)_{4}}_{3} + 3 MnO + 3 H_{2}O$ 308.7 260.8 503.7 212.6 54.0

An aqueous suspension of MnO_2 , prepared from 35 g. of $MnSO_4$. 7 H₂O, 5.6 ml. of Br₂ and 20 g. of NaOH and purified by decantation, is added slowly with constant shaking to a freshly prepared solution of Fe(CO)₄H₂. The color of the reaction mixture changes immediately to a deep green. The excess MnO_2 is dissolved by addition of FeSO₄ in sulfuric acid or of NaHSO₃. At the end, 100 ml. of sulfuric acid (1:1) is added, resulting in a vigorous evolution of gas. After completion of the gas evolution, the solution is refluxed on a water bath for about 30 minutes. This coagulates the Fe(CO)₄; because it is hydrophobic, it floats on top of the solution as a dark green, crystalline mass. The product is collected on a fritted-glass filter, washed with hot, dilute H₂SO₄, H₂O, ethanol, and petroleum ether, and weighed in a desiccator. Yield; 90% (15-16 g.).

PROPERTIES:

Deep-green, nearly black, strongly dichroic square plates. Insoluble in water; slightly soluble (dark green color) in organic solvents such as benzene, petroleum ether, ether and acetone; more soluble in Fe(CO)₈ and Ni(CO)₄; in contrast to the other iron carbonyls, very sensitive to air. d^{16} 1.996; crystal structure: tetragonal.

BEFERENCES:

 W. Hieber. Z. anorg. allg. Chem. 204, 171 (1932); R. B. King and
 F. G. A. Stone in: Inorg. Syntheses, Vol. VII, New York-London, 1963, p. 193.

Cobalt Carbonyls

Decomposition of the hydride $Co(CO)_4H$ above its melting point gives $[Co(CO)_4]_2$:

 $2 \operatorname{Co}(\operatorname{CO})_4 H = [\operatorname{Co}(\operatorname{CO})_4]_2 + H_2$ 344.0 342.0 22.4 I.

The hydride Co(CO)_H (see p. 1753) is slowly evaporated enter CO from a bath at an initial temperature of -30°C, which

may be left unattended. Beautiful crystals of orange-red [Co(CO). is remain as a residue.

Alternate method: Direct high-pressure synthesis from Co metal and CO [L. Mond, H. Hirtz and M. D. Cowap, Z. anorg, Chem. 68, 215 (1910)].

PROPERTIES:

Orange crystals, m.p. 51°C. Insoluble in H_3O ; soluble in ethanol, ether and other organic solvents. Decomposes in air to the violet, basic Co carbonate. Melting of Co(CO)₄ results in a very slow decomposition to cobolt tricorbony! [Co(CO)₃]₄; this reaction is clearly observable at 53°C and proceeds so fast at 60°C that it is complete after two days. After recrystallization from benzens, the tricarbonyl, formed according to the equation Co(CO)₄ = Co(CO)₃ + CO, consists of deep black crystals.

CALCO MAN SAL

REFERENCE:

W. Hieber, F. Mühlbauer and E. A. Ehmann. Ber. disch. chem. Ges. <u>65</u>, 1090 (1932).

Nickel Carbonyl

Ni(CO);

Forms even under such mild conditions as the reaction of CO with an alkaline solution of NiS. However, the reaction of CO with a solution of nickel sulfoxylate-ammonia complex, NiSO₂ · (NH₃)x, is especially recommended. This solution is easily prepared from NiSO₄, NH₃ and Na₂S₃O₄.

The apparatus shown in Fig. 345 comprises a large gas-liquid mixing flask to which the shaking vessel shown in Fig. 344 can be attached. This mixing flask is attached to a large U tube filled with pea-sized calcium chloride granules and P_2O_5 deposited on glass beads. This tube is in turn attached to three condets for traps, two tees with stopcocks, and a bubble counter at the support the train. The individual parts of the apparatus may be condeted at by short pieces of rubber, provided glass touches glass; however, a ground-glass connection is required at s (this allows attaching the two condensing traps k, which are fused to each other, to a vectors line).

The mixing flask is charged with a solution of 14.0 g. (0.05 moles) of NiSO4 • 7 H₂O in 400 ml. of water and 60 ml. of 25% aqueous ammonia. The carefully predried shaking vessel is charged with 12.5 g. of 80% Na2S2O4; then 30 ml. of concentrated ammonia solution and 80 ml. of water are added under flowing nitrogen. The materials are dissolved by shaking, and the shaking vassel is attached to the mixing vessel by means of a rubber stopper, as shown in the figure. At this point CO, carefully preparified to remove traces of iron carbonyl and oxygen, is passed through the clear blue nickel (II) salt solution; after a few minutes. a dropwise flow of the ammonial dithionite solution is started. (Pressures must be constantly equalized.) The dithionite solution is added over a period of about 20 minutes. The Ni(CO)4 forms instantly and is condensed in the traps by cooling the latter with Dry Ice-acetone (or ethanol) mixture; the unreacted CO may be burned at t_2 after a reasonable flow rate has been established.

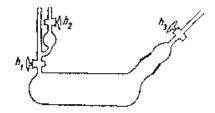


Fig. 344. Shaking vessel for work in the absence of air.

The nickel salt solution becomes nearly colorless in about 5 hours; a slight amount of decomposition, shown by the deposition of a mirrorlike layer of NiS_x on the glass walls, can not be avoided. Redistillation of the carbonyl (which condenses primarily in the first trap) in a stream of CO gives a completely pure product. Yield: 7.5 g. (5.5-6.0 ml.) of Ni(CO)₄ = 85-90\%.

PROPERTIES:

Coloriese liquid. M.p. -25°C. b.p. 43°C; d²⁰ 1.310. Crit. **See approximately 200**°C. crit. pressure 30 atm. Insoluble **in water, soluble in organic** solvents. Readily oxidized in air;

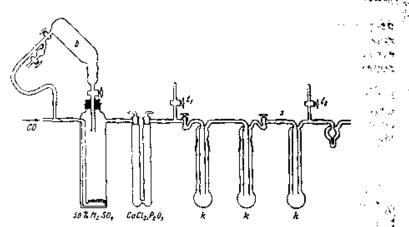


Fig. 345. Apparatus for the preparation of nickel carbonyl, carbonyl hydrides, and nitroyl carbonyls. b shaking vessel from Fig. 344; k condensing traps

burns with a luminous flame when ignited. A mixture with air is explosive. A bright Ni mirror is formed on passage through a heated tube at 180-200°C. The vapor is extraordinarily toxic.

REFERENCE:

W. Hieber, E. O. Fischer and E. Böckly. Z. anorg. allg. Chem. 269, 308 (1952).

> Dipyridine Chromium Tetrocarbonyl, Tripyridine Chromium Tricarbonyl

> > Cr(CO), py1, Cr(CO), py1

..... States

Up to one half of the CO contained in metal carbonyls one frequently be replaced by pyridine, o,o'-dipyridyl and phenanthroline.

| | | 2 py 156.2 | Cr(CO), py , 322.3 | + | 2 CO 44.81 | 90. 19 |
|------------------------------|---|---------------|-----------------------|---|-----------------|-----------|
| Cr(CO) ₈ 220.1 | + | Зру 287.3 | Cr(CO)3 py 3 373.3 | + | 3 CO 67.3 I. | • . |

A mixture of 1 g. of $Cr(CO)_6$ and 5 ml; of pure anhydrolinpyridine is heated in a sealed tube for 2 hours at 200 C. A. Fraction fraction of the $Cr(CO)_6$ separates unchanged on could be F. SEEL

theorem brown solution. The solution is filtered into a small distilling **experatus and most of the pyridine is quickly distilled off in a stream of N_R.** On cooling the residue, crystals of $Cr(CO)_4py_2$ **separate out; addition of petroleum ether increases the yield.**

If 10-15 ml, of pyridine is used in the above experiment and the heating is repeated after discharge of the CO, the product is $Cr(CO)_{3}py_{3}$. Pyridine can be substituted into $Mo(CO)_{8}$ more readily than into $Cr(CO)_{8}$; the $Mo(CO)_{8}$ is converted into $Mo(CO)_{3}py_{3}$ on heating with pyridine for several hours at 135 °C.

PROPERTIES:

 $Cr(CO)_{4}py_{3}$: Blunt, yellowish-brown prisms. On heating, loses pyridine and turns brownish-black. $Cr(CO)_{3}py_{3}$: Yellowish-red to red prisms, stable in air; gives up pyridine very readily.

REFERENCE:

W. Hieber and F. Mühlbauer. Z. anorg. allg. Chem. <u>221</u>, 341 (1935).

a-Phenanthroline Nickel Dicarbonyl

$Ni(CO)_z C_{tt} H_s N_t$

 $\begin{array}{rcl} Ni(CO)_{s} + C_{12}H_{s}N_{2} = C_{12}H_{s}N_{2} \cdot Ni(CO)_{s} + 2 CO \\ 170.7 & 180.2 & 294.9 & 44.8 \, l. \end{array}$

Readily formed from solutions of equimolar quantities of the components in acetone or absolute ethanol. The almost immediate CO generation is preceded by a blood-red color of the reaction mixture. As the gas evolution increases, the compound separates in long needles (of the order of 1 cm.). After suction-filtration, the compound is washed with absolute ethanol, followed by petroleum ether.

PROPERTIES:

Ruby-red needles with high luster; very stable. Decomposed by air only in the presence of moisture (slow process, accompanied by a green color).

SETERENCE:

W. Hieber, P. Mühlbauer and E. A. Ehmann. Ber. dtsch. chem. Ges. 55, 1098 (1932).

Iron Tetracarbonyl Halides

Fe(CO)₄X₂

I. The simplest method consists of reacting the halogens with $Fe(CO)_{B}$ in organic solvents.

Pure $Fe(CO)_4Cl_2$ can be obtained only at -20°C by slow passage of Cl_2 through a 1M solution of $Fe(CO)_5$ in petroleum ether; the slight decomposition of the $Fe(CO)_5$ does not affect the purity of the product. The product (yield ~ 60%) is a yellow powder, which loses CO at room temperature and turns gray.

 $Fe(CO)_4Br_3$ is prepared by slowly adding the reactants to a 2M petroleum ether solution, while cooling in ice and conducting the reaction under anhydrous conditions. The product is a reddishbrown powder. Yield: 75%.

 $Fe(CO)_4I_2$ is obtained in anhydrous ether solution using a slight excess of $Fe(CO)_5$ [the ether solution is 2M in $Fe(CO)_5$ and 0.5M in I_2]. On evaporation, the compound separates in large, black crystals. Yield: quantitative,

PROPERTIES:

The iron carbonyl halides are light-sensitive: water converts them to the corresponding Fe (II) salt solutions (the chloride and bromide react instantaneously, the iodide only upon heating). The thermal decomposition of iron carbonyl halides is a convenient way to produce fine powders of anhydrous Fe(II) halides.

II. $Fe(CO)_{4}I_{3}$ can be obtained from anhydrous FeI_{3} and CO(4) pressures above 6.3 atm. Thus, it can be prepared in ordinary laboratory autoclaves.

443

118 1 141

 $FeI_2 + 4CO = Fe(CO)_4I_2$ 309.7 89.6 l. 421.7

The preparation proceeds in anhydrous etheral solution, using 50 ml. of ether/g, of FeL₂; the air is displaced from the autoclase by evacuating and flushing with CO (which may be taken directly from a cylinder). While the yield is quantitative, the duration of the CO absorption depends on the surface/volume ratio in CO solution. Thus, in unagitated systems the reaction maximum sionally take several days. REFERENCES:

W. Hieber and G. Bader. Ber. dtsch. chem. Ges. <u>61</u>, 1717 (1998); W. Hieber and H. Lagally. Z. anorg. allg. Chem. <u>245</u>, 395 (1940); W. Hieber and A. Wirsching. Ibid. <u>245</u>, 35 (1940).
 H. Hieber and H. Lagally. Ibid. <u>245</u>, 305 (1940).

Iron Tetracarbonyl Dihydride

Fe(CO)₄H₁

Solutions of alkali metal, alkaline earth metal, and ammonium salts of $Fe(CO)_4H_3$ may be produced by shaking solutions or suspensions of the corresponding hydroxides with $Fe(CO)_5$ in the absence of air. Addition of acid liberates the hydride.

 $\begin{aligned} Fe(CO)_{5} + 3 NaOH &= [Fe(CO)_{4}H]Na + Na_{2}CO_{4} + H_{2}O \\ 195.9 & 120.0 & 191.9 \\ [Fe(CO)_{4}H]Na + H_{2}SO_{4} &= Fe(CO)_{4}H_{2} + NaHSO_{4} \\ 191.9 & 98.1 & 169.9 \end{aligned}$

The reaction may be conducted in the apparatus (Figs. 344 and 345) described for the preparation of Ni(CO)₄. After complete evacuation with an oil pump, the 200-ml. shaking vessel is charged with 7 ml. of Fe(CO)₅ (10 g., 0.1 moles), then with 25 g. of NaOH in 50 ml. of boiled water; the vessel walls are rinsed with some water and it is filled with oxygen-free nitrogen or CO. The reaction is complete after 5 hours of intensive mixing on a shaking machine. If no oxygen was present, a completely homogeneous, light-yellow solution of the sodium salt of Fe(CO)₄H₂ is produced. At this point, the mixing vessel is charged with 50 ml. of 50% colliuric acid, the shaking vessel is attached, and the entire apparatus is flushed with oxygen-free CO (which can be ignited at t_2 after a reasonable flow rate has been attained).

The mixing vessel is then cooled to -10 to -15 °C (ice-salt mixture) and the cold traps to -80 °C (Dry Ice-acetone). The hydride solution from the shaking vessel is then decomposed by slow, dropwise addition to the mixing vessel. The liberated hydride is carried by the CO stream into the cold traps, where it condenses as a solid (if this fails to occur, the temperatures of the cooling baths are too high or the CO flow too high). Upon termination of the decomposition the apparatus is flushed with CO until a "carbonyl flame" is no longer visible on burning at t_{23} this takes about one hour [see the section on Ni(CO)4]. The hydride collected in the first two condensation traps is not yet

pure. It contains the products of its own decomposition, $Fe(CO)_{\phi}$ and $Fe(CO)_3$, and occasionally its oxidation product $Fe(CO)_{\phi'}$ Repeated fractionation in high vacuum at -40 °C, with condensation at -80 °C, is necessary for complete purification. The removal of the last traces of $Fe(CO)_5$, which is frequently still present in small quantities (since it is re-formed during the distillation due to the extreme instability of the hydride), is achieved by repeated rapid distillation into a liquid-nitrogen-cooled vessel.

Since the isolation and purification of the free carbonyl hydride require considerable time, the acid decomposition should be started at the beginning of a full working day. $Fe(CO)_{4H_2}$ can be stored indefinitely, provided it is placed in suitable containers which are evacuated and cooled with liquid nitrogen.

PROPERTIES:

At the temperature of liquid nitrogen, a completely colorless, crystalline substance. M.p. -70 °C. The autodecomposition

$$2 \operatorname{Fe}(\operatorname{CO})_{a} \operatorname{H}_{a} \approx \operatorname{Fe}(\operatorname{CO})_{s} + \operatorname{Fe}(\operatorname{CO})_{s} + 2 \operatorname{H}_{s}$$

of the water-white, mobile liquid is already observed at -10° , as is indicated by a slight reddish color [Fe(CO)₃], but is completed only at higher temperature. The presence of even traces of Fe(CO)₃ and Fe(CO)₆ in the hydride is indicated by a weak red or yellow color; absence of color (only below -10° C) is a sensitive test for the purity of the product. The gaseous hydride has an extremely nausealing odor.

W. Hieber and H. Vetter, Z. anorg. allg. Chem. 212, 145 (1933).

An ether-soluble iron carbonyl hydride Fe₄(CO)₁₃H₂ was isolated from the reaction of pyridine-iron carbonyl with acids [W. Hieber and R. Werner, Chem. Ber. <u>90</u>, 286 (1967)].

Cobalt Tetracarbonyl Hydride

Co(CO)₄H

An alkaline suspension of $Co(OH)_2$ absorbs CO in the presence of a small amount of cyanide to form a solution of the alkaline

na Sta Ta of Co(CO), H. The hydride is then liberated from this solution with acid.

 $\begin{array}{rcl} 3 \operatorname{Co}(\operatorname{NO}_3)_{4} &+ & 11 \operatorname{CO} &+ & 12 \operatorname{KOH} \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & & \\$

The same apparatus as is shown in Figs, 344 and 345 (see preparation of Ni(CO)4) is used. Since the acid decomposition of the alkaline hydride solution produces considerable foaming, a second mixing vessel, placed in series with the first one, is recommended. The evacuated shaking vessel is charged with 14.6 g. (0.05 moles) of $Co(NO_3)_3 \cdot 6 H_3O$ in 30 ml. of water, 22.4 g. of KOH in 22 ml. of water, 10 ml. of water, 3.2 g. of KCN in 6 ml, of water (in this order), and finally with 10 ml, of water. Then stopcock h_1 is connected to a gas-liquid mixing vessel equipped with a fritted disk and containing an alkaline pyrogallol solution. The vessel is connected to a calibrated gasometer containing 6 liters of CO. After flushing the inlet piece via stopcock h_2 , the gas is admitted to the shaking vessel; the latter is flushed briefly via h_3 , h_3 is closed again, and the assembly is shaken on a machine under CO pressure. The CO absorption may be observed via the pyrogallol wash bottle: it varies with the intensity of shaking and even quantitative absorption may occasionally be achieved. During the absorption, the initially brown suspension is converted into a yellow solution which, in the case of absorption of the theoretical amount of CO, is hearly free of suspended matter and consists of a solution of Co(CO) K.

The free hydride is isolated in the same way as described in the preceding preparation of $Fe(CO)_4H_2$. On the same scale of preparation, the acid decomposition requires 50 ml. of 50% sulfuric acid. The hydride is finally sublimed from a bath maintained at -30°C to a cooler condensing trap.

PROPERTIES:

The pure solid hydride is completely coloriess and crystalline; it melts at -26.2°C to a light-yellow solution which changes to dark yellow at slightly higher temperature {beginning of decomposition to [Co(CO)₄]₂}. In gas form Co(CO)₄H has a nauseating elevant is extremely toxic. REFERENCES:

W. Hieber and H. Schulten. Z. anorg. allg. Chem. <u>232</u>, 29 (1937); A. A. Blanchard and P. Gilmont. J. Amer. Chem. Soc. <u>62</u>, 1192 (1940).

iron Carbonyl Mercury

Fe(CO)₄Hg

 $Fe(CO)_{s} + HgSO_{4} + H_{2}O = Fe(CO)_{s}Hg + CO_{e} + H_{t}SO_{e}$ 195.9 296.7 368.5

A solution of 7.5 g. (0.025 moles) of HgSO₄ in 50 ml, of 10% H_2SO_4 is shaken with 3.5 ml. (5 g.) of Fe(CO)₅ at room temperature to yield a dark-yellow, microcrystalline precipitate of $Fe(CO)_4$ Hg. The precipitate is collected by filtration, washed several times with dilute H_2SO_4 , 2-3 times with 2N HCl, then with water and acetone, and dried in vacuum,

PROPERTIES:

Insoluble in common solvents. Decomposes at about 150° C into Fe, Hg and CO. Reaction of HgCl₂ with Fe(CO)₅ gives Fe(CO)₄ Hg₂Cl₂.

REFERENCE:

H. Hock and H. Stuhlmann. Ber. dtsch. chem. Ges. <u>61</u>, 2097 (1928); <u>62</u>, 431 (1929).

Cobalt Carbonyl Mercury

[Co(CO)₄]₂Hg

Produced by reaction of solutions of a salt of $Co(CO)_{4}H$ with Hg (II) salts. The optimum preparative method requires work in an ammonia solution.

 $2 [Co(CO)_{4}]NH_{4} + HgCl_{2} = [Co(CO)_{4}]_{2}Hg + 2 NH_{4}Cl_{378.0} 271.5 542.8$

The potassium salt of Co(CO)₄H is prepared as described on page 1754. However, only one half the amount is needed. The shaking vessel is evacuated, and 25 ml. of a saturated NH164 solution (corresponding to about 10 g. of NH_4Cl) and 3.5 g. of $HgCl_2$ in 100 ml. of water are added in that order. The instantly formed ochre precipitate consists of $[Co(CO)_4]_2Hg$, $HgNH_2Cl$ and traces of Hg. The reaction flask is immediately opened; the precipitate is collected by filtration (without any special protective measures) and washed twice with water, dilute hydrochloric acid (to dissolve HgNH_2Cl) and finally again with water. The crude product is dried in a desiccator and dissolved in some acctone; water is added until persistent turbidity. The product is left in a refrigerator to crystallize.

Alternate method: Precipitation from a solution of $[Co(CO)_4]NH_4$, as prepared by the dithionite method [see section on Ni(CO)_4, p. 1747 f.] [W. Hieber, E. O. Fischer and E. Böcky, Z. anorg. alleg. Chem. 269, 308 (1952)].

PROPERTIES:

Orange needles; very stable; insoluble in water and dilute **nonoxidizing** acids; readily soluble in ethanol, ether, acetone, **benzene** and other similar solvents [in contrast to Fe(CO)₄Hg]. An easily prepared compound and an excellent starting material for the preparation of other cobalt carbonyl compounds. Thus, $[Co(CO)_4]_3$ Hg may be converted by alkali sulfides into alkali salts of Co(CO)₄H, from which the hydride itself and Co(CO)₄ may be obtained.

In a similar manner, other heavy metal derivatives of $Fe(CO)_4H$ and $Co(CO)_4H$ may be obtained by this double decomposition. Derivatives of $Co(CO)_4H$ and Zn, Cd, Hg, In, Tl are obtained directly from the metals and CO in high-pressure syntheses.

REFERENCES:

W. Hieber and H. Schulten, Z. anorg. alig. Chem. <u>232</u>, 24 (1937);
 W. Hieber and E. Fack. Ibid. <u>236</u>, 101 (1938); W. Hieber and U. Teller. Ibid. <u>249</u>, 43 (1942).

Ethylenediamine Iron Carbonyl

[Fe en;] [Fe;(CO);]

This and the next compound are complex salts of polynuclear iron carbonyl hydrides.

 $\begin{array}{rcl} 3 Fe(CO)_{6} &+ & 3 en = & [Fe en_{5}] [Fe_{4}(CO)_{6}] &+ & 7 CO \\ \\ & 567.7 & 180.2 & 571.8 & 156.8 \ . \end{array}$

This compound can be successfully prepared only under completely antydrous conditions. The ethylenediamine (not ethylenediamine hydrate) and the solvent pyridine must be completely free of water. The presence of pyridine is essential to the reaction. The apparatus shown in Fig. 346, consisting of the reaction vessel a, fritted-glass filter attachment g, and dropping funnel and adapter t, is recommended.

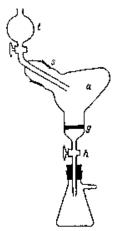


Fig. 346. Preparation of ethylenediamine iron carbonyl. *a* reaction vessel; g fritted-glass filter; *h* stopcock; s ground joint adapter; *t* dropping funnel attachment.

With vessel a pointed downward, a solution of 1.4 g. of the diamine in 20 ml. of pyridine is mixed with 8 g. of $Fe(CO)_{s}$; vessel a is closed with a ground-glass stopper at s and connected to the atmosphere via the stopcock h and a wash bottle filled with conc. $H_{3}SO_{4}$. The reaction mixture is then heated on a water bath to 80°C for four to five hours. After about one hour of heating the (now red) solution starts evolving gas bubbles and continues to do so until the reaction is finished. At end of the reaction, the solution is cooled, the dropping funnel t is connected to s, and the product, which forms in copious quantities, is filtered through g. It is washed on g with pyridine and anhydrous ether; for a final purification, it is again triturated with ether and reflitered. Xield: 2.6 g. (60% on the basis of the diamine).

SYNONYM:

Triethylenediamine iron (II) octacarbonyl diferrate (II).

PROPERTIES:

Brick-red monoclinic (or triclinic) and very shiny prisms requires stable; insoluble in organic solvents, including pyriding.

ترقد حاء

REFERENCES:

W. Hieber and F. Sonnekalb. Ber. dtsch. chem. Ges. <u>61</u>, 563 (1928);
 W. Hieber, J. Sedlmeier and R. Werner. Chem. Ber. **90**, 278 (1957).

Pyridine Iron Carbonyi [Fe pys] [Fes(CO);s] 5 Fe(CO); + 6 py = {Fe pys] {Fes(CO);s] + 7 CO \$39.4 474.6 1117.9 156.8 l.

This substance must be prepared in complete absence of air and under nitrogen; this is best done in the apparatus shown in Fig. 346.

The bulb is charged with 5 g, of $Fe(CO)_4$; the latter is then freed of the always present traces of Fe_3O_4 . This is done by pouring over it some methanol and then heating with 20% HCl on a water bath for four to six hours (no oxygen may be present). The solution is suction-filtered through the fritted glass and washed with dilute HCl, dry methanol and dry ether; the residue is dried in a high vacuum. For this final drying, the dropping funnel is replaced by a stopper at s and the apparatus connected at h to a cooled trap and the vacuum pump.

The purified $Fe(CO)_4$ is then reacted at $0^{\circ}C$ with 6 ml. of dry and air-free pyridine, the reaction taking place in the evacuated apparatus. The reaction is accompanied by foarning and evolution of CO, and ends in a short while, the green color of the $Fe(CO)_4$ solution turning intense red.

After 0.5 hour the product is collected by filtration, washed briefly with pyridine, then with dry petroleum ether and absolute ether, and dried in a high vacuum. Yield: 2.3 g. (70%), the remainder being retained in the mother liquor.

Allernate method: Direct synthesis from $Fe(CO)_5$ and pyridine in a sealed tube at 120-140 °C.

STNONYM:

Hexapyridine iron (II) tridecacarbonyl tetraferrate (II).

PROPERTIES:

Nearly black or deep-red crystals, extremely pyrophoric.

REFERENCES:

W. Hieber and E. Becker. Ber. dtsch. chem. Ges. <u>63</u>, 1414 (1930);
 W. Hieber and F. Mühlbauer. Ibid. <u>65</u>, 1088 (1932); W. Hieber and E. Werner. Chem. Ber. <u>90</u>, 286 (1957).

Potassium Nitrosyl Tricarbonyl Ferrate

[Fe(CO)₄NO]K

$Fe(CO)_{5} + KNO_{2} = [Fe(CO)_{5}NO]K + CO + CO_{2}$ 195.9 85.1 209.0

The reactor in this case is a one-liter, three-neck flask fitted with stirrer, reflux condenser and gas inlet tube. To start with, the air is completely displaced with very pure nitrogen; then, 45 g. of KNO2 is dissolved in 400 ml, of methanol with vigorous stirring (the KNO₂ is premelted and then cooled on a cold porcelain surface to give small droplets). Following this, 67 ml. (0.5 moles) of freshly distilled Fe(CO)5 is added via the condenser and the mixture is cautiously heated to 30-35°C. The reaction starts in a short while and is accompanied by vigorous evolution of gas; since the reaction is highly exothermic, it must occasionally be moderated by cooling in cold water. The gas evolution slows down in about three hours; the mixture is heated at 60°C for 30 minutes and then cooled. Finally, the stirrer and the reflux condenser are replaced by stoppers, and the solvent and unreacted carbonyl compound are distilled off in aspirator vacuum. To shorten this distillation somewhat, it is permissible to heat slightly (but very carefully).

The dry crude product can be used immediately for the preparation of $Fe(NO_2)(CO)_2$. However, there may arise a need to purify it, especially to remove excess nitrite and decomposition products. In this case, the crude product is extracted (in the absence of air and light) in a Soxhlet apparatus with 200 ml. of ether until the reflux is colorless. Evaporation of the extract under reduced pressure yields a bright-orange mass. Addition of toluene or xylene to the ether solution gives the salt as fine crystals. Yield: 60 g, of crude product, which on careful workup yields 45 g, of pure substance.

PROPERTIES:

Orange-yellow salt, very sensitive to light and air, especially when in solution. All operations, including the purification, should be conducted in a darkroom under red light. The product is kept in a vacuum desiccator lined with black paper; the desiccator is prefiushed several times with nitrogen, and is then evacuated When stored under such conditions, the preparation is stable for some time.

The socium solt is obtained in nearly quantitative yield by reaction of $Fe(CO)_s$ with NaNO₂ in absolute methanol in the presence of 2 molar equivalents of NaOCH₃ per mole of Fe(CO)₈₅.

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ALTERINCES:

W. Hieber and H. Beutner, Z. Naturforschg. <u>15b</u>, 323 (1960);
 M. J. Hogsed, C.A. <u>53</u>, 9592 (1959), U. S. Pat. 2,865,707 (1967).

Iron Dinitrosyl Dicarbonyt

Fe(NO)_t(CO)_t

KNO, - $(Fe(CO)_{3}NO)K + CO_{2} + H_{2}O - Fe(CO)_{3}(NO)_{2} + 2 KHCO_{3}$ 83.1 209.0 171.9

This compound is prepared in the same apparatus as nickel carboxyl (p. 1747 ff.; Figs. 344 and 345). First, the shaking vessel, which in this case is used as a dropping funnel, is charged with 42 g. (0.2 moles) of $[Fe(CO)_3NO]K$; after evacuation, a solution of 17 g. of KNO₂ or 14 g. of NaNO₂ in 150 ml. of water is added. Then, the shaking bulb is attached to the gas-liquid mixing vessel and the entire apparatus flushed with a moderately fast stream of air-free CO₂.

The brown nitrosyl carbonyl vapor appears the moment the solution is allowed to flow into the mixing vessel; the vapor is condensed in the Dry Ice-cooled traps, where it deposits as a bright orange coating. To speed up the transfer of the vapor to the traps, the reaction flask is heated in a water bath. However, the flask temperature should not exceed 35° C. If, as may happen (especially at the start of the experiment), some of the vapor condenses in the connecting tubes, it is driven into the cold traps by gentle heating with a hair dryer. The brown vapor disappears after a while, the preparation is stopped, and the CO₂ in the apparatus is displaced with pure nitrogen. The produce may be resublimed onto P₂O₅ in high vacuum; from there, it may be driven into ampoules, which are then stored in a freezer and protected from light to avoid decomposition. The yield is approximately 20-25 g. (60-70%).

PBOPERTIES:

beautiful deep-red crystals. M.p. 18,5°C. The liquid has a **tendency** to supercool; decomposes at 50°C. Insoluble in water, **soluble** in organic solvents; readily oxidized by air. Can be **distilled** witnout extensive decomposition only at temperatures **below** 15°C.

RESTRENCES:

W. Hieber and J. St. Anderson. Z. anorg. alig. Chem. 208, 238 (1932); 221, 132 (1933); F. Seel. Ibid. 269, 40 (1952).

Cobait Nitrosyl Tricarbonyl

Co(NO) (CO)₂

Prepared in the same way as Fe(NO)2(CO)2, that is, by reaction of the solution of Co(CO),K obtained in the cyanide process with nitrite and CO2.

 $[C_0(CO)_4]K + KNO_2 + 2CO_2 + 2H_2O = CO(NO)(CO)_4 + 2KHCO_4$ 210.1 85.1 171.0

PROPERTIES:

Cherry-red, very volatile liquid; m.p. --1.05°C, b.p. 48.6°C, decomposition temperature 55°C. Insoluble in water and very stable if kept under water; miscible in all proportions with ethanol, ether, acetone, benzene and other organic solvents,

REFERENCES:

W. Hieber and J. St. Anderson. Z. anorg. allg. Chem. 208, 238 (1932); 221, 132 (1933); F. Seel. Ibid. 269, 40 (1952).

Dinitrosyl Cobalt Halides

(NO)₂CoCl, (NO)₂CoBr, (NO)₂CoI

 $2 \operatorname{CoCl}_{2} + Z_{\mathrm{II}} + 4 \operatorname{NO} = 2 (\operatorname{NO})_{2} \operatorname{CoCl} + Z_{\mathrm{II}} \operatorname{Cl}_{4}$ 364.8 259.8 65.4 89.6 l $2 \operatorname{CoBr}_{2} + \operatorname{Zn} + 4 \operatorname{NO} = 2 (\operatorname{NO})_{2} \operatorname{CoBr} + \operatorname{ZnBr}_{2} + \cdots$ 453.8 437.6 . :**:**₽ $2 \operatorname{CoI}_{t} + 4 \operatorname{NO} = 2 (\operatorname{NO})_{t} \operatorname{CoI} + I_{t}$ 547.8 625.6

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The apparatus consists of a 70-cm,-long, 2-cm,-O.D. glass tube surrounded by a 15-cm.-long metal block with a thermometer well. The block is heated with a gas burner, the temperature being controlled automatically by means of a relay-actuated valve in the gas line, which in turn is tripped by a bimetaline element in the thermowell. The reactor tube is connected to a tee so that either dry N2 or NO2 may be passed through. The NO is generated from NaNO2 and 20% H2SO4, washed free of NGa with 50% KOH, and dried in a train consisting of flask filled with conc. H₂SO₄, CaCl₂, NaOH and P₂O₅ (in that order). All parts

of the apparatus are either connected with ground joints or fused together.

The raw material for the iodine compound consists of about 2 g. of anhydrous Col_2 placed in a porcelain boat, which is then inserted into the front part of the glass tube; the latter is then closed off with a wash bottle containing conc. H_2SO_4 . The traces of moisture carried in with the Col_2 are then removed by heating to 130°C (by means of the metal block) while passing through a stream of N_2 . After cooling, the N_3 is displaced with NO and the temperature is again raised to 70-80°C. At this point, the reaction of NO with Col_2 is so rapid that the pressure in the apparatus drops to below atmospheric; at the same time copious amounts of iodine are given off. The substance sinters and takes on a violet sheen. The temperature is now raised to 105°C and maintained at that level for 15-20 hours, that is, until the iodine vapors are displaced by brown vapors of the nascent (NO)₂CoI. The final residue in the porcelain boat is a viscous, blackishbrown mass.

The product must be sublimed. Thus, the boat is transferred, in a countercurrent stream of N_2 , to the other end of the reactor tube and the temperature is raised to 115°C. The beginning of the sublimation is noticeable by a brown deposit; at a later stage, beautiful, flexible, deep brown-black, glittering crystals, up to 15 mm, long, are formed.

The chlorine and bromine compounds are prepared in the same way, except that a halogen-trapping metal (such as Zn dust or Co powder) must be added in 20% excess.

PROPERTIES:

Formula weight of $(NO)_2CoCl$: 182.4; $(NO)_2Br$: 226.9; $(NO)_2CoI$: 273.9. After sublimation, these compounds form beautiful blackbrown needles with a diamondlike glitter; these are often 1 cm. long. Melting points: $(NO)_2CoCl$: 101°C; $(NO)_2CoBr$: 116°C; $(NO)_2CoI$: 131°C. The freshly prepared compounds are stable for some time in air; however, the crystals lose their surface sheen in several hours and then decompose over a period of days with loss of NO. The solubility in water increases in the sequence I-Br-Cl (partial decomposition).

in an analogous fashion iron (II) halides yields the dinitrosyl ime halides, (NO)₂FeX, upon which Roussin's salts are based.

REFERENCES:

W. Hieber and R. Marin. Z. anorg. allg. Chem. <u>240</u>, 241 (1939);
 W. Hieber and R. Nast. Ibid. <u>244</u>, 23 (1940).

Sodium Dinitrosyl Thioferrate*

Na[(NO),FeS] · 4 H₂O

$$2(NH_4)[(NO)_3Fe_4S_3] + 6 NaOH(·H_4O)('/_{10}): 113.1 24.0= 6 Na[(NO)_3FeS] + 2 Fe(OH)_3 + N_2O + 2 NH_3 + H_4O(·4 H_4O)145.8$$

A mixture of 10 ml. of 10% NaOH with 3 g. of Roussin's black ammonium salt is prepared and heated on the water bath at 80° C; the heating is continued until the ammonia odor disappears (in about 15 minutes). The Fe(OH)₃ precipitate is removed by suction filtration through a fritted-glass funnel and the reddishbrown solution is evaporated over CaCl₃ under reduced pressure. It is left standing for one day; beautiful black-red crystals separate. These are collected on a fritted-glass funnel, washed with 0.1% sodium hydroxide solution, and dried between filter papers.

SYNONYM:

Roussin's red sodium salt.

PROPERTIES:

Formula weight of $Na[(NO)_aFeS]$ 170.92; of $Na[(NO)_aFeS]$ 4 H₂O 242.99. Reddish-black crystals or reddish-brown powder, soluble in water and ethanol; insoluble in ether. Upon removal of excess base, the compound is converted in a short time to the black Roussin's salt.

REFERENCES:

O. Pawel. Ber. dtsch. chem. Ges. <u>12</u>, 1953 (1879); <u>15</u>, 2607 (1882).

^{*}The nomenciature used here and in the following preparations is justified by the nature of these complex salts, in which the NO group is bound in the same way as in the nitrosyl carbonylis. See F. Seel, Z. anorg. alig. Chem. 249, 308 (1942).

Ammonium Heptanitrosyl Trithiotetraferrate

NH4[(NO)7Fe4S3] · H4O

A solution of 8 g. of NaNO₂* in 40 ml. of water is mixed with a solution of (NH4) 2S, prepared by saturating 5 ml. of 22% ammonium hydroxide with H₂S adding 5 ml. of ammonium hydroxide of the same concentration, and siluting with 30 ml. of water. The final mixture is heated to the boil and thus becomes a dark-Now, a solution of 20 g, of FeSO₄ · 7 H₂O in 160 ml. brown. of water is added at once and the mixture is quickly reheated to a vigorous boil. The reaction starts even before the boiling point is reached [precipitation of Fe(OH)3 and S is evident from the color change to black and brown]. Almost simultaneously the mixture starts evolving nitrous fumes. If a good yield is desired, it is essential that the gas evolution be suppressed by addition of 25 ml. of ammonium hydroxide (in small portions) during the entire boiling operation. After boiling for 15 minutes, the hot solution is filtered as quickly as possible through two Buchner funnels (moderate vacuum). The small crystals of Roussin's black ammonium slat already begin to precipitate in the filtrate during the filtration. To obtain larger crystals, the filtrate is placed in a hot water bath, heated until the salt is completely dissolved, and allowed to cool in the bath, Yield: about 1.7 g.

SYNONYM:

Roussin's black ammonium salt.

PROPERTIES:

Formula weight of $NH_4[(NO)_7 Fe_4S_3] \cdot H_2O$: 565.7. Hard, monoclinic crystals with a diamondlike glitter; soluble in water, giving dark-brown solutions; stable to 80°C.

The corresponding elkeli selts are obtained by a similar procedure; however no excess of nitrite is necessary in this case.

This is about double the theoretical amount; this compensates for the decomposition of the NH₄NO₂ present in the solution.

REFERENCES:

O. Pawel. Ber. dtsch. chem. Ges. 12, 1953 (1879); 15, 2607 (1882).

Ethyl Dinitrosyl Thioferrate [(NO),Fe SC,H₄],

 $2 \text{ FeSO}_4 + 4 \text{ KOH} + C_2 H_3 \text{SH} + 2 \text{ NO}$ (-7 H₂O) 224.462.1 556.0 44.81. $= (NO)_{t}FeSC_{t}H_{s} + Fe(OH)_{s} + K_{t}SO_{4} + H_{t}O$ 177.0

The shaking vessel shown in Fig. 344 is charged with 27.8 g. (0.1 moles) of FeSO4 • 7 H₂O and evacuated. Then, 140 ml. of boiled water is aspirated in, the salt is dissolved by shaking, and finally a solution of 11.2 g. of KOH and 3.1 g. of C2H5SH (3.7 ml., 0.05 moles) in 25 ml. of water is added. The apparatus is now connected to a calibrated gas-measuring flask containing 2.5 liters of NO stored over some solid KOH; the gasometer is then shaken on a machine. The initially sirupy, off-color slurry of Fe(OH)2 and Fe(SC2H5)2 becomes a deep olive-green liquid. Toward the very end of the NO absorption (which goes very fast at the beginning and takes about 1.5 hours), the color changes to a light brown. A small amount of deep-black crystals are evident at the bottom of the flask and sometimes at the surface of the liquid. The NO is displaced with N2 and the flask is opened. The black crystals can be separated from the Fe(OH)3, which has a lower specific gravity, by decantation and slurrying; however, better yields (up to 80%) are obtained by centrifugation, washing in the centrifuge tube (once with absolute ethanol and 3-4 times with ether), and recrystallization of the substance from hot absolute ethanol with slow cooling.

PROPERTIES:

Glittering black monoclinic crystals, m.p. 78°C. Insolubie in water; soluble with difficulty in ethanol; more readily soluble in ether; readily soluble in CS₂, CHCl₃ and C₆H₆, giving yellowishred solutions.

REFERENCES:

K. A. Hofmann and O. F. Wiede. Z. anorg. Chem. 9, 308 (1895); H. Reihlen and A. von Friedolsheim. Liebigs Ann. 45?, 71 (1927).

1.18

Potassium Dinitrosyl Thiosulfatoferrate

K[(NO):FeStO1] · HtO

 $3 FeSO_4 + 4 K_3 S_2 O_3 + 4 NO = 2 K[(NO)_8 FeS_2 O_3] + K_2 S_4 O_6 + 2 K_2 SO_4$ + T H_0 (+H_3 O) = 556.0 761.2 \$9.61. 516.2

This derivative of Roussin's red salt is prepared by shaking a mixture of the concentrated aqueous solutions of 28 g. (0.1 moles) of FeSO₄ \cdot 7 H₂O and 40 g. of K₂S₂O₃ under NO, as described in the previous preparation. During the first hour, the gas is absorbed especially rapidly and the solution turns intensely brown. Later, K[(NO)₂FeS₂O₃] \cdot H₂O separates out in leaflets of brass-like glitter. The substance is collected by filtration, washed with ethanol, and dried in vacuum over conc. sulfuric acid.

PROPERTIES:

Formula weight of $K_1(NO)_2$ FeS₂O₃] · H₂O: 258.1. Only slightly soluble in cold and warm water; decomposes in boiling water.

The same procedure is used to prepare the sodium salt, $Na[(NO)_3FeS_2O_3]$. In this case, crystallization is slower due to the greater solubility of the product.

Finally, the same method may be used for the preparation of the corresponding cobalt and nickel compounds $K_3[(NO)_2Co(S_2O_3)_2]$, and $K_3[(NO)Ni(S_2O_3)_2]$.

REFERENCES:

K. A. Hofmann and O. F. Wiede. Z. anorg. Chem. 8, 319 (1895);
 W. Manchot. Ber. dtsch. chem. Ges. 59, 2445 (1926).

Potassium Nitrosyl Cyanomolýbdate

 $K_4[(NO)Mo(CN)_5] \cdot H_2O$

$$\begin{aligned} M_0O_1 + 5 \text{ KCN } + 6 (\text{NH}_3\text{OH})\text{Cl} + 5 \text{ KOH} \\ 144.9 & 325.6 & 417.0 & 280.5 \\ &= K_4[(\text{NO})\text{Mo}(\text{CN})_4] + 2 N_2 + \text{NH}_3 + 6 \text{ KC}] + 12 \text{ H}_2\text{O} \\ & \begin{array}{c} (-H_1\text{O}) \\ & 412.4 \end{array} \end{aligned}$$

The reaction is based on reduction with $NH_{2}OH$ and disproportionation of the latter into NOH and NH_{3} . Thus, 5 g, of

5767

MoO3 powder is treated with 10 ml. of a solution of 25 g. of KOH in 20 ml. of water; the mixture is stirred to the point where everys thing just dissolves. A saturated aqueous solution containing 20 av of KCN is then added and the mixture filtered through a medium. porosity fritted-glass funnel. Then, 17.5 g. of (NH3OH)Cl is added. to the filtrate and the mixture stirred until the (NHsOH)CI is dissolved. The red solution is now heated on a water bath for 30 minutes; then, an additional 10 ml. of conc. KOH is added. At this point, the red color changes to a light yellow and then slowly turns to violet. The appearance of the violet color is accompanied by the evolution of NH3 and is quickly followed by the separation of the violet NO compound. The latter is collected (after cooling) by filtration, washed with alcohol and ether, redissolved in a minimum of hot water, and quickly filtered into cold, 50% potassium hydroxide. The deep-violet, crystalline compound reprecipitates (the mixture must sometimes be left standing overnight); it is washed with ethanol and ether and dried in vacuum. Yield: 40%.

PROPERTIES:

Hygroscopic; decomposes in air, becoming lemon-yellow. May be stored indefinitely under nitrogen; in vacuum, may be heated up to 180°C without decomposition or loss of water of crystallization.

Readily soluble only in water; insoluble in all the usual organic solvents such as ethanol, ether, benzene, acetone, pyridine, chloroform, CCl₄ and CS₂. The aqueous solution is quite unstable and decomposes after a short time with loss of color.

REFERENCE:

W. Hieber, R. Nast and G. Gehring. Z. anorg. allg. Chem. <u>256</u>, 173 (1948).

Potassium Nitrosyl Cyanomanganate Ks{(NO)Mu(CN),}

 $\begin{array}{r} K_{s}[Mn(CN)_{s}] + 2(NH_{s}OH)Cl + 3KOH \\ 328.3 & 139.0 & 168.3 \\ = K_{s}[(NO)Mn(CN)_{s}] + KCN + 2KCl + NH_{s} + 4H_{s}O \\ 332.3 \end{array}$

A solution of 16.4 g. (0.05 moles) of K₂[Mn(CN)s] in 100 pd. of a 15% KCN solution is treated (in this order) with 7 gr starting (till_SOR)C) and a solution of 8.4 g, of KOH in 20 ml. of water. The mixture is then slowly heated, whereby it becomes brown, then violet. At this point flocculent $Mn(OH)_3$ appears occasionally due to hydrolytic cleavage of the $K_3[Mn(CN)_a]$. The end of the reaction is indicated by a dark-violet color of the solution and termination of the NH₃ evolution. After cooling, the solution is made weakly acidic by addition of acetic acid, and 18.5 g, of $Mn(CH_3CO_3)_3 \cdot 4 H_3O$ in 60 ml, of water is added to give a copious but readily filtered rose-red precipitate of $Mn_3[(NO)Mn(CN)_5]_3$:

The precipitate is carefully washed and digested with a solution of 35 g. of K_2CO_3 in 120 ml. of water:

' $Ma_{s}[(NO)Mn(CN)_{s}]_{s} + \frac{1}{2}K_{s}CO_{s} = K_{s}[(NO)Mn(CN)_{s}] + \frac{1}{2}MnCO_{s}$ 307.4 207.3 332.3

After slight heating the solution may be filtered, if necessary; it is then made weakly acidic with acetic acid, and a large excess of ethanol is added. On standing for a few days, the initially flocculent precipitate changes to fine, deep-violet crystals, which are collected and washed with ethanol. When kept over $P_{s}O_{s}$, the substance loses all water of crystallization and is converted to the analydrous K₃[(NO)Mn(CN)₆]. Yield: 80-90%.

REFERENCE:

W. Bieber, R. Nast and E. Proeschel. Z. anorg. allg. Chem. <u>256</u>, 167 (1948).

Sodium Nitrosyl Cyanoferrate

Nas[(NO)Fe(CN)s] · 2 H2O

$$\begin{split} \mathbf{K}_{\bullet}[Fe(CN)_{\bullet}] + \theta HNO_{s} &\simeq H_{2}[(NO)Fe(CN)_{\bullet}] + 4 KNO_{s} + NH_{4}NO_{s} + CO_{s} \\ & (\cdot 3 H_{\bullet}O) \\ & 422.4 \\ & H_{2}[(NO)Fe(CN)_{\bullet}] + Na_{2}CO_{s} = Na_{2}[(NO)Fe(CN)_{\bullet}] + H_{2}O + CO_{2} \\ & (\cdot 2 H_{2}O) \end{split}$$

298.0

A 400-ml. beaker is used to dissolve 40 g. of $K_4[Fe(CN)s]$. **5 E₄O in 60 ml. of water (slight heating).** Then, 64 ml, of nitric

acid (d 1.24) is added (stirring). The mixture is digested one water bath at moderate temperature until a test drop of the brown solution reacts with FeSO₄ solution to give a dark green (rather than blue) precipitate. After standing for 1-2 days, the mixture is just neutralized with Na₂CO₃ (an excess must be avoided). The neutralized solution is heated to the boil, filtered and quickly concentrated to a small volume. After cooling, an equal volume of ethanol is added to precipitate most of the KNO₃. This is separated by filtration, and the solution is quickly reconcentrated to remove the ethanol. The dark-red solution yields crystals on standing; these are suction-filtered and washed with some cold water. Further crystalline material is obtained by repeating the evaporation of the mother liquors.

SYNONYM:

Sodium nitroprusside.

PROPERTIES:

Ruby-red orthorhombic-bipyramidic crystals. One part is soluble in 2.5 parts of water at 16°C.

REFERENCES:

L. Vanino, Handb, d. präp. Chem. [Handbook of Preparative Chemistry], Inorganic Part, Stuttgart, 1925, p. 355; R. Wild. Arch. Pharm. <u>131</u>, 26 (1865).

Sodium Carbonyl Cyanoferrate

$Na_1[(CO)Fe(CN)_5]$

Easily prepared via reaction of CO with Na₃[Fe(OH₂)(CN)₆], which in turn is obtained from sodium nitroprusside.

a) $Na_{2}[(NO)Fe(CN)_{3}] + (NH_{3}OH)Cl + Na_{2}CO_{3}$ (.2 H₃O) 69.5 106.0 = $Na_{3}[Fe(OH_{2})(CN)_{3}] + NaCl + N_{2}O + CO_{2} + H_{2}O$ 272.9 58.5

A solution of 20 g. of sodium nitroprusside and 10 g. of Na₂CO₃ in 80 ml. of water is prepared; the reaction flask is placed in the and 7 g. of (NH₃OH)Cl is some water is added. Gas evolution begins, immediately and the solution turns a greenish brown. After one **bour, the product is precipitated as a brown tar with three volumes** of ethanol. By repeated solution in water and reprecipitation with methanol, Na₂[Fs(OH₂)(CN)₅] is obtained as a yellow powder. It is important to keep the temperature below 5°C to avoid formation of Na₄[Fe(CN)₆] and iron hydroxides.

b) $Na_{3}[Fe(OH_{s})(CN)_{s}] + CO = Na_{3}[(CO)Fe(CN)_{s}] + H_{s}O$ 272.9 222.41, 282.9

The freshly prepared aquo complex (13 g.) is dissolved in 35 ml. of boiled water and introduced into an evacuated three-neck flask fitted with a vacuum-tight mercury-seal stirrer, a dropping funnel, and gas inlet and outlet tubes. By repeated flushing and evacuation, the flask is filled with carbon monoxide (prewashed with an alkaline pyrogaliol solution). When vigorously stirred, the solution starts to absorb CO at a fast rate; after 24 hours and absorption of 98% of the stoichiometric quantity of CO, the reaction is complete. The flask must be protected from light during the reaction. The product is precipitated from the greenish-blue solution by addition of 200 ml. of ethanol containing 0.5 g. of NaOH; it is filtered in air. After washing with some absolute ethanol, the complex is obtained in analytical purity.

Since $Na_3[(CO)Fe(CN)_5]$ is somewhat soluble in ethanol, it is recommended to work up the aqueous-alcoholic filtrate. To this end the filtrate is evaporated to dryness at 12 mm. and 40-50°C (bath temperature), the residue dissolved in the minimum amount of water, and all Fe(OH)₃ filtered out. The filtrate is concentrated to crystallization in a vacuum desiccator over conc. H₂SO₄; a very small quantity of mother liquor should remain. The crystals are collected by filtration, washed with some ethanol, and dried at 110°C. Yield: up to 90%.

PROPERTIES:

Pale-yellow needles, surprising stable.

REFERENCE:

W. Hieber, R. Nast and C. Bartenstein. Z. anorg. allg. Chem. <u>272</u>, 32 (1953).

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SECTION 5

Alloys and Intermetallic Compounds

G. BRAUER

General Remarks

The usual laboratory preparation of alloys consists of fusion of the metallic components. This method allows a simple control over the quantities of reagents so as to reach the desired composition. If the changes of the phase diagram of the metal system are known as a function of the temperature, this method also allows, in most cases, the preparation of definite intermetallic compounds. Occasionally, however, it is difficult to obtain the required homogeneity in the product because some of the reagents may burn, evaporate or react with the fusion vessel.

By comparison, other methods for the preparation of alloys are less used in the laboratory, although in special cases the optimum methods may involve reduction (chemical or electrolytic) of metallic compounds. In addition, some intermetallic compounds are best obtained as residues remaining after the corresponding basic alloys are dissolved. However, a knowledge of the temperature-induced transformations of the phase diagram is of the greatest importance in all cases; thus, the literature references below must be consulted, if at all possible.

Due to the enormous number of possible and known alloys and intermetallic compounds, a full description of all preparative methods is, of course, impossible. It is even less feasible to cite all the most important compounds separately. This section therefore contains only a selection of typical laboratory procedures; these are examples which may be adapted to other cases, even if the latter are unrelated. Only a few individual preparations are given in detail.

Further, it should be pointed out that preparative methods for metallic compounds overlap those for semimetals and nonmetallic compounds. For this reason, many of the methods cited here are derived from those for nonmetallic compounds; others, which stem from metallurgy, may also be applied is other substances. REFERENCES:

Collected phase diagrams of metallic systems:

 Mansen and K. Anderko. Constitution of Binary Alloys, New York-Toronto-London, 1958; Landolt-Börnstein, Zahlenwerte und Funktionen [Numerical Values and Functions], Vol. II, Part 3, 6th Ed., Berlin-Göttingen-Heidelberg, 1956; W. Hume-Rothery et al. Metallurgical Equilibrium Diagrams, London, 1952; E. Janecke. Kurzgefasstes Handbuch aller Legierungen (Short Handbook of Alloys], Heidelberg, 1949; T. Lyman (Amer. Soc. Metals). Metals Handbook, Cleveland, 1948 (Binary and Ternary Alloys); J. L. Haughton. Bibliography of the Literature Relating to Constitutional Diagrams of Alloys, London, 1942; M. von Schwarz. Metall- und Legierungskunde [Metals and Alloys], Stuttgart, 1929 (Binary, Ternary and Quaternary Alloys).

Preparation of Alloys by the Use of Heat

Purity of the Starting Materials

Except for special cases where some purification is achieved by the vaporization that occurs at relatively high temperatures, one should not expect that the product alloys will be purer than the starting metals. Therefore, the latter should be as pure as possible and should contain a minimum of dissolved impurities ("internal" impurities). The "external" impurities also cannot be neglected. Thus, oxide loyers must be removed by scraping or grinding, or by chemical etching with suitable acids. Industrial metals comminuted by mechanical means (powders, shavings) are frequently contaminated by traces of lubricants. These must be removed by extraction with organic solvents; otherwise, they tend to interfere with the alloy formation and form carbides. Water and all organic solvents must be removed by careful drying.

The optimum methods sometimes involve metal hydrides rather than pure metals. The procedure is useful mainly in the case of metals that form stable hydrides (alkali and alkaline earth metals. Ti to Th, V to Ta, Pd). The hydrides are readily reduced to powders and the contact of the latter with the other components of the alloy is much better than it would be otherwise. The thermal decomposition of the hydrides proceeds so easily that the formation of alloys is not only not slower than in the case of pure metals, but is faster due to the small particle size of the material. In addition, the hydrogen liberated from the hydride may reduce the oxide impurities. One disadvantage inherent in the use of hydrides is that the commercial materials are usually less pure than the corresponding metals.

Form of the Starting Materials

The starting material may consist of ohunks, ingots, shavings or powders. Large chunks have relatively small surface areas, thus introducing fewer "external" impurities; they usually leave less material on the container walls. On the other hand, mixtures of large chunks may sometimes be difficult to reduce to a homogeneous melt, especially if the components of the alloy differ greatly in density or melting points. While homogeneous mixtures of powders already in the solid state can be prepared, the oxide skin frequently prevents junction of the particles even when sufficient heat is applied; in addition, powders have a greater tendency to cling to the container walls, again because of surface oxides. The metal hydrides may be found advantageous in this case, as mentioned above. The formation of alloy from powders, shavings or thin wires is greatly improved by pressing the mixture into pellets prior to heating (suitable dies are described in Part I, p. 103). (They are made from shape-retaining "oil-tempered" steel and are hardened only after machining and careful fitting of the die and the matrix.)

Metals which readily acquire a surface oxide layer may be cut into a potlike shape on a lathe. The other alloy components can then be hammered into the hollow to assure an intimate contact from the very start.

When two components with widely differing melting points are fused, the fusion pot should be arranged so that the lowermelting metal must run through the higher-melting one.

Preparation of Starting Mixtures

It is desired to obtain the desired alloy composition by weighing out theoretical quantities of the components but, for various reasons, this composition cannot always be achieved that simply. Frequently a number of successive preliminary experiments must be carried out, whereby one gains the necessary experience.

The most important causes of deviation of the product from the desired composition are losses of metal by vaporization, oxidation or side reactions with the material of the fusion pot. In such cases the expected losses of a component are balanced by adding an extra quantity of that component to the starting mixture. A rough approximation of the extra quantity required is obtained from the fact that when the preparation is conducted properly and in closed crucibles (see below), not even the very reactive mixtures of alkali metals lose more than 5% of the startise ing weight. An especially clean way to measure out cikal; metals consists in melting the latter in small, sealed glass ampoules, from which they can easily be removed by remelting (see the section on Alkalj Metals, pp. 961-967).

Crucible and Ampoule Methods

The alloy components, weighed out with the above considerations in mind, are combined by fusion in crucibles or ampoules. Some method must always be devised to minimize losses due to burning or vaporization. In simple cases, where open vessels are used, this is achieved by covering the charge with a protective layer of a salt or salt mixture which also melts in the process. Alternatively, the mixture may be protected by a blanket of an inert gas; crucibles may be closed by a lid and ampoules by fusing the constricted neck. If the closure is gas-tight, some inert or reducing gases may be included and a vacuum may even be maintained.

Several low-melting solts and solt mixtures suitable for laboratory use are given in Tables 1-3 (for further references, see Guertler [1]). Many such protective agents are commercially available for industrial use and they can also be employed.

Table 1

Melting Points of Some Salts Suitable for Use in Protective Layers

| Salt | M.p., °C | Salt | М.р., °С |
|---|--|---|---|
| LiNO, NaNO, KNO, LiCI MgCi, NaB,O; CaCi, KCI NaCi KF | 255 307 334 613 708 741 772 778 801 880 | LiF NarSO, KBO; BaCI, NaBO, K,SiO, NaF NaF NaF,SIO, CaF; | 870 884 947 962 963 976 988 1088 1360 |

Hygroscopic salt mixtures sometimes react with the molten alloys, evolving hydrogen and interfering in the reaction. This effect can be reduced by adding KOH.

The type of protective atmosphere depends on the metals of the alloy, Hydrogen is frequently used, except when large quantities of hydride-forming alkali, alkaline earth or rare earth

Table 2

| WL, % | Sa <u>i</u> t í | ₩£ % | Sait II | M.p., °C | Wt, R | Salt I | Wit, | Seit II | M.p. |
|---|---|--|---|---|--|---|---|---|--|
| $\begin{array}{c} 73\\ 55.3\\ 46\\ 57\\ 61.4\\ 12\\ 03.8\\ 73.5\\ 45.8\\ 73.5\\ 45.8\\ 73.5\\ 45.8\\ 73.5\\ 45.8\\ 73.5\\ 45.8\\ 73.5\\ 26\\ 85\\ 85\\ 85\\ 85\\ \end{array}$ | KNO ₄ NaNO ₃ LiCl LiCl KCl NaCl NaCl KF KCl NaCl NaCl NaCl NaCl NaCl NaCl NaCl Na | 27 44.7 54 38.6 58 67.2 66.3 54.2 26.5 37 65. 55.8 37 65 4.2 26.5 37 65 4.2 26.5 4.2 26.5 37 65 4.2 27 4 55.4 37 65 4 57 4 57 4 57 4 57 4 57 4 57 55 57 54 57 57 54 57 57 54 57 55 55 57 57 57 57 57 57 57 57 57 57 | LiNO, LiNO, KCl MgCl ₃ MgCl ₄ LiCl CaCl ₂ LiCl AlF, CaCl ₄ Li,SO, KF Na ₂ CO ₄ Na ₄ P ₂ O, Na ₄ P ₂ O, Na ₄ P ₂ O, CaCl ₄ CaCl ₄ CaCl ₄ CaCl ₄ | 132 208 352 580 426 430 500 562 565 600 601 605 620 620 620 620 624 640 644 | 32.8 51 77.8 45 35.8 72 51 32.4 35.4 83.7 52.8 61 21.5 90.4 87.8 78.8 | KCI LiBO: NaCI NaCI LiF NaF LiF LiF LiF LiF NaF NaF NaF SaF, BaF, | 67.2 49 22.2 55 64,2 28 49 50 67.8 64.6 36.3 47.2 39 78.5 9.6 12.2 21.2 | BaCl ₇ NaBO: BaCl ₇ KCI MgF ₇ NaF K ₅ CO ₄ KF AlF ₃ AlF ₃ AlF ₄ MgF ₇ MgF ₇ MgF ₇ | 645 648 654 660 669 875 690 700 710 710 710 710 710 810 915 835 835 835 890 930 |

Meiting Points of Some Binary Salt Mixtures with Uniform Melting Points

metals are present; in other cases, nitrogen is used, except when nitride-forming Li, Be, Mg, Ca, Sr and Ba, or the rare earth metals, Ti, Zr, Hf, Th, V, Nb and Ta are present. If no carbides can form, CO may be used to advantage; however, CO_2 and SO_3 may occasionally oxidize the metals at high temperatures. Noble gases, especially argon, which is commercially available in cylinders at 150-200 atmospheres pressure, are the best but also the most expensive protective agents. For real protection the gas should be very pure: oxygen is undesirable even in traces. Gas purification methods are given in various sections of this handbook (H₂: p. 111 ff.; N₂: p. 457 ff.; noble gases: p. 82 ff.). Occasionally, H₂, N₂ and Ar are available in high purity (99.99%) from commercial sources, sometimes on special order.

High, narrow crucibles are preferred. Useful crucible materials are a) metals, b) ceramics and c) glasses (for ampoules).

A) METALS:

For obvious reasons, only high-melting metals which do not tend to form alloys are suitable for crucibles. Iron and various types of steel, as well as molybdenum and tonicium, are frequently used. Molybdenum is very serviceable but also much more expensive and less easily worked than Fe. These metals are preferentially used for smelting alloys of the "B" group of

10

G. BRAUER

elements and for the extremely reactive alkali and alkaline earth metals (see Table 4).

Table 3

Melting Points of Some Ternary Salt Mixtures with Uniform Melting Points

| WL K | Salt I | WL R | Sait II | WL K | Salt III | М.р., С |
|---|--|---|--|--|---|--|
| 16.4 76.4 24 5 53.3 10.1 15.9 20.5 | NaCl BaCl NaCl NaCl AJF, AJF, AJF, AJF, | 24.6 14.0 37 9 13.2 34.4 26.7 51.7 | KCI KCI KCI KCI CaF ₂ CaF ₂ CaF ₂ | \$9.0 9.6 39 86 33.2 55.5 57.4 27.8 | BaCl, Na₂CO, Na₃CO, Na,B ₄ O, NaF NaF NaF NaF | 540 542 640 705 780 825 1095 |

Table 4

Metallurgical Classification of Elements

| Alk and fail car | al- Transition metals | | | | | | | : | | ₿Ę | leme | ncs | | | | | |
|---------------------------|-----------------------|------|----|----|----|------------|----|-----|----|----|------|------------|----|----|----|----|------------|
| Fr | Ra | Ac | ΊЪ | Pa | U | – – | | | - | | - | • • • • | | | | | |
| Cş | Ba | R.E. | H{ | Ta | w | Re | Os | lr. | Pt | Au | Hg | TI | Pb | Bi | Po | At | Em (Rn) |
| RЬ | Şr | Y | Zı | Nb | Mo | Τc | Ru | Rh | Pd | Ag | Cď | In | Sn | 56 | Te | ī | х |
| K | C4 | Sc | Τi | ۷ | Çı | Μn | Fe | Co | Ni | Çu | Zn | Ga | Ce | As | Se | Br | Kr |
| Na | | | | | | | | | | | Mg | A 1 | Si | P | js | CI | Ar |
| ម | | | | | | | | | | | ße | В | ¢ | N | 0 | F | Ne |
| | | | | | | | | | | | | | | | | н | He |

Metallic Pt, Ag and Ni, which are normally chemically inert and time are used as vessel materials under corrosive conditions, cannot be used in crucibles because of their intrinsic and promunced tendency to form alloys.

The preparation of alloys of the so-called transition metals virtually always requires ceramic crucibles (see also below).

1776

A gas-tight seal for an iron crucible can be obtained in administraber of ways. An iron lid may, for instance, be put on and sealed in place by means of flanges; the lid may also be in the form of a threaded cap or plug, which yield a firmly closed circular seal. Two types of screw caps are shown in Fig. 273, p. 990. Tubular. crucibles with fitting lids (or plugs) can frequently be welded shut for a gas-tight seal. In this case, the plug closely fits the LD. of the crucible and has the shape of a tube with one end closed. Examples of this are given in Fig. 347. Even though the crucible may contain a protective gas blanket, the gas-filled space above the material to be alloyed should be kept at a minimum. With this in mind, the inner cylinder serving as a plug in the crucible of Fig. 352b should be hammered down (after charging) as far as possible, sawed off near the rim of the outer crucible and then welded to the outer rim. A plug shaped as a hollow cylinder is easier to weld at the rim than a solid plug. The hollow plug should be slightly tapered (into a cone) near its upper rim. Alternately, its rim should be turned down slightly after it is driven in (it thus forms a flange surface). In either case, the aim is to close off the seam and prevent welding gases from penetrating into the crucible. If generation of a large amount of heat is expected on welding and if it is undesirable to trigger the reaction until the crucible is tightly sealed, its lower section may be cooled in water during welding. This would have to be done, for instance, in welding crucibles containing the very volatile alkali and alkaline earth metals when they are to be alloyed with "B" metals.

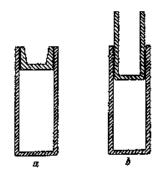


Fig. 347. Tubular steel crucible. When small quantities of alloy are needed (for instance, in crystal structure studies) the following dimensions have proved useful-0.D. 20-25 mm., wall thickness 1-2 mm., height #0-90 mm. as the Sec. 6 18 3 6

1. 2.1

Prior to closure of the crucible, the protective gas may be introduced through a parrow tube. A better method is to put the

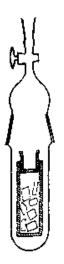


Fig. 348. A method for evacuating a metai crucible and filling it with a protective gas blanket. charged crucible, with the lid loosely in place, into a large-diameter glass tube, which is closed at one end and fitted with a ground glass joint and stopcock (Fig. 348). The tube is then alternately evacuated and filled with the protective gas. This arrangement displaces the air very efficiently.

After fusion and cooling, the iron crucibles are opened by sawing off the top and bottom, and the alloy is then punched out of the open cylinder. In another method, the crucible is placed on a lathe, clamped at the stopper end, and its wall turned down to 0.1-0.3 mm. This thin wall can then be stripped off with a pair of pliers in the same manner as the top of a can of sardines. Since this can be done very rapidly, even those alloys which are very sensitive to air can be isolated without too much damage and can be rapidly transferred to a storage vessel filled with a protective gas. The method is also useful in cases where the alloy

ingot adheres firmly to the crucible walls because of local welding.

Alloys which are extremely sensitive to air, especially those with high concentrations of alkali and alkaline earth metals, require special methods for the removal of the ingot from the iron crucible [2]. In the device of Zintl and Harder (Fig. 349) a tubular iron crucible can be opened while completely surrounded by a protective gas.

The iron tube r is connected via the standard-taper joint s to a source of pure N_2 as well as to other devices for further treatment of the alloy. The tubular crucible t, whose wall has already been machined down on a lathe (see above) so that it is now thin, is positioned in r by means of the screws a in such a way that its bottom may be sawed off through the slit c while still under N_2 (the length of the circumferential slit c is equal to only 2/3 of the diameter of tube r). After the crucible bottom is sawed off, the crucible is pushed to the right by means of a thick wire (which passes through an axial hole in the cover plate e) and repositioned by means of screws a. The top of the crucible **that is**, the plug) is now sawed off; the cover plate e is taken off for a moment and the debris removed. The alloy is now contained in an iron tube (casing) which is open at both ends. The iron filings still adhering to the tube and ingot are tapped out. The alloy can now be pushed out of the casing by a steel rod passed through the hole in e. In certain cases the casing tube (including the alloy inside) may be used directly in further workup, e.g., an extraction. The protective gas should escape through only one hole at a time; the slit c for the saw can be closed off by collar d, the hole in eby means of a rubber stopper. This apparatus was originally used for the preparation of Na-Pb and Na-Sn alloys.

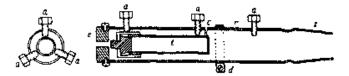


Fig. 349. Opening of a tubular iron crucible in the absence of air. r iron tube with standard-taper joint s; t crucible; a screws to fasten the crucible in place (nine such screws are arranged, in groups of three, along the circumference of r, the angles between the screw axes being 120°, as indicated in the insert); c slit for the introduction of a hacksaw; d collar for closing the slit when not in use; e cover plate for the tube r.

In the arrangement of Klemm and Dinkelacker, described in greater detail in Fig. 353 and on p. 1788 f., complete removal of the ingot from the tube is unnecessary; only quantities needed for immediate use need to be drilled out.

B) CERAMIC MATERIALS

Crucibles made of various kinds of ceramic materials can be used. The reader is referred to the text and tables in Part I, p. 12 ff., especially Table 7. Recently, crucibles of Ce and Th Sulfides have proved advantageous for the fusion of nearly all metals, the exception being Pt. They can be used up to 1800°C [3]. Crucible shapes frequently used in the study of alloys are

Crucible shapes frequently used in the study of alloys are the conical (the so-called high shape) and the long, cylindrical (Tammann tubular crucible), both with a rounded or, less frequently, a flat bottom. Ceramic crucibles may be fitted with lids of the same material, but these can usually not provide a gas-tight seal by themselves (some sealing compound must be provided). Only alumins (Al₂O₃) can be fused and then only in the case of very small tubular crucibles (about 15 mm. O.D.). In this case a well-fitting plug may be fused to the crucible wall with an



Fig. 350. Tubular alumina crucible. O.D. about 15 mm., length 65 mm.

acetyleas-oxygen flame (welding torch) [4]. Thus, a crucible of the type illustrated in Fig. 350 is charged to a quarter of its height with the metal, closed off with the loosely fitting plug, and evacuated and filled with a suitable inert gas in the apparatus of Fig. 347. The crucible is then surrounded by moist sand to one half of its height, and the top section, including the plug, is carefully heated, using first a city gas-air mixture, then the acetylene-oxygen flame. The flange of the plug eventually fuses to the rim of the crucible (m.p. of $Al_2O_3 = 2050$ °C). The entire closed crucible is then cooled carefully and uniformly. Some experience is necessary to avoid cracking during the fusion and, especially. during the cooling.

Tubular crucibles made of Pythagoras mass* may be closed off in the same way as an ampoule, that is, by pulling to a small diameter and sealing the top end in a hydrogen-oxygen or acetylene-oxygen flame (see ampoule methods, p. 1782).

In another method, the crucible is lined with other materials. This method allows using, in the preparation of alloys, chemically resistant materials that cannot be shaped like a ceramic when unsupported.

Thus, CaO linings are suitable for work with Co olloys and, in general, with calcium metal, which is extremely corrosive when hot. The Jander method of lining iron crucibles with CaO (already mentioned in Part I, p. 13) consists of the following.

The crucibles are 12 cm. high and 2.5 cm. L.D., with a wall 1 mm. thick. A thick paste of freshly prepared quicklime (from precipitated CaCO₃) and water is partly poured in and partly painted on the inside of the crucible so that there is a layer 1-2 cm. thick at the bottom and a wall lining 0.3-0.4 cm. thick. Rotating the crucible and careful pressing with a spatula produce a good and even coat. The crucible is then very slowly dried at room temperature or at 30-40 °C; any cracks that appear are filled by pressing with a spatula (this can be done as long as the cake is

^{*}Pythagoras mass is a low-melting porcelain used for laboratory ware and electrical resistor casings, useful for temperatures not exceeding 1500 °C. Its melting point is about 1730 °C (Houben-Weyl, Allgemeine Laboratoriumspraxis [General Laboratory Practheel, 4th ed., part 2, Georg Thieme Verlag, Stuttgart, 1959, p. 634).

still moist). Cracks that appear after this cannot be remedied; very fine cracks do no harm, as experiments with cracked CaO linings have shown. After the initial drying the temperature is increased to dark red heat, which transforms the Ca(OH)₂ to CaO. Dry CaO does not adhere well to iron. Since its coefficient of expansion differs from that of iron, the crucible must be heated very carefully and treated very gingerly even after the lining process. The crucible is charged with the reactants, and an iron lid, also coated with CaO, is welded on.

Coatings of LiF are suitable for work with lithium olloys and metallic lithium at temperatures below 800° C. These coatings adhere relatively well to zirconia (ZrO_2) crucibles [6]. Thus, several grams of LiF (m.p. 870° C) are placed in a ZrO_2 crucible which is positioned in a small, movable electric furnace. The crucible is firmly seated in the furnace by means of asbestos wool. A clear melt is produced on heating; the current is then shut off and the melted LiF evenly distributed over the crucible walls by tilting the furnace. This is continued until the crucible cools sufficiently for the material to set. Afterward, the furnace is allowed to cool slowly at a low current (from 700°C to 300°C in one hour). The lithium fluoride lining thus formed has a thickness of 1-2 mm. If the cooling is too rapid, it will have large cracks; small cracks are nearly unavoidable, but are not deleterious because of the high surface tension of most metals.

Other lining materials, such as Nucerite, which can be directly bonded to metals, under certain conditions withstands temperatures up to 650 °C, and is resistant to many gases, are also on the market. In addition, such materials as Pyroceram will be quite useful in the high-temperature laboratory.

Of late, many new ceramic materials have been developed for use in the various military and space programs. It is not possible to list them in this short section. Besides, this field is undergoing very rapid changes and new materials appear almost monthly. The reader is therefore advised to spend some time consulting the pertinent trade literature before proceeding with the experiment. He may find such investment of time very worthwhile, because it may result in a simpler, better, more convenient and cheaper experimental arrangement.

Ceramic crucibles may also be placed in glass, quartz or ceramic combustion tubes (one end open) so that the material may be in a vacuum or an inert gas atmosphere during the heating. Such an arrangement is shown in Fig. 272, p. 984.

Ceramic crucibles are frequently enclosed in slightly larger iron crucibles, which are then hermetically sealed with a weldedon plug; this arrangement combines the chemical resistance of ceramics, especially the oxides of Be, Mg, Ai, Zr and Th, with the ease of sealing of iron crucibles. Finally, all the crucible types mentioned above may be sealed into glass ampoules: this permits maintaining a vacuum or a desired gas atmosphere during the fusion.

C) INPOPLES.

All types of glass, especially the high-melting glasses (see Part I, p. 5 ff.) and quartz, as well as tubes of Pythagoras mass, can be formed into ampoules (bomb tubes) and used for alloying of metals by fusion. The glass type used depends on the maximum working temperature. Pyrex can be used up to 560°C, Vycor up to 800°C under normal conditions and 1100°C for a short time, fused silica up to 1150°C, and Pythagoras mass up to 1400°C without danger of deforming. The metal reactants are changed into a - long combustion tube of the appropriate ampoule material. The tube will normally have an I.D. of 10-20 mm., a wall thickness of 1.5-2 mm., and a round bottom of uniform thickness. The tube must be thoroughly cleaned and dried. It is then constricted just above the charge, but not so close to the latter that a reaction will be set off by the heat applied during sealing. The wall must be fairly thick at the constriction. The tube is evacuated and sealed at the constriction, thus forming an ampoule containing the metals under vacuum. The constricting and sealing are done with suitable torches (city gas-air, H₂-O₂, etc.), depending on the softening temperature of the ampoule material,

The ampoule can also be filled with a protective gas. However, the thermal expansion of the gas must be taken into account in this case. For this reason, the ampoule is filled with the requisite gas at less than atmospheric pressure at room temperature.

After fusion and resolidification, the ampoule is broken up and the metal ingot isolated. The composition of the alloy may then be calculated (approximately) from the weights of the reactants and the product. However, only careful chemical analysis can give the true composition.

Heating and Cooling

The required reaction or fusion temperature is determined from the phase diagram. As a minimum, this temperature must be higher than the liquidus point of the alloy product. Preferably, however, it should exceed the melting points of all the reacting metals. The best temperature is one which exceeds the liquidus point by 30-50°C over the entire range of compositions of the system. Such a temperature will certainly ensure proper reaction conditions.

Heat sources may be furnaces of various types (see Part **1**, **pp. 32-42).** In general, the materials may be heated up as

rapidly as desired. The temperature increase due to the heat of reaction may be neglected. The heating time should be as short as possible to avoid reactions between the metal and walls of the reactor, and should in no case be longer than the time absolutely necessary to achieve a uniform composition. For this reason, the furnace should be preheated to approximately the desired temperature prior to the introduction of the vessel with the reactants. This vessel must, of course, be heated slowly enough to avoid stresses which would produce breakage. This applies particularly to glass ampoules and ceramics of low thermal conductivity. In any case, well-designed protective glosses or goggles must be worn during these operations.

When the desired melting temperature is reached; the homogenization of the mixture is promoted by mechanical means. Open crucibles are stirred with a rod of suitable material; tightly closed vessels (crucibles with a screwed-on or welded-on lid, ampoules) are taken out of the furnace and shaken or tumbled a few times; in the case of crucibles which are open but surrounded by a second protective vessel and which thus cannot be shaken or tumbled, at least some motion of the melt can be induced by external tapping or vibrating. All such agitation procedures must be followed by a short reheating to the maximum desired temperature.

Cooling also depends on the phase diagram as well as the intended use of the alloy. If there is no danger of separation of mixed crystals (with subsequent alteration of the composition of the alloy) and no peritectic reactions are expected, or if the composition achieved at the high temperature is the one desired in the solid, the material is quickly cooled in air. Materials in metal or quartz vessels may also be quenched in water or oil.

On the other hand, when a reaction must be completed at a lower temperature or it is desired to produce single crystals for studies on structure, then a slow, controlled reduction of the temperature is required. The type of cooling procedure thus depends on the application.

The formation of large single crystals from the melt may be favored by quiet, vibrationless cooling. Sometimes, however, motion of the melt during crystallization is desirable. The heating and cooling methods used for single crystals of pure metals are also applicable to single crystals of intermetallic compounds that exhibit congruent melting (see Part I, p. 94 ff., and [7]).

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Alloy Synthesis under Pressure

Special methods are required when one of the constituent metals of the alloy has a very low boiling point (Zn, Cd, Hg; see also p. 1789) while the other constituent has a high melting point (platinum metals and other transition metals; see Table 4, p. 1776). In this case, if the pressure is atmospheric pressure, one metal tends to vaporize before the other liquefies. Nowotny et al, have designed a special furnace which allows heating such metal combinations in a protective gas at high pressures. The apparatus is essentially a closed iron bomb containing a resistance-heated tube which encloses the crucible (Fig. 351). The furnace mantle m is a thick-wall seamless steel tube whose lower section is threaded for 50 mm, and carries a screw cap v. This cap in turn carries a threaded adapter which is connected to the compressed gas cylinder, the pressure gage and one of the two electrical terminals. All screw connections are also sealed with lead gaskets b. The other end of mantle m is closed off by cover plate d (a 35-mm.-thick circular steel plate) held in place by flange (and connected to the second electrical terminal. The gasket ring r is made of insulation-grade asbestos, and the six flange screws are of high-strength nickel-chromium steel (the screws must also be insulated from the flange by sleeves and washers of electrically insulating asbestos or similar material). The inner walls of plate d and the cap v are threaded so as to support the brass collars h_1 and h_2 . The latter make the electrical connection between the plate and cap and the carbon resistance element which they support. To cotain good electrical contact between the brass collars and the carbon sleeve conductors g1 and g2, the I.D. of the collars is made 0.1 mm. smaller than the O.D. of the corresponding section of the carbon sleeve. The collar is then heated and slipped over the

sleeve while still hot. The heating tube k is made from electrographitized carbon and has a wall thickness of 1.5-1.8 mm, in the long middle section and 4 mm, at the ends. Its ends fit tightly into sleeves g_1 and g_2 .

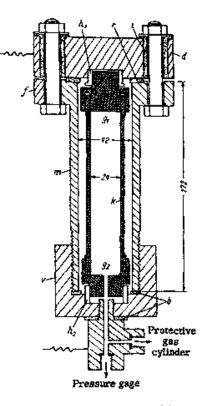


Fig. 351. Tubular furnace for high temperature pressure synthesis. k carbon tube; g_1 . g_2 special carbon sleeve conductors; h_1 , h_2 brass collars; m outer steel tube (mantle); f flange; d cover plate; v screwedon cap; b lead gaskets; r, i asbestos gasketing rings and sleeves. Dimensions in mm.

The narrow, high tubular crucible containing the charge is centered in k. The furnace is connected to a low-voltage transformer capable of delivering 600-900 amp. at 12 volts. The apparatus is filled with a protective gas $(N_{2} \text{ or } Ar)$ to 60-70 atm.; the pressure increases rapidly to about 150-200 atm. during heat-up but then decreases again during the actual fusion (it drops to about 70-100 atm. in 10 min.). The temperature cannot be measured direction

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in a series ant se it can only be estimated from the current consumption, assuming stherwise constant conditions (preliminary experiments are helpful).
 During the run, the furnace is immersed in running water up to the flange while the lid is cooled by spraying water from above. Electrographitized carbon is a useful crucible material for

Electrographitized carbon is a useful crucible material for preparation of alloys of Zn and Cd with Pt or Pd. Alumina crucibles do not last. The volatile-metal loss may approach 25%. The carbon tube and sleeves may last for 40-70 fusions (10 minutes each). Obviously, this furnace is not suitable for metals which readily form stable carbides.

REFERENCE:

H. Nowotny, E. Bauer and A. Stempfi, "Alfons-Leon-Gedenkschrift" der Allg. Bau-Zeitung, Vienna, 1951, p. 63.

Melting Without a Container

Under certain conditions it is possible to melt small quantities of metals, alloys and related compounds in such a way that they do not make or barely make contact with the wall of the container. Such a procedure becomes very desirable when one deals with corrosive elements or when products of very high purity are required. However, "containerless" fusion is possible only in special cases. For example, the sample may be heated to melting by means of an electric arc or a directional electron beam; in this case the sample rests in a shallow depression in a cooled copper plate. The molten sample contracts due to surface tension to form an oblate spheroid whose area of contact with the copper support is so small that no contamination occurs during the short fasion process. The resolidified sample is turned over and remelted on the other side. This procedure is called button melting. For heat sources, see Part I, p. 42.

Another melting method is the so-called levitation melting in which the sample is freely suspended in vacuum or in an inert atmosphere by a field developed by means of induction coils, which also supply the heat. This promising method is, however, still in the experimental stage, [E. C. Ocress, D. M. Wroughton, G. Commetz, P. H. Brace and J. C. R. Kelly, J. Appl. Phys. 23, 545 (1952); J. Electrochem. Soc. 29, 205 (1952)].

Comminution in the Absence of Air

Special precautions must be taken while studying alloys that are extremely sensitive to air, hygroscopic or readily exidized. This

G. BRAUER

1766

is especially true of operations in which one is trying to obtain comminuted material, shavings, etc., for density determinations or x-ray powder diagrams, where such material must be completely free of decomposition products. Devices for producing such comminuted alloys have been developed by Zintl et al. (I) and Klemm and Dinkelacker (II).

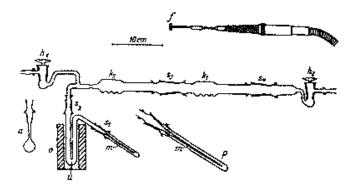


Fig. 352. Comminution of sensitive alloys in the absence of air. k_1 , k_2 working chambers for handling the alloy; h_1 , h_2 high-vacuum stopcocks; *m* capillary for x-ray sample; *u* glass tube for annealing the alloy powder; *o* electric furnace; *a* adapter with the analysis and sample storage bulb; *f* rotary milling tool.

I. The apparatus in Fig. 352 consists of several glass parts connected by ground joints s_1-s_4 . The assembly is connected via Schiff stopcocks h_1 and h_2 (see Part I, p. 59 f.) to a high-vacuum pump and a supply of pure, anhydrous inert gas.

The major constituent parts of the apparatus are two slightly oblate chambers k_1 and k_2 made of medium-wall glass tubing. The underside of each chamber carries three to four corrugations impressed with a carbon rod on the hot, soft tube. These corrugations prevent the alloy from slipping out of the chamber during workup. Depending on need, devices for annealing the comminuted material, for charging the glass capillaries which are used to hold the sample while examining its x-ray powder pattern, or for removal of analytical samples (analysis bulbs) may be added.

Before use, the entire apparatus is thoroughly evacuated over a period of several hours. At the same time, it is carefully heated (to promote removal of moisture) and then connected via stopcock h_1 to the protective gas supply. The blanketing gas is allowed to escape at h_3 . A small piece of the solid alloy is then introduced into chamber k_1 via the ground joint s_4 . A fast stream of the **protective gas is maintained while introducing the sample, following** which a loosely fitting rubber cap is put over joint s_4 . This permits the gas to escape while preventing air penetration into k_3 . The surface of the alloy in k_1 is cleaned by means of a small rotary milling tool i (5 mm. O.D.), set on a 12-cm.-long rigid shaft and introduced via s_4 . The rigid shaft is attached to the chuck of a flaxible shaft driven by a dental drilling machine. The alloy piece is cleaned on all sides and is then pushed into the chamber k_3 by means of a thick wire or a thin glass rod. The powdered waste material removed from the metal surface must not be entrained from k_1 into k_3 (it can be dislodged from the metal surface by tapping).

When the material is safely in k_2 , k_1 is disconnected at s_3 . The required quantity of clean shavings is then produced from the alloy in k_2 (a new, clean milling tool should be used). After this, s_3 is reconnected to h_2 . Turning and tapping the assembly transfers the fresh alloy shavings (or powder) to tube u (this tube must be prebaked and degassed in high vacuum). The alloy powder in u may then be annealed in the heat produced by furnace o. This treatment removes stresses and is frequently necessary in order to obtain good powder patterns with sharp interference peaks. If very sensitive alloys are handled, the temperature maintained during degassing of tube a must be higher than during the succeeding annealing of the sample. After the annealing, the required quantity of powder is transferred to the capillary tubes m, which are then melt-sealed prior to introduction into the x-ray powder pattern analyzer (the wide end of tube m is cemented to the adapter at s1, and a small side opening serves to equilibrate its pressure with that in the protective tube p).

If desired, tube u may be replaced by a bulb for sealing off analytical samples. The net weight of the empty bulb and its adapter (to u) is first established. The bulb is then filled with alloy powder and sealed off. It is then reweighed, and the total weight of the oxide-free metal powder can thus be accurately determined.

11. The arrangement of Klemm and Dinkelacker also utilizes a small rotary milling tool for cleaning of the surface and commission of the alloy chunk. In this method, however, the alloy is act removed from the crucible but is powdered while still in the crucible. The apparatus is shown in Fig. 353.

The thick-wall brass shell a houses vessel b, which can be rotated on axis i. The top of the crucible containing the freshly prepared alloy is sawed off, and the crucible is introduced via the ground-joint adapter c, which slopes upward. The crucible is then firmly fastened in b by means of a small screw r. Vessel b can be turned into any desired position by means of handle d. It is then fixed in that position by turning down screw s, which thus immobilizes axis t. Housing a can be evacuated via the groundmetal joint f, while additional vessels for further treatment of the alloy (analysis, powder pattern, density determination, etc.) can be

attached at a similar joint e. The apparatus can be completely sealed and evacuated if handle d is taken off and a standard taper cap pushed over the ground joint g.

The surface of the alloy in the crucible is cleaned by means of a small. rapidly rotating steel milling tool (5 mm. diameter), driven from a dental drill via a flexible shaft and introduced through joint c. The impurities removed from the surface of the alloy are dumped into c by turning b on axis I. A disposable rubber wiper blade ω cleans off all waste powder from the walls of a and pushes it into e. The waste is then removed from c. the joint is cleaned by blowing through it inert gas, and a new cutting tool is introduced through c. The clean alloy shavings (see the previous method) thus produced are removed through e.

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Distillation Method

If one component of a desired binary alloy is more volatile than the other and if the decomposition vapor pressure of the alloy is not too high, the alloy can be prepared by distilling or subliming the volatile component onto the other.

However, apart from a few exceptional cases this method is, for obvious technical reasons, restricted to alloys made of relatively volatile metals and metalloids, that is, those boiling below 1000-1100°C at 760 mm. This is because distillation at higher temperature tures is quite difficult in practice. (However, much less volatile

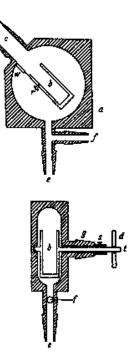


Fig. 353. Comminution of alloys in the absence of air without removing the alloy from the crucible. *a* brass housing; *b* vessel housing the crucible and able to rotate; *i* axis on which *b* rotates; *d* handle; *g* rubber wiper blade for scraping off loose particles. metals can be distilled in small amounts in high vacuum.) The method is therefore suitable for:

The special advantages of the distillation method are as follows: a) The volatile component is repurified by the distillation just prior to the reaction (this is important in the case of very reactive

metals). b) The reaction between the vapor of one component and the powder of the other proceeds quietly and smoothly (because of the limited amount of vapor present at any time).

c) Any excess of the volatile component can be distilled off after the reaction.

Each of the components is placed in a separate boat and the boats are positioned one behind the other in a horizontal tube. The choice of boat and tube materials is governed by the same considerations of thermal stability and chemical resistance as were discussed in the case of crucibles (see p. 1775 ff.). The tube must be gas-tight. For this reason, it is usually closed at one end and carries a ground joint on the other (the latter is for evacuation and filling with inert gas); alternatively, it may carry high-vacuum valves or stopcocks on both ends (see Fig. 354). To protect the glass, quartz or ceramic tube a against corrosion by the volatile metal, a liner tube b (made of glass, ceramic material or metal such as Fe or Ni) may be inserted. Boat s, contains an excess of the volatile component, while boat so is filled with the finest possible powder of the relatively nonvolatile reagent. Boat s1 is also surrounded by a test-tubelike cylinder c which acts as a vapor deflector.

At the start of the run, a high vacuum is created in tube a. Then the two short, tubular electric heaters are switched on and regulated in such a way that a temperature sufficiently high to maintain a reasonable rate of distillation exists in s_1 , while a slightly lower temperature exists in s_2 . The temperature in s_2 should be suffictently high to induce and maintain the reaction between the metal powder and the vapor arriving from s_1 . At the end of the run, the excess of the volatile component is distilled off and condensed in the cooler section of the tube. Finally, the product is removed from boat s_2 .

The above method is also useful for purifying a crude product distance from two components by the crucible or ampoule fusion methods. The excess of the volatile component may thus be remeved by vacuum distillation. In this case the vapor pressure of the free volatile component must, of course, be much higher than its pressure in the residual intermetailic phase. Examples of application of this method are preparations of silicides and germanides of alkali metals, and of Na₃As and K₃Sb.

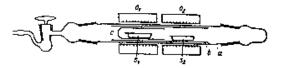


Fig. 354. Preparation of alloys by distillation. a reactor tube; b liner tube; c vapor deflecting cylinder; s_1 , s_2 boats; a_1 , a_3 tubular electric heaters.

The same principle can also be applied to the Faraday sealedtube system described in Part I, p. 76f. This system is completely closed and the only external influence consists of the temperature gradient; direct handling is not possible in this case. However, if the reactor tube material is resistant to corrosion by the reagents involved, the Faraday system produces an extremely pure reaction environment.

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Residue Methods

Occasionally, a pure component (α) phase may exhibit properties markedly different from those of the intermetallic phase which is vicinal to it on the constitutional diagram. Thus, the α -phase may dissolve more readily in a solvent or it may be attacked more readily by a reagent. In such cases it may be possible to use an excess of the pure component during the high-temperature synthesis and then liberate the intermetallic product by leaching out the matrix phase. Occasionally, also, slow cooling of the alloy meit may yield well-formed crystals of the intermetallic phase embedded in the pure component matrix, which may then be removed by some solvent. Depending on circumstances, the matrix phase may be removed by electrolytic oxidation, by aqueous acids, by bases, or by liquid NH₃. For example:

I. Electrolytic solution processes may be used to isolate semimetallic compounds from the matrix in which they are produced. Thus, for instance, Fe₃C may be isolated by electrolytic oxidation of the surrounding carbon-rich steel (see p. 1503). Other carbides such as (Fe, Cr)₃C, (Cr, Fe)₇C₃, (Fe, Mn)₃C, (V, Fe)₄C₃ and Fe₃Mo₃C are prepared in a similar manner. A procedure and an Fe₃Mo₃C are prepared in a similar manner.

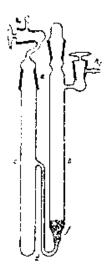


Fig. 355. Extraction of alkali metal alloys with liquid ammonia.

especially elegant apparatus have been developed by Klinger and Koch. This procedure has been employed primarily for the study of steels containing nonmetallic admixtures, but should be usable for a more general study of alloys.

II. Aluminum compounds such as Al_3Ti , Al_3Zr , Al_3Th , Al_3V , Al_3Nb , Al_3Ta , Al_4Ce , Al_4La , AlB_2 , etc., may be isolated from the Al-rich (matrix) products of the corresponding aluminothermic reactions, the solvents being dilute acids or bases. In a similar way, some silicides such as $ZrSi_2$, $ThSi_2$, VSi_2 , $NbSi_2$, $TaSi_3$, $MoSi_2$, WSi_2 and USl_2 may be produced in molten aluminum ''solvent'' and then isolated as residues from treatment of the respective aluminum alloys with acids or bases (see p. 1794).

III. A special case is the isolation of intermetallic compounds of alkali or

alkaline earth metals (except Be and Mg) by extraction with liquid ammonia. The alkali or alkaline earth metal, in considerable excess, is fused with the alloying component, the mixture is slowly cooled to obtain large crystals, and the solidified melt is then transferred without being exposed to air (the apparatus in Fig. 349 is quite appropriate here) into an extraction apparatus such as the one shown in Fig. 355. This device was developed on the basis of the arrangement of Biltz and Rahlfs (see Part I, Fig, 71). The alloy to be extracted is introduced through a and placed on top of the dense glass-wool filter f. The stopcocks h_1 and h_2 are both connected to a single vessel so that one can establish a high vacuum in the system, introduce NH3 to one (or both) tubes, or establish a connection between tubes b and c. Some NH₃ is condensed in b, where it contacts the alloy on f; the blue solution of the alkali metal is then allowed to pass via the intercon**necting tube** d into tube c. There NH₃ is evaporated, leaving behind the free alkali metal. The NH3 vapor is recycled to b for recondensation. Several repetitions of this operation allow exhenetive extraction of the alloy on f. The desired compound, which is completely resistant to or attacked only slightly by the $NH_{S'}$ remains as a residue on f.

The apparatus shown in Part I, Fig. 73 may also be used for the extraction of alloys with liquid ammonia.

The above method was used to produce Na_3As , Na_3Sb , Na_3Bi , $Na_{15}Pb_4$, $Na_{15}Sn_4$, $NaZn_{13}$ and Na_2Au . Pure, well formed single crystals were obtained.

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Special Processes

Intermetallic and metalloid compounds may also be prepared by methods other than those described in the preceding sections. However, these other processes have so far been used only in special cases, since the necessary conditions tend to limit their general applicability.

I. SIMULTANEOUS CHEMICAL REDUCTION OF NONMETALLIC

For instance, reduction of niobium oxide and nickel mixtures by means of hydrogen leads to Ni-Nb alloys [1]. Thermal decomposition of isomorphous mixtures of Fe, Co or Ni formates of oxalates, conducted under reducing conditions, gives fine, crystalline alloy powders. These alloys correspond to phase equilibria at comparatively low temperatures [2].

II. SYNTHESIS OF BINARY ALLOYS AND INTERMETALLIC COMPOUNDS BY COMBINING SOLUTIONS OF BOTH COMPONENTS

The solvent may be a third, more or less inert metal, usually with a low melting point (Hg, Al or Mg). The process temperatures

thus range between ambient and several hundred degrees. For basic data on the precipitation of intermetallic compounds, see [3].

The Hg solution method may be used for the preparation of many intermetallic compounds, as well as very reactive metals. This is because the Hg solvent can be distilled off at a comparatively low temperature. The method can thus be used for preparation of alloys which cannot be obtained by fusing or sintering at high temperatures (see Amalgam Metallurgy [4]).

Aluminum compounds (silicides, borides, and so forth) can be prepared in liquid Al (see p. 1797 ff.). Special silicides may be obtained in liquid Cu (see p. 1796).

Liquid NH₉ may also be used as a solvent, especially in the synthesis of alloys of alkali and alkaline earth metals. However, this method has so far been used mostly for nonmetallic or metalloid alkali compounds [5].

III. ELECTROLYTIC DEPOSITION OF ALLOYS FROM AQUEOUS SOLUTIONS.

The composition of the alloy depends on the composition of the electrolyte, the reaction conditions, and special additives which favor the precipitation. Just as in the case of solidification of melts, alloys precipitated by the electrolytic method consist of heterogeneous crystallizates, solid solutions, or some intermediate phases. They may differ from the alloys produced at high temperatures. The differences may show up in phase boundaries and in some physical and engineering properties [6].

The following binary alloy systems have so far been prepared in this way: Cu-Zn, Cu-Sb, Cu-Bi, Cu-Pb, Ag-Zn, Ag-Cd, Ag-Au, Ag-Bi, Ag-Pb, Au-Cu, Au-Ni, Ni-Zn, Ni-Cd, Ni-Fe, Zn-Cd, Pb-Sn, W-Ni, W-Co and W-Fe.

Some intermetallic or metalloid compounds may also be obtained by high-temperature electrolysis of liquid melts of the corresponding metal compounds. Secondary reactions sometimes play an important role in this case. This method, developed mainly by Andrieux and Dodero [7], has so far been used for horides (see p. 1798), silicides (see p. 1796 f.), phosphides, arsenides and carbides.

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1794

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Silicides

A summary of processes for the preparation of metal silicides is given in Table 5.

I. MOISSAN'S CLASSICAL PROCESS (FUSION OF THE ELEMENTS)

These reactions are usually highly exothermic; the charge thus heats up far above its melting point, and a closely controlled reaction becomes impossible due to interaction with the walls of the vessel and gases, as well as volatilization of reagents; product purity and the yield are usually poor.

a) Silicides of transition metals, especially those of metals of Groups IV to VII, may be successfully prepared by sintering mixtures of powders of the constituents at comparatively low temperatures (< 1500°C). In this case, external heating must be discontinued promptly at the beginning of the exothermic reaction to avoid melting of the charge. The starting materials must be extremely pure and have a particle size < 0.06 mm. The powder mixtures are either tableted or pressed into alumina or graphite crucibles. They are heated in argon or in vacuum. Under these crucibles, side reactions with the crucible materials are usually negligible.

Table 5

Preparation of Metal Silicides

| | Process | Reactions involved |
|-----|---|--|
| L | Synthesis from the elements | |
| | a) By fusion | M + Si →MSi, MH + Si → MSi + H ə |
| | b) By sintering or sin- tering under pres- sure | |
| п. | Reaction of metal ox- ides with Si or SiO_2 (silicates) and C | $ \begin{array}{l} MO + Si \rightarrow MSi + SiO \\ MO + SiO_2 + C \rightarrow MSi + CO \\ M \ silicate + C \rightarrow MSi + CO \\ (unfavorable: \\ MO + Si \rightarrow MSi + SiO_2 \\ MO + SiC \rightarrow MSi + CO \\ \end{array} $ |
| m. | a) Aluminothermic and magnesothermic processes | MO+Al(Mg)+SiO ₂ +S→ MSI (in Al)+Al(Mg)-S-containing slags |
| | b) Aluminum silicide process | Al-Si + M \rightarrow MSi (in Al) Al-Si + MF ₂ \rightarrow MSi (in Al) + AlF ₃ Al-Si + MO + NaF \rightarrow MSi (in Al) + Na ₃ AlF ₆ + Al ₂ O ₃ |
| | c) Copper silicide process | $Cu-Si+M \rightarrow MSi$ (in Cu) $Cu-Si+MO \rightarrow MSi$ (in Cu) + CuO • SiO ₂ |
| īv. | Electrolysis of a melt | K ₂ SiF ₆ + MO - MSi + KF |
| v. | Vapor-deposition proc- ess | $M + SiCl_4 + H_3 \rightarrow MSi + HC$ |

b) According to Kieffer and Cerwenka, the density of the material can be increased even during the heating process, the result being a better product. A Tammann furnace (see Part I, p. 39) is used. The powder mixture is pressed into strong, 15-mm.-I.D. graphite molds and heated at 200 kg./cm.² and 1100-1500°C. After cooling, the surfaces of the samples thus obtained are ground, yielding a material containing only 0.02-0.05% C.

B. REDUCTION OF METAL OXIDES WITH SI, SIC OR SIO₂ (SILICATES) IN THE PRESENCE OF CARBON

In general, this process requires very high temperatures and yields fused products from which it is difficult to isolate well-defined silicides. For this reason, this method is largely of historical interest. However, a modern variant is of some importance. In this variant, very pure Si is added to the metal oxide in the stoichiometric ratio. If the stoichiometric ratio is maintained exactly, all of the oxygen from the metal oxide will be bound to the Si, which then volatilizes as SiO. This method, which requires a vacuum but only relatively modest temperatures, yields very pure silicides.

The above process is applicable in all those cases in which both the metal and its oxide (which is reduced) have low vapor pressures at the reaction temperature (this is true of transition metals of Groups III to VIII). For instance, the process yields pure rare earth silicides, which are otherwise difficult to obtain. In this case the optimum reaction pressure is approximately 0.1 mm.

III. ALUMINOTHERMIC OR MAGNESOTHERMIC PROCESSES

The general method was invented by Hönigschmidt. It starts from metal oxides and SiO_2 and gives pure products if the nascent silicide is embedded in an excess of the reducing metal (preferably Al). This is achieved by using an excess of SiO_2 and of the embedding Al in the reaction mixture. Of course, the embedding aluminum metal becomes alloyed to some extent with the Si and the other metal of the mixture. The object of the embedding process is to form an ingot or nugget which can be easily separated from the surrounding nonmetallic slag. This separation is facilitated by the addition of fluxes (CaF₂, cryolite or CaO) to the reaction mixture (Al₂S₃, which was used by Hönigschmidt, is not recommended). The silicide can then be isolated from the nugget by reaction with dilute acid or alkali. It is obtained in the form of a crystalline powder.

Some processes for silicides start from the metal itself rather than its oxide. The metal is thus reacted with Si in the presence of a melt of a third metal which serves as the solvent. Aluminum is usually the optimum solvent. Another method employs components initially prealloyed with Ai (for instance, ThSi₃ is made from Th-Al and Si-Ai alloys). Still another process proceeds by stages, whereby the components of the silicide are prepared in situ from other compounds, primarily a metal fluoride or oxide and an alkali fluoride. The nascent components then form the silicide.

In all the above variants of the basic process, the silicide is always embedded in excess Al. The process has been used for NbSi₂, TaSi₂, ThSi₂, MoSi₂ and WSi₂.

The Lebeau process, which uses copper as a solvent and in at carrier, is no longer of any importance.

1798

Alternate methods:

IN. FLECTROLI'SIS

Silicides of Ti. Zr and Cr as well as those of the rare earth metals may be obtained by electrolysis of melts of the metals with silicates or fluorosilicates of suitable composition.

V. VAPOR DEPOSITION

Silicide layers may be obtained from H_2 -SiCl₄ mixtures by deposition of an incandescent filament.

Procedures for the preparation of silicides are also found in other sections of this book (see Alkali Silicides p. 989 f., magnesium silicide p. 921 f., calcium silicide p. 946 f., silicides of Ti, Zr and Th, p. 1249 f.).

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Borides

Table 6 lists the most important processes for the preparation of borides, especially those of the transition metals.

Table 6

Preparation of Metal Borides

| _ | Process | Reactions involved |
|-------|---|--|
| I, | Synthesis from the elements | · ·· |
| | a) Fusion | $M+B \rightarrow MB$, $MH+B \rightarrow MB+H_a$ |
| | b) Sintering or sinter- ing under pressure | |
| II. | Aluminothermic and magnesothermic processes | MO+B ₂ O ₃ +Al(Mg) → MB+Al(Mg) oxide |
| III. | Reduction of oxides with carbon | $MO + B_2O_3 + C \sim MB + CO$ |
| IV. | Boron carbide process | $MO(M, MH) + B_4C(C, B_2O_3) - MB + CO$ |
| v. | Electrolysis of a melt | MO+alkali (alkaline earth) borate+ alkali (alkaline earth) fluoride MB+alkali (alkaline earth) borate- fluoride |
| VI. | Vapor-deposition processes | M (M halide) + B halide + H₂ → MB + hydrogen halide |

I. Synthesis via fusion of the elements entails such high heats of formation that the reaction temperatures become very high. As a result, there is interaction with the material of the vessel and the product boride becomes contaminated. On the other hand, all borides may be prepared by sintering the appropriate mstal with amorphous boron powder, which should be as pure as possible (commercial grades now available contain 97-99% B). The reaction mixtures should be heated in alumina crucibles (W or Mo crucibles or boats may also be used) in vacuum (an argon atmosi phere is occasionally also used). The reaction, which is always exothermic, starts at temperatures of 700-1200°C; the highest temperature may lie above 2000°C. In some cases, sintering under pressure in carbon tubes (mentioned as a possible method of synthesis for silicides—see p. 1796) can be used.

II. Reduction with Al or Mg allows the use of oxides as starting materials and eliminates the preparation of pure boron. On the other hand, this method involves inconvenience of chemical separation of the product boride crystals from by-products. This separation becomes especially difficult in the case of products of the aluminothermic preparation of high-melting borides (those of transition metals of Groups III to VI). No solid ingot or nugget is formed in this case; the fine boride powder is occluded in Al_2O_3 slag. According to Andrieux and Peffen, an excess of B_2O_3 . CaO and Na $_{2}O$ should be added to the reaction mixture. The alumina slag thus becomes soluble in acids and may be separated more easily from the boride powder.

II. Originally the preparation of borides of metals such as Ti and Zr from B_*C involved a reaction in hydrogen:

or

$$7 Ti + 3 B_{4}C + B_{2}O_{3} = 7 TiB_{2} + 3 CO$$

 $3 Ti + 2 B_{4}C + TiO_{2} = 4 TiB_{2} + 2 CO$

Recently, however, a simpler process has been devised:

$$2 \text{TiO}_2 + B_4 \text{C} - 3 \text{C} = 2 \text{TiB}_2 - 4 \text{CO}$$

The mixture of starting materials is pressed into pellets and beated in a tubular carbon furnace under high vacuum. Maximum temperatures of 1400-1900°C are required to produce the metal boride within a reasonable time. The method has been tested for borides of Ti, Zr, V, Nb, Ta and W.

Alternate methods:

IV. Small quantities of pure boron compounds can be prepared by **electrolysis** of melts. Boron, which is evolved on the cathode **from alkali and alkaline earth borates**, combines with the simultaneously precipitated metal.

V. Passage of gaseous mixtures consisting of a metal halide, BBr_3 and H_2 over incandescent carrier metals on the average yields only boride layers inhomogeneous, and solid products.

REFERENCES:

- General: R. Kieffer and F. Benesovsky. Hartstoffe [Hard Materials], Vienna, 1962; R. Kieffer and F. Benesovsky. Metall <u>6</u>, 171, 243 (1952).
- H. Moissan. Der elektrische Ofen [Electrical Furnace], Berlin, 1900; F. Wedekind, Ber. dtsch. chem. Ges. <u>46</u>, 1198 (1913); Binet du Jassonneix. Comptes Rendus Hebd. Séances Acad. <u>Bci. <u>143</u>, 169, 897, 1149 (1906).
 </u>
- b. R. Klessling. Acta Chem. Soand. <u>4</u>, 209 (1950); P. Ehrlich. Z. aborg. Chem. <u>259</u>, 1 (1949); L. Brewer, D. L. Sawyer,

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D. H. Templeton and C. H. Dauben, J. Amer. Ceram. Soci De. 173 (1951); H. Nowotny, F. Benesovsky and R. Kieffer, Z. Metallkunde <u>50</u>, 258, 417 (1959).

- II. E. Wedekind, Ber. dtsch, chem. Ges. <u>46</u>, 1198 (1913); J. T. Norton, H. Blumenthal and S. J. Sindeband, Trans. AIME <u>185</u>, 749 (1949); S. J. Sindeband, Ibid. <u>185</u>, 198 (1949); J.-L. Andrieux and R. Peffen, French Patent 1,123,861 (1956).
- III. P. M. McKenna. Ind. Eng. Chem. 28, 767 (1936).
- IV. R. Kieffer, F. Benesovsky and E. R. Honak, Z. anorg. alig. Chem. <u>268</u>, 191 (1952); G. A. Meyerson and G. V. Samsonov, Zh. Prikl. Khimii <u>27</u>, 1115 (1954); C. T. Baroch and T. E. Evans, J. Metals <u>7</u>, 908 (1955).
- V. L. Andrieux. Thesis, Univ. of Paris, 1929; Rev. Métallurg. <u>45</u>, 49 (1948); G. Weiss. Thesis. Univ. of Grenoble, 1946; Ann. Chimie <u>1</u>, 446 (1946); J. T. Norton, H. Blumenthal and S. J. Sindeband. Trans. AIME <u>185</u>, 749 (1949).
- VI. M. Moers. Z. anorg. Chem. 198, 243 (1946); J. E. Campbell, C. F. Powell, D. Nowicki and B. W. Gonser, J. Electrochem. Soc. 96, 318 (1949).

Amaigams

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While some low-melting (< 1000 °C) metals fail to form alloys with mercury, the majority may be amalgamated simply by heating

Table 7

Solubility of Metals in Mercury at about 20°C (after Jangg and Bach)

| Metal | Solubility in weight % | Metal | Solubility in weight % | Metai | Solubility in weight & weight & weight |
|--|--|---|---|---|--|
| Ag Al As Ba Be Bi Ca Cd Co Cr Cu Fe Ce | $\begin{array}{c} 0.03 \\ 2.3 \cdot 10^{-3} \\ 0.24 \\ 0.13 \\ 0.83 \\ 1 \cdot 10^{-3} \\ 1.4 \\ 0.8 \\ \sim 5.0 \\ < 1 \cdot 10^{-5} \\ < 4 \cdot 10^{-7} \\ 2 \cdot 10^{-5} \\ < 5 \cdot 10^{-7} \\ 1 \cdot 10^{-3} \end{array}$ | In K La Mg Mo Ne Ni Pb Pb Pd Rb Rb | 57 0.38 0.013 0.036 0.31 $1.7 \cdot 10^{-3}$ $\sim 2 \cdot 10^{-6}$ 0.52 $2 \cdot 10^{-6}$ 1.5 0.08 $2 \cdot 10^{-3}$ 1.4 0.16 | Ru Sb Si Sn Sr TA Th Ti U V W Zn Ži | 0.35 2.9 10723 , 105 1 - 107 0.87 1.0 0.01; 4124 ms 0.016 ; 4124 ms 0.016 ; 4124 ms 1.107 1 |

with mercury in closed iron crucibles or glass ampoules. Under special circumstances, these vessels may also contain special insert crucibles (see p. 1774 ff.). This simple process applies to all permissible amalgam compositions.

Another general method for preparation of amalgams consists Another general method for preparation of amalgams consists of the electrolysis of solutions of the respective metal salts in cells comprising an Hg cathode. The concentrations of the respective metals in the amalgam reach very high levels so that solid phases may separate. The method is applicable even to metals with extremely low solubility in Hg (for example, Fe); in this case, the method gives suspensions of the metal in Hg which exhibit behavior very similar to that of "true" amalgams (see Table 7).

REFERENCE:

G. Jangg and H. Bach. Quecksilber- und Amalgammetallurgie, Handbuch d. techn. Elektrochemie [Mercury and Amalgam Metallurgy, Handbook of Engineering Electrochemistry], Vol. I, Leipzig, 1961.

It is sometimes desired to prepare liquid or semisolid amalgams of base metals for special purposes, especially for use as laboratory reducing agents. The following simple methods apply in these cases:

SODIUM AMALGAM (LIQUID; ABOUT 1% Na)

L Clean sodium metal (11.5 g.) is cut into 5-mm. cubes. The cubes are speared with a pointed glass rod and rapidly introduced below the surface of warm (30-40°C) pure mercury (1150 g. = 85 ml.) contained in a 500-ml. wide-neck Erlenmeyer flask. The flask is covered with cardboard to prevent spattering during the rather vigorous amalgam formation reaction.

II. In another method, 3,5 g, of Na protected by a layer of toluene (10-15 ml.) is melted in a 250-ml. Erlenmeyer flask placed on a hot plate. Then, 340 g. (25 ml.) of Hg is added in drops (stirring or shaking). The first few drops of mercury cause a vigorous reaction, but then the amalgam formation becomes less violent. The toluene boils during the entire addition; at the end, it is decanted or displaced with other liquids.

The following method for solid amalgams may be modified and adapted to other ratios of reagents.

SODIUM AMALGAM (SOLID; ABOUT 2-3% Na)

1. The Fieser procedure gives especially pure material: Clean ecdium pieces (6.9 g. for an amalgam containing 2% Na, 10 g. for one containing 3% Na) are placed in a 250-ml. three-neck

1962

round-bottom flask. The two side necks carry nitrogen inlet and outlet tubes, while the center neck carries a dropping funnel containing 340 g. (25 ml.) of Hg. The flask is thoroughly flushed with $N_{\rm H}$, and 10 ml. of Hg is then added. The flask is heated on an open flame until the start of the reaction. Additional Hg is then slowly added, with minimum additional heating. After the addition, the hot molten amalgam is poured onto a clean plate and broken up into pleces while still hot and brittle.

II. Another method is useful for preparation of larger quantities of amalgam. Thus, for example, 51 g, of clean, freshly cut sodium is heated in an enameled pot (about 18 cm. I.D.) under paraffin oil until molten (the thickness of the protective oil layer should be 1 cm.). Then, 1650 g. (122 ml.) of Hg is added slowly (constant stirring) from a dropping funnel. This reaction ends within 3-4 minutes, and most of the paraffin is decanted. The amalgam solidifies at about 250° C. During cooling, it is comminuted with a heavy pestle to form small beads. Alternatively, the hot liquid amalgam may be poured (together with the adhering oil) into a porcelain dish and allowed to solidify; the cake is then broken up to the desired particle size in a mortar. After complete cooling the oil is removed by washing with petroleum ether or benzene. The solvent is then evaporated, and the product stored in an air-free atmosphere.

PROPERTIES:

Amalgams containing less than 3% Na are not too sensitive to air; however they must be stored in an air-free atmosphere. Complete liquefaction occurs at the following (liquidus) temperatures: 0.5% Na, 0°C; 1.0% Na, 50°C; 1.5% Na, 100°C; 2.0% Na, 130°C; 2.5% Na, 156°C; 3% Na, 250°C; 4.0% Na, 320°C.

REFERENCES:

Organic Syntheses, Collective Volume 1, New York-London, 1941;
p. 539; W. R. Renfrow, Jr., and C. R. Hauser in: Organic Syntheses, Collective Volume 2, New York-London, 1950, p. 609; V. Deulofeu and T. H. Guerrero in: Organic Syntheses; Vol. 22, New York-London, 1947, p. 92; S. H. Babcock in: H. S. Booth. Inorganic Syntheses, Vol. 1, New York-London; 1939, p. 10; L. F. Fleser. Experiments in Organic Chemistry, New York, 1941, p. 419,

POTASSIUM AMALGAM

For preparation, see A. Roeder and W. Morawistz, Z. Elektrochem. 60, 431 (1956).

CALCIUM ANALGAM

The reactor is a small steel bomb b (Fig. 356). The vertical part of the top opening carries a flat thread into which is screwed the steel head k. While the two parts should fit each other well, one should be to unscrew k without too much difficulty. The conical extended surface above the thread provides additional scaling area. The seal should hold at better than 70 atm. The head k carries a pressure-reducing value r connected to pressure gage m and pressure tubing d, which leads to a compressed nitrogen cylinder.

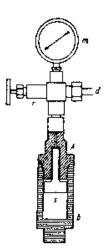


Fig. 356. Preparation of calcium amalgam. b steel bomb, 19 cm. long, 5.5 cm. I.D., 9 mm. wall thickness; capacity 45 mL up to the screw thread; s movable piston; t steel head; r pressurereducing valve; m pressure gage; d copper pressure tubing for in-

troduction of N2.

A piston s, located inside the bomb and actuated by the gas from the cylinder, fits the walls fairly tightly.

To start with, the bomb is charged with 35 ml. of pure Hg. Then, 7-10 g. of shavings of commercial Ca are added and the piston set in place. The bomb is tightly closed and nitrogen injected to a pressure of 60-70 atm, above the piston. The formation of the amalgam starts immediately, heat of reaction is evolved, and the bottom of the bomb becomes hot: the reaction ends in no more than 10-15 minutes. The pressure is released and the bomb is opened. The amalgam is rapidly transferred to a dry, wide-neck flask of about 60-ml. capacity, which is then tightly closed. The steel bomb is rinsed with some pure Hg. This material is added to the flask, which is then filled with Hg to just below the stopper (the amalgam in the flask heats up considerably on dilution with the Hg). The mixture is shaken well and allowed to cool.

PROPERTIES:

This amaigam contains about 1% Ca; sometimes solidifies in the coid; can be stored indefinitely in containers com-

pletely filled with mercury. According to data in M. Hansen and **K. Anderko**, Constitution of Binary Alloys, the liquidus curve in the Ca-Hg system rises to about 260°C at 2% Ca, 140°C at 1% Ca, and 25°C at 0.3% Ca; most of this amalgam solidifies at the peritectic point of -39°C. REFERENCE:

A. Brukl. Angew. Chem. <u>52</u>, 151 (1939).

STRONTIUM AND BARIUM AMALGAMS

Strontium and barium amalgams are prepared by electrolysis of solutions of the corresponding chlorides on mercury cathodes. The directions for the compound are each applicable to the other.

STRONTIUM AMALGAM

The cell a of the apparatus shown in Fig. 357 contains about 300 ml, of a saturated solution of pure SrCl₂, made weakly acidic

with HCl (if contaminated with traces of Na and Fe the salt must be prepurified). The cathode b consists of 600 g. (45 ml.) of pure, distilled Hg. The thick Pt wire c, which dips into the mercury pool, is the current lead. The anode is a graphite rod e (10 mm. O.D.) suspended in a porous clay cell d which dips into the liquid. The electrolysis proceeds at a current of 6.5 amp. (that is, at 1.7 amp./in.2, considering the 24 cm,² of cathode surface). The passage of the current causes a sharp temperature rise and the electrolyte is maintained at the optimum temperature of 38-40°C by means of cooling coils g and f wound on the outer surface of cell a and immersed in the solution. The liquid in the anode space is replaced every 15 minutes to prevent accumulation of Cla and its penetration into the cathode space. The Sr content in the Hg reaches 1.3% in 90 minutes; at this point the amalgam becomes a siurry because

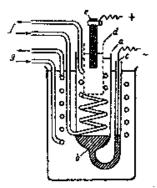


Fig. 357. Preparation of strontium amalgam. *a* electrolysis cell; *b* mercury cathode; *c* current lead (Pt wire); *d* porous clay cell; *e* anode (graphite rod); *f*, *g* water-cooled colls.

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the liquidus point for this composition is reached. The current is shut off and the electrolyte is poured out from the cell. The amalgam is then removed, washed several times with water, and dried with filter paper.

PROPERTIES:

Silvery, shiny, solid at room temperature. Must be stored in air-free atmosphere.

HOR.

REFERENCE:

L. Holisck and W. Noddack, Angew. Chem. 50, 819 (1937).

RARIUM AMALGAM (APPLICABLE ALSO TO STRONTIUM AMALGAM)

The cell consists of a 250-ml. beaker. The cathode is a pool of 250 g. (18 ml.) of pure mercury. A Pt wire, all of it except for the tip sealed in glass to prevent contact with the electrolyte, dips into the mercury pool and serves as the current lead. The anode is a horizontal sheet of Pt, 5-10 cm.² in area.

The cell is filled with 100 ml. of saturated $BaCl_2$ solution. The electrolysis proceeds at a current of 1.75-2.5 amp. and 6-7 v. The current should be shut off after 2.5 hours, since beyond that time there occurs a sharp voltage rise, evolution of gas at the cathode and decomposition of the amalgam. Sometimes, crystalline amalgam particles deposit on the mercury surface and interfere with the electrolysis. This deposition may be prevented by slow agitation with a stirrer, or the crystals may be pushed into the body of the mercury with a glass rod.

At the end of the run the solution is decanted and the amalgam is thoroughly washed with distilled water, followed by ethanol and ether. It contains about 3% Ba. Is is stored in an air-free atmosphere.

REFERENCES:

G. McPhail Smith and A. C. Bennett, J. Amer. Chem. Soc. <u>31</u>, 804 (1909); B. C. Marklein, D. H. West and L. F. Audrich in: H. S. Booth. Inorg. Syntheses, Vol. 1, New York-London, 1939, p. 11.

ZINC, CADMIUM, TIN, LEAD AND BISMUTH AMALGAMS (LIQUID)

The liquid zinc amalgam (2-3% Zn) is prepared from 4 g, of zinc (gramules, shavings; preferably, however, foil). The zinc is degreased with ether, thoroughly washed with dilute H_3SO_4 , placed in a 100 ml, flask, and heated on a water bath together with 200 g. (14.0 ml.) of Hg and 2 ml. of 1N H_3SO_4 . The Zn dissolves completely in about 20 minutes. The liquid amalgam is repeatedly washed with very dilute H_3SO_4 , cooled and separated in a dropping function from solid particles (β or γ phase, composition approx. HgZe₂). These solids may be used to enhance the Zn concentration of sublights that have lost some Zn during use. The liquid Cd and Bi consignment (each containing about 3% of the respective metal) are prepared in an analogous fashion. However, the Bi amalgam is prepared with hydrochloric rather than sulfuric acid. The Sn amalgam (8% Sn) is prepared by heating Sn granules with Hg under hydrochloric acid. The liquid Pb amalgam (3% Pb) by heating dry. Pb with the stoichlometric quantity of Hg (the starting Pb must be freed of surface oxide by treatment with conc. HCl). The amalgam product is washed with water.

PROPERTIES:

The above liquid amalgams are very stable and may be stored for a long time under weakly acidic water, with which they react extremely slowly.

Used as reducing agents in volumetric analyses.

REFERENCES:

E. Brennecke. Flüssige Amalgame als Reduktionsmittel in der Massanalyse [Liquid Amalgams as Reducing Agents in Volumetric Analysis], in: Brennecke, Fajans, Furmann, Lang and Stamm. Neuere Massanalytische Methoden [New Methods of Volumetric Analysis], Stuttgart, 1951; also contains references to original publications. C. Winterstein, Z. anal, Chem. <u>117</u>, 81 (1939).

AMALGAMS OF BARE EARTH METALS

Amalgams of rare earth metals (3% of the metal) are readily obtained by electrolysis of alcoholic solutions of the corresponding anhydrous chlorides at an Hg cathode and a graphite anode. These amalgams may be then further concentrated by distilling off the excess Hg.

REFERENCES:

E. E. Jukkola, L. F. Audrieth and B. S. Hopkins in: H. S. Booth, Inorg. Syntheses, Vol. 1, New York-London, 1939, p. 15.

ALUMINUM AMALGAM

The normal procedure is to deposit only a surface layer of amalgam on the metal, in order to activate it for use in some specific reaction [H. Adkins, J. Amer. Chem. Soc. 44, 2175 (1929)]

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Potassium-Sodium Alloy (liquid)

The constitutional diagram of the K-Na system shows a liquidus curve minimum at -12.5 °C corresponding to 77.3 wt. % K. All alloys with compositions near this point (45-90 wt. % K) are liquids at room temperature and are much more reactive than the pure metals.

Alloys such as these are prepared by carefully heating, for instance, 3 g. of clean pieces of K and 1 g. of clean pieces of Na (or other required quantities of these metals) under anhydrous toluene or xylene, while kneading the two metals with a flat-end glass rod.

According to Lecher, the metals may be combined even at room temperature provided some ethanol is added to the protective fluid in order to activate the metal surface. The vessel is a Schlenk flask, which consists of a two-neck glass bulb (one of these necks is narrow and vertically centered, the other is inclined and somewhat to the side of the flask). An alloy useful in organic reactions may be obtained from 0.35 g. of Na and 1.6 g. of K, which are combined under weakly alcoholic ligroin while a stream of nitrogen is introduced via the side neck (the metals are kneaded by means of a flat-end glass rod introduced through the vertical neck). After a liquid alloy has been obtained, the nitrogen purge is continued while the alcoholic ligroin (including the impurities suspended in it) is replaced by clean, anhydrous ligroin.

The Schlenk flask may, of course, be replaced by other devices which allow work in the absence of air. The liquid alloy ignites spontaneously and must always be protected by an inert fluid and an inert gas (N_3, CO_4) .

REFERENCES:

E. Lecher. Ber. dtsch. chem. Ges. <u>48</u>, 524 (1915). For constitutional diagrams and crystal structures of the K-Na and other binary systems of alkali metals, see also A. Helms and W. Klemm. Z. anorg. allg. Chem. <u>242</u>, 201 (1939).

Low-Melting Alloys

Low-melting alloys are often required for special purposes such as for heating baths or manometers, sealing in other liquids or gases, cementing, and for flowout devices. Some of these siloys, all of which are reasonably stable in air ar their melting peints and somewhat above, are listed below.

5. ALLOYS AND INTERMETALLIC COMPOUNDS

| Designation | М,р,, °С | Composition, wt. % |
|---|----------------|---------------------------------|
| Bi-Cd-Pb-Sn eutectic (Wood's Lipowitz metal) | 71 | 49.5 Bi/10.1 Cd/27.3 Pb/13.1 Sn |
| Bi-Cd-Pd eutectic | 91.5 | 51.7 Bi/8.1 Cd/40.2 Pb |
| Bi-Pb-Sn eutectic (Newton's Rose metal) | 9 6 | 50 Bi/31.2 Pb/18.8 Sn |
| Bi-Cd-Sn eutectic | 103 | 54 Bi/20 Cd/26 Sa |
| Bi-Pb eutectic | 125 | 56.5 BI/43.5 Pb |
| Bi-Sn eutectic | 139 | 58 Bi/42 Sn |
| Cd-Pb-Sn eutectic | 145 | 18.2 Cd/32 Pb/49.8 Sn |
| Pb-Sn eutectic | 183 | 37.7 Pb/62.3 Sn |
| Sn-Zn eutectic | 198.6 | 91.1 Sn/8.9 Zn |
| Cd-Zn eutectic | 266 | 82.6 Cd/17.4 Zn |
| Ag-Pb eutectic | 304 | 2.5 Ag/97.5 Pb |

Further special alloys can be obtained with Ga and In:

| Designation | M.p., °C | Composition, wt. % |
|----------------------|-------------|-------------------------------|
| Ga-In-Sn-Zn eutectic | 3 | 61 Ga/25 In/13 Sn/1 Zn |
| Ga-In-Sn eutectic | 5 | 62 Ga/25 In/13 Sn |
| Ga-In-Zn eutectic | 13 | 67 Ga/29 In/4 Zu |
| Ga-In eutectic | 16 | 76 Ga/24 In |
| Ga-Sn eutectic | 20 | 92 Ga/8 Sa |
| Ga-Zn eutectic | 25 | 95 Ga/5 Zn |
| L 46 | 46.5 | 40.6 Bi/8.2 Cd/18 In/22.4 Pb/ |
| | | 10.8 Sn |
| L 58 | 58 | 49 Bi/21 In/18 Pb/12 Sn |
| In-Sn eutectic | 117 | 52 In/48 Sn |

An exhaustive review of alloys melting between --39°C and +419°C is given by Spengler. If the low-melting alloys are used as cements or solders for nonmetallic objects, or if they are melted in nonmetallic vessels, then the thermal expansion coefficients must be carefully considered. For instance, Wood's metal may, on cooling and resolidification, burst glass vessels in which it is contained for use as a bath liquid.

REFERENCES:

H. Spengler, Metall 9, 682 (1955); Z. Metallkunde 46, 464 (1955); J. D'Ans and E. Lax. Taschenbuch f. Chemiker and Physics (Randhook for Chemists and Physicists], Berlin-Göttingen-Heidelberg, 1959; M. Hansen and K. Anderko. Constitution of Binary Alloys, New York-Toronto-London, 1958; C. J. S. Smithells. Metals Reference Book, London, 1949; M. T. Ludwich (The Indium Corp. of Amer.), Indium etc., New York, 1950; W. Kroll. Metallwirtschaft <u>11</u>, 435 (1932).

Formula Index

pp 1-992: Vol. 1; pp 1003-1810: Vol. 2

NOTE: Rare earth elements (lanthanides) are designated by the common symbol Ln (except in special cases where R.E. has been used). Thus, for their compounds see under Ln.

Ag₂Se 1041

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Ag 1029, 279, 1028 Ag₂C₂ 1047 Ag(CF3COO) 205 Ag2C4H4O6 1049 AgCN 661 Ag₂CN₂ 1047 Ag2CO3 1048 AgClO3 1037 [Ag(dipyr)3](ClO4)2 1050 [Ag(dipys)2]NO3 1050 [Ag(dipyr)3](NO3)2 1051 [Ag(dipyr)2]S2O8 1051 AgF 240 AgF₂ 241 Ag₂F 239 AgI 1035 AgMnO4 1463 AgN₃ 1045 Ag3N 1046 AgNCS 671 AgNH₂ 1043 AgNO2 1048 Ag2N2O2 493, 514 Ag2O 1037 Ag₂O₂ 1038 Ag20.4WO3.aq 1728 $A_{g}PO_{2}(NH_{2})_{2}$ 582 [Agphen_]S2O8 1050 Ag₂S 1039 Ag₂SO₃ 1043 Ag₂SO₄ 1042

Ag2SiO3 705 Ag₂Te 1042 AlAs 831 AlAsO4 831 AlB₂ 772, 1792 AlB₁₂ 772 AlBr3 806, 813 AlBr3-H2S 819 Al4C3 832 AI(C₂H₅)₃ 810 Al(C₂H₅)₂Br 809 AI(CH₃COO)₃ 835 $Al(C_2 \Re_5)_2 Cl \cdot O(C_2 H_5)_2$ 811 AI(C₂H₅)₂H 811 AI(C5H7O2)3 836 Al(C2H5)3.O(C2H5)2 611 Al(CN)3-O(C2H5)2 834 Al₄Ce 1792 AICl3 680, 805, 812 Al₂Cl₃H₃ 808 AlCl3-6H2O 815 AICI3-NH3 817 AlCla-PCIs 818 AICI3-SO2 817 Al2Cl6-SOCl2 818 AlF3 225 AIF3-3H2O 225 AlH3-N(CH3)3 809 AlH3-2N(CH3)3 809 (AlH3)0-x0(C2H5)2 807 -S. 14-11-18 Alla 814 🗧

All 3.6NH3 819 AlaLa 1792 AIN 827 AI(N3)3 829 Ai₃Nb 1792 Al₂O₃ 824, 1660 Al(OCH₃)₃ 888 Al(OC₂H₅)₃ 834, 835 AI(OC2H4)3N 835 Al(OD)3 134 AI(OH)3 676, 810, 820 AlOOH 820 Al203-2S02-H20 824 Al2O3-3SO2-xH2O 824 A)P 829 4 H , હું તુને A)PO4 831 Al₂53 134, 700, 823 ALSE 831 同業課 Al₂Se3 825 20,00 Al₃Te 1792 Al2Te3 826 п. Al₃Th 1792 Al₃V 1792 Al₃Zr 1792 Ar 82 Aa 591 ' AsBr3 597 AsCl3 596 🖓 🖓 AsF3 179, 197 AsF₅ 198 AsH3 593 As2R4 594 Asl<u>s</u> 598 Ani 597

Aug03 600 AngOg 681 AngOs-10120 601 Asp05-68003-aq 1736 AsyOs-188603-49 1735 As2S5 603 Az4S4 603 AsyZe3 594 Au 1052 Au₂C₂ 1063 AuCN 1064 AuCI 1055 A=Cl₃ 1056 A=203 1059 Ac(OH)3 1060 AuS 1062 Au₂S 1061 An₂S₃ 1063

B

B 770 B₂AI 772 B12AI 772 BAsO4 797 BBr3 770, 781 B(CH₃)₃ 798 B(C₂H₅)₃ 799 B(C, R₂₌₊₁)₃ 800 BCl; 780 BCl₂(C_nH_{2n+1}) 803 BF 3 219 BF2(=-C4flg) 802 BF3-2820 784 BF 3-NH 3 785 BF3-O(C2H5)2 786 B-16 773 **R**3 782 BN 789 BEN 2)3 476 779 والو**الوال**و **179 Ja** 779 B₂O₂ 167

B(OCH₃)₃ 797 B3O3(CH3)3 800 B3O3(n-C4H9)3 801 B(OH)2CH3 800 B(OH)2(n-C4H9) 801 B2O3-24WO3-ag 1716 BPO4 796 B₂S₃ 788 Ba 922 BaBr₂ 930 Ba(BrO3)2-H2O 316 BaCO₃ 933 BaCS₃ 674 BaCl₂ 930 Ba(CIO3)2-H2O 314 Ba(ClO₄)₂ 320 $B_{0}(C|O_{4})_{2}-3H_{2}O=320$ Ba₂CrO₄ 1393 Ba₃(CrO₄)₂ 1394 Ba₂[Cu(OH)₆] 1685 BaF₂ 234 $Ba_3[Fe(OH)_6]_2$ 1691 Ba2[Fe(OH)7].1691 BeO 893 BaGeF₆ 215 BaH₂ 929 Ba3H4(IO6)2 326 Be(H2PO2)2-H2O 557 BaH₂P₂O₆ 2H₂O 562 Bal₂ 930 Ba(MaO₄)₂ 1462 Ba(N₃)₂ 942 Ba(N₃)₂-H₂O 942 Ba₃N₂ 940 BaO 933 BeO₂ 937 BaO2-8H2O 936 3BaO-P2O5-24McO3-89 1732 10BaO-P2Os-24V2O5-aq 1740 3BaO-P2O5-24WO3-aq 1721 Ba3(PO2S2)2.8H2O 572 BaPt(CN)4.4H20 1576 BaReO4 1485 Ba(RcO4)2 1485 Ba3(ReO5)2 1487

BaS 938 Ba(SO₃F)₂ 173 BeS205-2H2O 397 BeSO₄-KMnO₄ 1463 BaSe 939 BeSeO₄ 939 BaSi 947 BaSiO₃ 706 BeSi2Os 706 Ba[Sn 2O(OH)4] 1696 BaTe 940 Be 887 BeBr₂ 891 BeC₂ 899, 900 Be₂C 899 Be(CH₃COO)₂ 901 BeCO₃ 893 BeCl₂ 889 BeF₂ 231 Bel₂ 892 $Be(N_3)_2$ 899 Be3N2 898 Be40(CH3COO)6 901 Be₄O(C₂H₅COO)₆ 902 Be(OH)₂ 894 Be4O(HCOO)6 902 BeS 895 BeSe 897 BeTe 897 Bi 620 BiBO₃ 2H₂O 627 BiBrg 623 BiCl₂ 622 BiCl₃ 621 BiF3 201 BiF₅ 202 Bil₃ 624 BiICl₂ 622 Bi₂O₃ 620 Bi2O4+aq 629 BiOBr 624 BiOCI 622 BiOI 625 BIONO₂ 626 BiONO2-1/1 H2O 626 BiONO₃ 620

 pp 1-992: Vol. 1; pp 1003-1810; Vol. 2

 BiPO₄ 626
 CNI 666

 BiPO₄-3H₂O
 626
 C₁₂Na(N

 Br₂ 275
 CO 645

 BrF3
 156
 C₃O₂ 64

 BrF3
 156
 COCl₂ 44

 BrF3
 156
 CoCl₂ 64

 BrF3
 156
 COCl₂ 4

 BrA
 20 276
 COCl₂ 4

 BrN₃ 476
 COClF 2

 BrO₂ 306
 COIF 2

 Br₂O 307
 (CONH)₃

 [BrPy_x)ClO₄ 328
 COS 65

 [BrPy₂]F 328
 COSe 6

 [BrPy_x]NO₃ 328
 C₈Rh 6

С

C 630 C30AIC14-2AIC13 644 C₈8r 643 CCIF₃ 205 CCl₂F₂ 151, 205 C2Cl2F4 205 C₂Cl₃F₃ 205 C₈Ca 635 C24C9 635 C36Cs 635 C48Cs 635 C12Cs(NH3)2 637 CF 640 CF₄ 203, 207 C4F 641 C₂HCl₃F₂ 205 CHF₃ 204 C24HSO4+2H2SO4 642 CIF₃ 205 C₈K 635 C24K 635 C36K 636 C48K 636 C12K(NH3)2 637 C12Li(NH3)2 637 (CN)2 661 CNBr 665 CNC1 662

CNI 666 C₁₂Na(NH₃)₂ 637 CO 645 CO₂ 647 C₃O₂ 648 COBrF 210 COCl₂ 650 COCIF 208 COF₂ 206, 210 COIF 211 (CONH)3 668 COS 654 COSe 655 C₈Rb 635 C24Rb 635 C36Rb 635 C48Rb 635 C12Rb(NH3)2 637 CS₂ 652 C₃S₂ 653 C3S2Br6 653 CSe2 656 Ca 922 Ca(AlH₄)₂ 806 CaBr₂ 930 CeC₂ 943 CaCN₂ 946 CaCO₃ 931 CaCl₂ 930 Ca(ClO₄)₂ 320 Ca(ClO₄)2-4H₂O 320 CsF₂ 233 CaGe 948 CaH₂ 929 Cal₂ 930 Ca₃N₂ 940 CaO 931 CaO₂ 936 CaO2-8H2O 936 Ca(OH)₂ 934 Ca₃P₂ 942 Ca10(PO4)6(OH)2 545 Ca2PbO4 760 CBS 938 CaSe 939 CaSeO4 939

CeSi 946 CaSi₂ 946 CaTe 940 Cd 1042 CdAs₂ 1103 Cd₃As₂ 1103 CdBr2 1096 Cd(C2H5)2 1103 Cd(CH3COO)2 1105 Cd(CN)2 1105 CdCO3 1104 CdCi2 1093 CdCl2-KCl-H2O 1095 CdF₂ 243 CdFe₂O₄ 1107 CdI₂ 1096 Cd₃N₂ 1100 Cd(NH₂)₂ 1100 Cd(OB)₂ 1097 Cd(OH)Ci 1094 CdP₂ 1101 CdP4 1101 Cd3P2 1101 CdS 1098 Cd(SCN)₂ 1106 CdSe 1099 Cd₂SiO₄ 1107 1² CeF3 247 25 CeF₄ 247 CeO₂ 1132 Ce2O3 1151 CeS 1155 Cl₂ 272 (CIBNH)3 779 CICN 662 CIF 153 ClF₃ 155 Cl2-6H2O 274 , **`**1∜¦ CIN₃ 476 CIN(SO3K)2 508 ClO₂ 301 Cl₂O 299 111100 Cl₂O₈ 303 Cl207 304 ClO₂F 165

1-332: Vol. 1; pp 1003-1810; Vol. 2 CIO₃F 166 CIO+F 167 (CIPy, 1003 328 Co 1513 CoAl₂O₄ 1525 CoBr2 1517 CoBr2-6820 1517 Co2C 1531 [Co(CO)3]4 1746 [Co(CO)4]2 1746 Co(CO)4H 1753 CoCl₂ 267, 1515 [Co en 3]Br3 1538 [Co en]Br3-2H2O 1539 [Co ++3]Br3+3H2O 1538 CoF₂ 267 CoF3 268 Col 2 1218 Col2-6H2O 1518 CoN 1529 Co2N 1529 Co(NH₂)₃ 1526 [Co(NH3)4CO3]2SO4--3H₂O 1535 [Co(NH3)6]C12 1516 [Co(NH₃)6]Cl₃ 1531 (Co(NH3)5C1)C12 1532 [Co(NH₃)₄Cl]Cl₂ 1536 [Co(NH₃)₄C]₂]Cl. ·%H2O 1536 (Co(NH₃)₄Cl₂]Cl. ·H₂O 1537 $[Co(NH_3)_5(H_2O)]_2$ (C204)3-4H20 1532 (Co(NH3)4(H20)2]2 (504)3-3820 1537 (CoONH_3) (NO3)3 1526 C.C.H. 3) 5NO2]C12 1524 Co^m(NH 2)5(02)Co^{(V} 000 25 1504)2 504H. **78**20 1540

{Co(NH₃)₅ONO]Cl₂ 1535 Co(NO)2Br 1761 Co(NO)(CO)3 1761 Co(NO)2Ci 1761 Co(NO)21 1761 [Co(NO2)6]Na3 1541 $[C_0(NO)_2(S_2O_3)_2]K_3$ 1766 CoO 1514, 1519 Co3O4 1520 Co(OH)2 1521 CoO(OH) 1520 CoP 1530 CoP₃ 1530 Co2P 1530 CoS 1523 CoS₂ 1523 Co₃S₄ 1523 CogS8 1523 CoSO2+3H2O 393 Co₂(SO₄)₃, 18H₂O 1524 Cr 1334 CrBr₂ 1340 Cr8r3 1341 Cr(C6H6)2 1397 Cr(C₁₂H₁₀)₂ 1397 $[Cr(C_{12}H_{10})(C_6H_6)]$ 1398 Cr2(CH3COO)4-2H2O 1368 [Cr(C6H6)2][1395 [Cr(C12H10)2][1396 [Cr(C₆H₅NC)₆] 1363 Cr(C₅H₇O₂)₃ 1383 Cr(C2H50CS2)3 1383 Cr(CO)6 1741 CrC₂O₄·2H₂O 1370 Cr(CO)3Py3 1749 Cr(CO)₄Py₂ 1749 CrCl₂ 1336 CrCl₃ 1338 [CrCl₃(C₂H₅OH)₃] 1380 [CrCl en 2]Cl 1357 [CrCl2 eB2]C1-H2O 1356 [CrCl₃(NH₃)₃] 1381 [CrC1(NH 3)5]Cl2 1352

[CrCi₃(OH₂)₃] 1380 $[CrCl(OH_2)_5]Cl_2 H_2O$ 1350 [CrCl₂(OH₂)(NH₃)₃]Cl 1358 [CrCl₃Py₃] 1381 [Cr(Dipy)3] 1363 [Cr(Dipy)3]ClO4 1362 [Cr(Dipy)3](ClO4)2 1361 (Cr en3)C13-3.5H2O 1354 [Cr en₃](SCN)₃-H₂O 1354 [Cr en 3]2(SO4)3 1354 CrF₂ 256 CrF₃ 258 CrF-3H₂O 258 CcF4 258 Crl₂ 1341 Crl 3 1344 CrN 1347 Cr(NH₂CH₂COO)₃ 1382 {Cr(NH₃)₆}Cl₃ 1351 [Cr(NH₃)₆](NO₃)₃ 1351 [Cr(NH₃)₅(OH)Cr(NH₃)₅ Cl₅ 1359 [Cr(NH₃)₅(OH)Cr(NH₃)₄ (OH₂)]Cl₅ 1360 $[Cr(OCN_2H_4)_6]Cl_3 3H_2O$ 1359 CrO₂Cl₂ 1384 CrO₂(ClO₄)₂ 1387 CrO₂F₂ 258 Cr(OH)3-nH2O 1345 [Cr(OH2)6](CH3COO)3 1371 [Cr3(OH)2(CH3COO)6] (CH₃COO)-nH₂O 1371 [Cr3(OH)2(CH3COO)6] Cl-8H₂O 1371 [Cr(OH₂)6]Cl₃ 1348 [Cr(OH)6]Ne3 1688 CrO₂(NO₃)₂ 1386 CrO3-2Py 1385 CrPO₄ 1364

pp 1-992: Vol. I; pp 1003-1810: Vol. 2 CrS 1346 Cr₂S₃ 1346 $[Cr(SCN)_4(C_6H_5NH_2)_2]$ NH4-1%H2O 1378 [Cr(SCN)2en2]SCN 1357 CrSO4+5H2O 1365 Cs 958 CsAI(SO₄)₂.12H₂O 956 CsBrCl₂ 294 CsCg 635 CsC24 635 CsC36 636 CoC48 636 Cs2CO3 987 CsCl 951, 955 Cs₂CrO₄ 1389 $C_{s_2}C_{r_2}O_7$ 1389 CsGe 989 CsH 971 CsIBr₂ 297 CslCl₂ 296 CsMn(SO4)2-12H2O 1468 CeN₃ 476 Cs(NH3)2C12 637 CsO₂ 981 Cs20 974 CsOH 983 Cs2S2 369 Cs₂S₃ 369 Cs₂S₅ 369 Cs2S6 369 Cs2SeCl6 425 CsSi 989 2Cs20.SiO2.12MoO3.eq 1730 Cs2TeCl6 444 Cs3(Tl2Cl9) 874 Cu 1003, 1633 CuBr 1006 CuBr₂ 1009 Cu2C2-H2O 1026 CuCO₃,Cu(OH)₂ 1024 2CuCO3-Cu(OH)2 1025 EuCl2 1150. CuCl 1005 CuCl₂ 1008

CuF₂ 238 CuF2.5H20.5HF 238 CuH 1004 Cu₂HgI4 1110 Cul 1007 Cu(N₃)₂ 1022 Cu₃N 1021 [Cu(NH3)4]SO4-H2O 1021 CuO 1012 Cu₂O 1011 Cu(OH)₂ 1013 [Cu(OH)4]Nu2 1684 CuP₂ 1024 Cu₃P 1023 Cu2P4012 553 CuS 1017 Cu₂S 1016 Cu₂SO₄ 1020 Cu₂Se 1019 Cu2Te 1019 D D₂ 121 DBr 131 DCI 129 DF 127 DH 126 DI 133 0₂0 119 D₃PO₃ 132 D₃PO₄ 138 D₂S 134 D₂SO₄ 135 Е EuBr₂ 1149 EaCO3 1137

EuO 1156 EaS 1155 -a. H EuSO4 1137 へは EuSe 1155 EuTe 1155 F F₂ 143 · F₂O 163 F₂O₂ 162 FSO₂NO 186 Fe 1490 FeBr₂ 1493 FeBr3 1494 Fe₃C 1503,1792 [Fe3(CH3COO)6(OH)2] CH3COO-H2O 1508 [Fe(CN)5(CO)]Na3 1769 [Fe(CN)5NH3]Na24H2O 1512 [Fe(CN)5NH3]Na3-3H2O. 1 1511 [Fe(CN)5(NO)]Na2-2H2O 1768 [Fe(CN)₅(OH)₂]Ne3 1769 [Fe(CO)₄]₃ 1745 Fe(CO)5 1743 . 1 Fe₂(CO)₉ 1744 Fe(CO)4Br2 1751 28 #1 Fe(CO)4Cl2 1751 + A Fe(CO)4H2 1752 Fe(CO)4Hg 1755 Fe(CO)412 1951 42/13) [Fe(CO)3NO]K /17591 24 FeCl₂ 1491 🖬 🖓 FeC13 1492 1944 [Fe eng][Fe2(GQ)8]449 1756 FeF₂ 266 EuCl₂-2H₂O 1136 Fel₂ 1495 EaF2 248 (State of Feat 1502 . . .

1815

10 1-316: Yel. 1: 10 1003-1810: Yel. 3 Fe(NO)2(CO)2 1760 (F+(NO)2SC2H512 1765 F+00)2SN+4H20 1763 [F+(NO)2S2O3]K-H2O 1766 [F.(NO)2S2O3]Na 1766 FeO 1497 FegO, 1661 Fe304 1499 FeOC) 1501 Fe(OH)2 1498 [Fe(OH)4]Na2 1686 [Fe(OH); Na4-2H2O 1689 [Fe(OH)g]Na5-5H2O 1690 FeO(OH) 1499 3Fe 203-4SO 3-9H 20 1507 [FePy6][Fe4(CO)13] 1758 FeS 1502 [Fe(SCN)5]Na3-12H2O 1511 Fe3(SO4)2(OH)5-2H2O 1507

G

Ga 837 GaBr₂ 846 GaBr₃ 845 Ga(CH₃)₃ 840 Ga(CH₃)₃.N(C₂H₅)₃ 841 Ga(CH₃)₃.N(C₂H₅)₃ 841 Ga(Cl₂ 846 Ga(Cl₃ 843 Ga(Cl₀)₂.6H₂O 839 GaF₃ 227 Ga₂H₆ 840 Ga₂H₂(CH₃)₄ 840 Gal₃ 845 Gall₃ 845 Gall₃ 845 Gall₃ 76

Ge(NO3)3 856 Ga₂O 849 Ge103 848 Ga(OH) 3 847 GaO(OH) 847 G8P 857 GaS 851 Ga₂S 652 Ga₂S₃ 850 GaSb 857 GaSe 854 Ga₂Se 854 Ga2Se3 654 GaTe 855 Ga2Te3 855 Ge 712 GeBr4 718 Ge(CH3COO)4 726 GeCH3[3 722 GeCl₂ 716 GeCl₄ 207, 715 GeF₄ 215 GeH4 713 Ge₂H₆ 713 Ge 3Hg 713 GeHCl₃ 717,721 Gel₂ 720 Gel4 719 Ge₃N₄ 722 Ge(NH)₂ 723 Ge₂N₃H 723 GeO 711 GeO₂ 706 Ge(OC₂H₅)₄ 725 GeS 723, 724 GeS₂ 723

H

 $\begin{array}{l} H_2 \quad 111 \\ HAIB_{r_4} \cdot 20(C_2H_5)_2 \quad 817 \\ HAICI_4 \cdot 20(C_2H_5)_2 \quad 816 \\ H_3A_8O_4 \quad 601 \\ H_3A_8O_4 \cdot 501 \\ H_3A_8O_4 \cdot 501 \\ H_7A_8O_6 \quad 601 \end{array}$

HAuCl4-4H2O 1057 HBF₄ 221 H(BF2(OH)2] 784 NBO₂ 791 HBr 282 ∦ВrО₃ 315 HCN 658, 668 H₂CS₃ 674 HC1 280 HCIO 308 HClO3 312 HCIO₄ 318 B₃Co(CN)₆ 1542 H₃C₀(CN)₆·5H₂O 1543 $H[C_{H}(SCN)_4(NH_3)_2]$ 1377 HD 126 HF 145 H₃Fe(CN)₆ 1510 H₄Fe(CN)₆ 1509 H21rCl6 1593 HI 286 HIC14-4H2O 299 HIO₃ 316 H5IO6 322 HIO3-I2O5 307 H₂M₀O₄·H₂O 1412 HN3 472 HNCO 667, 668 HNCS 669 HNO₃ 491 H2N2O2 492 HNbO4-nH2O 1324 H₂O 117 H₂O₂ 140 H₃PO₂ 555 H₃PO₃ 554 H₃PO₄ 543 H₄P₂O₆ 558 H4P206-2H20 559 H4P207 546 HPO2C12 538 HPO2(NH2)2 582 H₂PO₃NH₂ 579 H₃PO₃S 568 H2PtCl4 1570

pp 1-992: Vol. 1; pp 1008-1810: Vol. 2 lo 857 Hg 28 H₂PtCl₆.6H₂O 1569 HgBr₂ 1109 ІлАв 86⁄7 H₂S 344 H₂S₂ 350 Hg(C2H5)2 1118 1n.Br 862 Hg(CH3COO)2 1120 H₂S₃ 350 JaBr₂ 861 H₂S₄ 353 Hg2(CH3COO)2 1120 InBrz 859 Hg(CN)₂ 1121 H₂S₅ 353 inCl 862 H₂S₆ 353, 855 HgCO3 243 InCl₂ 861 H₂S₇ 353, 355 HgCl2 4HgO 1108 InCl₃ 858 H2S8 353, 355 InF3 228 HgCl₂ 2NH₃ 1114 H₂S_x 346 HgF₂ 244 Inl 862 ini₂ 861 H₂SO₅ 388 Hg2F2 243 H₂S₂O_B 389 Hg2(NH)Br2 1115 Inlg 860 InN 866 $H_2S_{x}O_{3}$ 405 HgNH2C1 1114 H₂S_xO₆ 405 [Hg(NS)₂]_x 1118 In₂O 863 HSO3CI 385 [Hg2(NS)2], 1117 In₂O₃ 863 HSO3F 177 In(OH)3 862 HgO 299 HgS 1111 InP 867 HSO₃NH₂ 508 IoS 864 HSbCl6-4.5H2O 611 $H_{g}(SCN)_{2}$ 1123 In₂S 864 H₂Se 418 Hg₂(SCN)₂ 1122 HgSe 1113 ln₂S₃ 864 H₂SeO₃ 430 laSb 867 H₂SeO₄ 432 HgSeF4 180 InSe 865 H₂SiF₆ 214 H2Si2O3 694, 699 In₂Se 865 F In₂Se₃ 865 H2Si2O5 699 (n₂Te 865 H4SiO4 697 12 277 in2Te3 865 H₂SnCl₆-6H₂O 730 IBr 291 lr 1590 HTaO4 nH2O 1324 [I(C5H5N)2]ClO4 327 IrCl₃ 1592 H₂Te 438 ICN 666 IrF4 271 H₂TeO₃ 449 ICI 290 IrF6 270 H6TeO6 451 ICi 3 292 IrO₂ 1590 H4TiOs 1219 I(ClO₄)₃ 330 IrO2+2H2O 1591 H(TIC14)-3H2O 872 IF₅ 159 Ir203-xH20 1592 HTI(SO4)2-4H2O 882 IF₇ 160 HV(SO4)2-4H20 1282 I(IO₃)₃ 331 H0.5WO3 1423 ĸ I(NO₃)₃ 329 H2WO4 1424 I2O4 333 He 82 K 958 1205 307 Hf 1172 K2[A12O(OH)6] 1693 -I4O9 331 HfBr2 1204 K₃AS 986 12O5-HIO3 307 HfBr3 1204 KA9H2 595 I207-12MoO3-sq 1738 HfBr4 1203 K[Au(CN)2] 1065 (IO)2SO4-H2O 342 HfC 1245 KAuCl4-%H2O 1058 [IPyx]CIO4 328 HfCl4 1203 KAuO2-3H2O 1062 [IPy2]F 328 HIN 1233 KBF4 223 [IPyx]NO3 328 HfO₂ 1221 KBF30H 223 868 I2(SO4)3 329 HfOCl2-8H2O 1213

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10 2-382: Vol. 1: pp 1003-1810: Vol. 2 K.B. 944 KB103 10130 638 **KB**+F₄ 237 KB:0-3H20 311 **XCs 63**5 KCN 635 EC.36 635 KC48 635 K₂CO₃ 987 K2C4(CN)4 1106 K_{Co(CN)6] 1541 K3CoF7 369 K_[Cr(CN)6] 1373 K3[Cr(C2O4)3]-3H2O 1372 K2CrF6 269 K₃CrO₈ 1391 K[CrO₃C1] 1390 K[CrO3F] 1390 K3(Cr(SCN)5)-4H2O 1374 K[Cr(SCN)+Py2] 2H20 1379 K3CaF6 269 KC=02 1014 KF 236 KF·HF 237 K2FeF6 269 K₂FeO₄ 1504 KFeS₂ 1507 KGe 989 K2GeF6 216 **KH** 971 KHF₂ 146 KHM_0O6-2H2O 1414 K7(ENb6019-aq) 1706 KHPO3NH2 579 K2Hg(CN)4 1122 KHgi - H2O 1110 Lala(SCN)4 1124 L₂hCl₆ 1593 K≠Cl₆-382₂O 1595 Q 200 105r2 2% EICI, 295 SICI, 290

KIF6 238 Kl₃-H₂O 294 KIO4 325 K₃Ma(CN)6 1474 K₅Mn(CN)₆ 1472 K₄Mn(CN)₅-3H₂O 1473 K₃[M₀(C₂O₄)₃]-3H₂O 1470 $K_{2}[Mn(C_{2}O_{4})_{2}(OH)_{2}]$ -2H₂O 1471 K₂MnCl₅ 1464 K₂MnCl₆ 1464 K2MnF6 264,269 K₂MnO₄ 1461 K4[Mo(CN)8]-2H2O 1416 K₃M₀Cl₆ 1408 KN₃ 476 KNH₂ 1044 K(NH₃)₂C₁₂ 636 K₃{(NO)₂Co(S₂O₃)₂] 1766 K[(NO)2FeS2O3]-H2O 1766 $K_3[(NO)Mn(CN)_5]$ 1767 K4[(NO)M6(CN)5]-H2O 1766 K₃[(NO)Ni(S₂O₃)₂] 1766 K₂NbF₇ 255 K₃NbOa 1325 K₃NbO₈-55H₂O 1325 K8[Nb6O 19 8q] 1706 K2[Ni(CN)4]-H2O 1559 K₂NiF₆ 269 KO₂ 981 K₂O 974 3K20-A5205-24MoO3-29 1734 K₂O-3CrO₃ 1709 K₂O-4CrO₃ 1710 3K20-P205-18McO3-aq 1733 11K20.2P205.24V205. -aq 1740

3K2O.P2O5.21WO3.aq 17223K20.P205-24W03.aq 1721 7K2O·P2O5·22WO3-49 17222K20-SiO2-12WO3-ng 1718 7K20-2SiO2-20WO3-89 1719 K₂O-3V₂O₅ 1704 K₂OsO₄·2H₂O 1604 K(OsO₃N) 1605 KPF6 196 K₃PO₄ 8H₂O 545 K4P2O8 562 K₂PbCl₅ 753 КРЫ₃ 754 КРЫ₃-2H₂O 754 K₂PdCl₄ 1584 K₂PdCl₆ 1584 K₂Pt(CN)₄-3H₂O 1576 K₂PtCl₄ 1572 K₂PtCl₆ 1571 K₂Pt(OH)₅·xH₂O 1575 K2ReCl6 1478 K₂[RhCl₅(H₂O] 1588 K₃RhCl₆·H₂O 1588 KRuO4 1600 K₂RuO₄ H₂O 1600 K₂S 360 K₂S₂ 363 K₂S₃ 364 K₂S4 366 K₂S₅ 367 K₂S₆ 368 KSCN 739 K₂S₂O₈ 392 K₂S₃O₆ 398 K₂S₃O₁₀ 1714 K₂S₄O₆ 399 K₂S₅O₆ 1%H₂O 401 K₂S₆O₆ 403 KSO₂F 178 K₂SO₃ (NO)₂ 504 K₃Sb 986, 1791

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pp 1-992: Vol. 1; pp 1003-1810: Vol. 2 KSbCl6-H2O 612 K₂Se 421 K₂SeCi₆ 425 KSi 989 K₂SnCl₆ 731 K₂TaF₇ 256 K3TaO8 1325 K₃TeO₈, %H₂O 1326 K2Te 441 K₂TeCl₅ 444 $K_2(TICI_5H_2O)$ H_2O 874 K₃(T1Cl₆)-2H₂O 873 $K_4(U(C_2O_4)_4) - 5H_2O$ 1450 K₂UO₄ 1445 K₂VF₆ 269 K₃V(SCN)₆ 1291 KV(SO₄)₂ 1283 K₃[W(CN)₈] H₂O 1430 K4[W(CN)8]-2H2O 1429 K₃₩₂Cl₉ 1427 K₂Zn(CN)₄ 1068

L

LaF₃ 246 Le₂S₃ 1153 La₂Se₃ 1154 La2Se4 1154 Li 956 Li₃Al 830 Li3AlAs2 831 LiAI(CN)₄ 833 LiAlH₄ 680, 805 Li3AIN2 828 Li3AIP2 830 Li3As 985 LiBH₄ 775 LiBH4.0(C2H5)2 775 Li38i 985 Li₂C₂ 987 Li2CO3 950, 987

Li3Cr(C6H5)6. ·2%(C2H5)20 1375 Lif 285 LiFeO₂ 1504 LiGaH₄ 842 LiH 971, 805 LiN3 475 Li₃N 984 LiNH₂ 463 Li2NH 464 Li(NH3)2C12 636 Li_2Q Li2O2 975, 979 LiOH 983 LiOH-H₂O 983 Li₃P 985 Li₃Sb 985 Li₂Si 991 Li₄Si 991 Li2SiO3 705 LiUO₃ 1445 Li2UO4 1445 LaBr3 1148 Ln(C5H5)3 1159 LnCl3 1146 ևոլց 1149 LaN 1157 Ln(NO₃)₃ 1158 Ln(OH)₃ 1152 Ln\$ 1155 Ln₂(SO₄)₃.nH₂O 1156 LaSe 1155 LnTe 1155 LaX₂ 1150

М

Mg 903 Mg3As₂ 917 MgBr₂ 909 MgC₂ 920 MgC₂ 920 MgCl₂ 905 MgCl₂ 6H₂O 906

MgCl2-NH4Cl-6H2O 906 Mg(ClO₄)₂ 320 Mg(ClO₄)₂.6H₂O 820 MgF₂ 232 Mg2Ge 922 MgH₂ 905 MgI₂ 910 Mg(N₃)₂ 917 Mg₃N₂ 916 MgO 911 Mg(OD)2 137 $M_{\rm g}(\rm OH)_{2}$ 912 [Mg(OH)4]Na2 1683 Mg3P2 917 MgS 913 Mg3Sb2 606 MgSe 915 Mg2Si 921 MgTe 915 Ma 1454 Ma(CH₃COO)₃ 1469 Ma(CH3COO)3-2H2O 1469 [Mn(CN)5(NO)]K3 1767 MnF₂ 262 MpF3 263 Ma4N 1468 . $Mn_3[(NO)Ma(CN)_5]_2$ 1768 1.0 MnO 1455 MnO₂ 1458 . S. C. Mn₂O₃ 1457 Ma₂O₇ 1459 Mn(OH)2 1456 1.17 MaO(OH) 1457 1.1 MnS 1465 いった話録 Mn2(SO4)3 1467 . MAR Mo 1401 MoBra 1407 🔅 😹 🍂 [MoBr3Py3] 1408 Mo(C6H6)2 1401 {Mo(CN)5(NO)]K4-H2O; if 19 A 49 A 49 1766 Mo(CO)6 1741 MoCl3 1404

ap 2-488: Val. 1: pp 2003-1810: Vol. 2 **26.Cl**5 1405 MagClg 1403 **Mar**s 259 1409 1409 **141**23 1412 MagO21 1410 MeOC15[(NH4)2 1413 120.aq 1711 20003-3(NH4)20-P205--**eq** 1730 Ma4010(OH)2 1411 MesOs(OH)10 1411 MoOg[Za(NH3)4] 1414 NoS2 1415 $M_{0}S_{4}(NH_{4})_{2}$ 1416 MoSig 1792, 1796

N

Nz 457 N₃Br 477 NBr3-6NH3 480 NCI3 479 N₃CI 476 (NCI)3(SO)3 412 NCI(SO₃K)₂ 508 ND₃ 137 NF₃ 181 NH₃ 460 ¹⁵NH₃ 461 N2E4 469 N2H4-H2O 469 MIL4AIF 4 227 CUI_4)3AIF6 226 CGH4)3AsO4.3H2O 602 ONH4)3ABS4 604 (NH4)2BeF4 232 ME₂Br 480 0014)2CS2 674 NEI₂Cl 477 **Mi_CiO**3 313 **600**₂)₂CrO₄ 1392 **644**2Cr2012-2H20 1292

NH₄[Cr(SCN)₄(NH₃)₂]. -H₂O 1376 NH₄F 183 NH4F-HF 183 (NH4)4Fe(CN)6 1509 (NH₄)₃GaF₆ 228 $NH_4Ga(SO_4)_2 \cdot 12H_2O$ 854 NH4HPO3NH2 584, 588 (NH4)2HPO3S 584 NH₄HS 357 (NH₄)₃InF₆ 229 (NH₄)₂hCl₆ 1594 NH4I 289 (NH₄)₂[M₀OCl₅] 1413 (NH₄)₂MoS₄ 1416 NR₂NO₂ 496 $NH_4[(NO)_7Fe_4S_3] \cdot H_2O$ 1764 3(NH4)20.As205.24WO3-•aq 1725 3(NH₄)₂O·Cr₂O₃-12MoO₃-•aq 1737 NH₂OH 501 (NH₃OH)₃AsO₄ 501 (NH₃OH)₂C₂O₄ 501 (NH₃OH)Cl 498 (NH₃OH)HSO₄ 499 (NH₃OH)₃PO₄ 500 5(NH4)20-12MoO3-aq 1711 3(NH₄)₂O·P₂O₅-24M₀O₃. •aq 1730 5(NH₄)₂O-2P₂O₅. ·24V2O5·aq 1740 3(NH4)20.P205-18W03. -aq 1723 3(NH₄)₂O·P₂O₅·24WO₃· -aq 1721 5(NH4)20-12WO3-aq 1713 NH2OSO3H 511 (NH₄)₂O₈Cl₅ 1603 NH4PF6 195 (NH4PO3), 580 NH4PO2F2 196

(NH₄)₂P₂O₅(NH₂)₂ 588 (NH₄)₂PbCl₅ 751 (NH₄)₂PdCl₄ 1584 (NH₄)₂PdCl₆ 1586 (NH₄)₂PtCl₆ 1570 NH4ReO4 1484 (NH₄)₂[RhCl₅(H₂O)] 1588 (NH4)3RhCl6-H2O 1588 (NH₄)₃[Rh(NO₂)₆] 1586 (NH₄)₂RuCl₆ 1599 (NH₄)₂S₅ 369 NH₃SO₄ 510 (NH₄)₂S₂O₈ 390 N2H6SO4 468 NH₂SO₃H 508 NH(SO3K)2 506 NH₂SO₃K 507 N₂H₂(SO₃K)₂ 504, 509 $N_2H_2(SO_3NH_4)_2$ 509 $N_2H_2(SO_3P_y)_2$ 510 (NH₄)₂SbBr₅ 615 (NH₄)₂SeCl₆ 425 (NH₄)₂SnCl₆ 731 (NH4)2TeCl6 444 (NH₄)₂TiCl₆ 1199 $(NH_4)_4[UO_2(CO_3)_3]$ 1449 NH4VO3 1272 $NH_4V(SO_4)_2$ 1283 NH4V(SO4)2-12H2O 1284 (NH₄)₂Z₀Cl₄ 1072 (NH4)22a(SO4)2.6H2O 1077 NH_{g2}Br 1117 NHg2OH-xH2O 1116 NI₃-NH₃ 481 NO 485 NO₂ 488 N₂O 484 N₂O₃ 487 N₂O₄ 488 N₂O₅ 489 NOBF₄ 224 NOBF4-H2O 224

pp 1-992: Vol. 1; pp 1003-1810: Vol. 2 NO₂[BF₄] 187 N₂O₅ BF₃ 187 NOBr 513 NOC1 511 NO₂CI 513 NOCIO₄ 320 NO₂CIO₄ 321 NOF 184 NO₂F 186 NO₃F 187 [(NO)₂FeSC₂H₅]₂ 1765 (NO)HSO4 406 NOH(SO3K)2 503 NO2NH2 497 NO₂NHCOOK 497 NOSO₂F 186 NO(SO3K)2 504 NO(SbC16) 612 NO₂(SbCl₅) 612 $N_2(SO_3K)_2$ 510 N(SO₃K)₃.2H₂O 506 Na 958 Na₃AgO₂ 1039 NaAlCl₄ 816 Na4[A1(OH)7]-3H2O 1692 Ne4[AI4O3(OH)10] 1693 Na6[A16O4(OH)16] 1693 Na₃As 986, 1791, 1793 NaAsH₂ 595 Na3AsO2S2-11H2O 605 Na 3AsO 3S-12H2O 605 Na3AsS4.8H2O 604 Na₂Au 1793 Na[B(C6H5)4] 803 NaBF4 222 NeBH4 776 NaBH4-2H2O 777 NaBO₂ 791, 793 NaBO2.%H2O 791 Na802-2H20 791 NeBO2-4H2O 791 NaBO2-H2O2-3H2O 796 NaBO3-4H2O 795 NaB508.5H2O 795 Na2B407 794 Ne2B4O7.2H2O 794

Na2B4O7-4H2O 794 Na2B4O7-5H2O 793 Na2B407-10H20 793 Ne3BO3 790 Na4BeO3 895 Na₃Bi 986, 1793 NaBiO3 627 NaBiO3.nH2O 628 NaBrO-5H2O 310 Na₂C₂ 987 Ne₂CO₃ 988 Na₃[(CO)Fe(CN)₅] 1769 NaCIO 309 NaClO 5H 20 309 NaClO2-3H2O 312 Na3[Co(NO2)6] 1541 Na3[Cr(OH)6] 1688 NaCrS₂ 1394 Na₂[Co(OH)₄] 1684 NaF 235 $Ne_2[Fe(CN)_5NH_3] \cdot H_2O$ 1512 Na₃[Fe(CN)₅NH₃]·3H₂O 1511 Nn₂[Fe(OH)₄] 1686 Ne3[Fo(OH2)(CN)5] 1770 $Na_4[Fe(OH)_7] \cdot 2H_2O$ 1689 Na5[Fe(OH)8]-5R2O 1690 Na3Fe(SCN)6-12H2O 1511 NaGe 989 NaGeH₃ 714 Na2GeH2 714 NaH 971 NaH2AsO4-H2O 602 Na3H2As3O10 1709 NaHB(OCH₃)₃ 777 Na₃H₂IO₆ 323 Na7[HNb6O19-aq] 1706 Na3HP207 548 NaH2PO4+2H2O 544 Na2H2P2O6 6H2O 560 NaHS 357 NaHSe 419

Na2H4TeO6 453 Na2H4TeO6-3H2O 454 NaIO3 323 NaIO₄ 323, 324 NelO4-3H2O 324 Na₂[Mg(OH)₄] 1683 -Na3MaO4+%NaOH-12H2O 1460 NaN3 -474 Na¹⁵N₃ 466 NaNH₂ 465 Na¹⁵NH₂ 466 Na(NH3)2C12 636 NaNO 514 Na₂NO₂ 515 Ne₂N₂O₃ 517 Na2N2O2.9H2O 495 $Na_2[(NO)Fe(CN)_5] \cdot 2H_2O$ 1768 Na[(NO)2FeS]-4H2O 1763 Na[(NO)2FeS2O3] 1766 Nas[NbsO19-aq] 1706 NaO₂ 980 Na₂O 974 Na₂O₂ 979 Na2O-As2O5-6MoO3-sq-1736 3Na 20 As 205 - 18MoO3-•sq 1785 5Na2O-B2O3-24WO3 ag. 1 1717 NaOD 121 1. A. . 5Na20-1207-12MoO3-49. 1738 - - <u>-</u> - - }* Na20-4MoO3-aq 1712(, ** 5Na20-12MoO3-aq: 1710 -10Na20-P205-24V205:491 1739 3Na20-P205-24703-000 7 1720 2Na20-SiO2-12MoO3-\$4 1729 6.5 Na20.V205-aq 1703 + #* 2Na20.V205.aq 17020 2 3Na20-5V205-49 3898

pp 1-352: Yel. 1: pp 2003-1810: Vol. 2 Neg0-4803-49 1727 Stag0-12003-49 1712 MagOnCla-2H2O 1602 NayP 986 NoPH₂ 590 NoPH2-2NH3 530 Ne_PH 530 (NaPO3), 549 (NePO3), 550 (NaPO3), 551 Na3P309-6H20 552 Na4P206-10H20 561 Na₄P₄O₁₂-nH₂O 553 NesP3010 547 Na5P3010-6H2O 547 Na6P4013 548 (Ne2PO3)3N 590 Na₂PO₃NH₂ 588 Na2PO3NH2.6H2O 581 Na4P205NH 589 Na4P206NH-10H20 589 Na3POS3-11H2O 571 Na3PO2S2-11H2O 570 Na3PO3S-12H2O 569 NaPOS(NH₂)₂ 589 N=3PS4-8H20 572 Na15Pb4 1793 Na₂PbO₃ 758 Ne4PbO4 759 Nag[Pb(OH)6] 1694 Na₂PdCl₄ 1584 No2PtCl6 1571 Na2PtCl6-6H20 1571 Na2Pt(OH)6-xH20 1575 Na2BeO3 1483 Na 3RhCl 6-12H 20 1587 Na₂S 358 Na₂S₂ 361 Na254 365 RepSy 367 Ma25204-2H20 393 Ma25206-2H20 395 Reg 6 966, 1793 HezSi6+9120 619 No₂6e 421 Refer 2421

Na2SeO3 SH2O 431 Na2SeO4 433 Na2SeS406-3H20 434 NaSi 989 Na2SiO3 704 Na2SiO3-9H2O 704 Na2Si2O5 704 Na15Sn4 1793 Na4SnO4 739 Na[Sn(OH)3] 1687 Na₂[Sn(OH)₆] 1694 Na₂SnS₃.8H₂O 742 Na4SnS4-18H20 743 Na7[Ta5016-aq] 1708 Nag[TagO19-ag] 1708 Na₂Te 441 Na₂Te₂ 442 Na₂TeO₃ 449 Na₂TeO₄ 449, 453 Na6TeO6 453 Na2TeS4O6-2H2O 454 NaUO3 1445 NaZn₁₃ 1793 Na[Zn(OH)3] 1681 Na₂[Zn(OH)₄] 1682 NbBr₂ 1309 NbBr₃ 1309 NbBr5 1311 NFC 1333 NbCl₂ 1296 NbCl₃ 1297 NbCl₄ 1299 NbCl₅ 1302 NbFs 254 NHH 1296 NM₂ 1314 Nbia 1314 NH4 1314 Nbls 1315 Nb-N 1328 NbO 1317 NbO₂ 1318 Nb₂O₅ 1318 NbOBr3 1313 NbOC13 1307 [Nb6019-aq]Nas 1705

NbP 1330 N6P₂ 1330 Nb_S 1327 NbSi₂ 1792, 1797 Ne 82 Ni 1543 NiBr₂ 1545 NiBr2-6H2O 1546 Ni₃C 1556 NiCO₃ 1557 NiCO3-6H2O 1556 Ni(CO)4 1747 Ni(CO)₂C₁₂H₈N₂ 1750 NiCl₂ 1544 NiF₂ 269 Nil₂ 1547 Nil₂-6H₂O 1547 Ni₃N 1555 Ni₃N₂ 1555 $Ni(NII_2)_2$ 1554 [Ni(NH₃)₆]Cl₂ 1545 [Ni(NO)(S₂O₃)₂]K₃ 1766 NiO 1548 Ni(OH)₂ 1549 [Ni(OH)₆]Sr₂ 1686 NiO(OH) 1549 Ni₃O₂(OH)₄ 1551 NiS 1551 NiS₂ 1554 Ni(SCN)2 1558 NiS₂(C₆H₅-CSS)₂Ni(SSC--C₆H₅)₂ 1558

0

 $\begin{array}{c} O_2 & 334 \\ O_3 & 337 \\ OF_2 & 163 \\ O_2F_2 & 162 \\ [OS(N)Cl]_3 & 412 \\ Os & 1601 \\ OsCl_4 & 1601 \\ OsO_2 & 1603 \\ OsO_4 & 1604 \end{array}$

| pp 1-992: Vol. I; pp 1003-18. | 10: Vol. 2 | |
|---|--|---|
| | DC/httr > | RLC . cos |
| | R A | RbC ₂₄ 635 |
| P 518 | Pb 748 | RbC ₃₆ 635 |
| PC12F 191 | Pb(CH ₃) ₄ 763 | RbC48 635 Rb2CO3 987 |
| PC12F3 192 | Pb(C2H5)4 765 | |
| PCI4-PF6 193 | Pb(CH3COO)4 767 | |
| PF ₃ 179, 189 | PbCO3 766 | Rb2CrO4 1388 5.0 Rb2Cr2O7 1388 5.0 |
| PF5 190, 194 | 2PbCO3 Pb(OH)2 767 | DIO ARA |
| PH ₃ 525 | PbCl4 750 | RbH 971 |
| P ₂ H ₄ 525 | PbF ₂ 218 | RbN ₃ 476 |
| PH4[531 | PbF ₄ 219 | Rh(NH_)_C., 697 |
| PI3 540 | Pb(N ₃) ₂ 763 | Rb(NH ₃) ₂ C ₁₂ 637 RbO ₂ 061 |
| P ₂ I ₄ 539 | PbO ₂ 757, 1668 | RbO ₂ 981 - |
| P ₃ N ₅ 574 | Pb ₃ O ₄ 755 | Rb ₂ O 974 |
| (PNBr ₂) _n 578 | [Pb(OH)6]Na2 1694 | REON 983 |
| $(PNCl_2)_n$ 575 | Pb2P2O6 558 | 2Rb2O-SiO2-12MoO3-eq |
| $(PNF_2)_3$ 194 | PbS 760 | 1730 ··· |
| | | Rb ₂ S ₂ 369 |
| $(PNF_2)_4$ 194 | Pb(SCN) ₂ 769 Pb(SC) 263 | Rb ₂ S ₃ 369 |
| P_2O_5 541, 825 | Pb(SO ₄) ₂ 761 | Rb ₂ S ₅ 369 |
| POBr3 534 | PbSiO ₃ 705 | Rb ₂ SeCl ₆ 425 |
| $P_2O_3Cl_4$ 536 | Pd 1580 | RbSi 989 No. 1 |
| P ₄ O ₄ Ci ₁₀ 536 | [PdBr ₂ (NH ₃) ₂] 1585 | |
| POC1(OC6H5)2 579 | PdCl ₂ 1582 | Rb(T1Br4).H2O 876 |
| POC1 ₂ (OC ₆ H ₅) 582 | [PdCl ₂ (NH ₃) ₂] 1585 | Rb ₃ (TIBr ₆) %H ₂ O 876 |
| POF ₃ 179, 193 | [PdCi4]Na2 1584 | Re 1476 |
| PO(NH ₂) ₃ 584 | PdO 1583 | ReCl3 1476 |
| $P_2O_3(NH_2)_4$ 588 | PrO ₂ 1151 | ReCls 1477 |
| (PO(NH)NH ₂] _n 588 | Pt 1560 | ReF6 264 |
| [PO(NH ₂) ₂]NH 587 | PtCl ₂ 1568 | ReO ₂ 1480 |
| [PO(NH ₂) ₂ NH] ₂ PONH ₂ | PtCl ₃ 1567 | ReO3 1481 |
| 587 | PtCl ₄ 1567 | Re207 1482 |
| PONH2(OC6H5)2 577 | {PtCl ₂ (NH ₃) ₂] 1578 | ReOCl4 1479 |
| PO(NH2)2(OC5H5) 582 | [PtCl6]Na2 1571 | ReO3CI 1480 |
| P205-18MoO3-aq 1732 | [Pt(NH3)4]Cl2-H2O 1577 | ReS2 1486 |
| P205-24MoO3-89 1731 | {Pt(NH ₃) ₄][PtCl4] 1577 | Re2S7 1487 |
| P205-18W03-aq 1724 | [Pt(NO ₂) ₂ (NB ₃) ₂₁ 1579 | Rh 1585 |
| P205-24WO3-89 1720 | PtO 1573 | RhCl3 1587 |
| P ₂ S ₅ 567 | PtO2 xH2O 1574 | [RhCl(NH3)5]Cl2(15994+2 |
| P ₂ S ₅ .7NH ₃ 574 | [Pt(OH)6]Na2-xH2O 1575 | [RhCl(NH3)s](NO3) |
| P ₄ S ₃ 563 | PtS 1575 | 1590 |
| P ₄ S ₅ 565 | PtS2 1576 | [RhCls(H2O)](NH4)2 |
| P ₄ S ₇ 566 | ·· · · | 1588 |
| P ₄ S ₁₀ 567 | مريني المراجع | [RhCl6](NH4)3.H20: 0.4 |
| - 4-10 001 PSR-, 595 | κ | 1586 84 2013 2 28 |
| PSBr3 535 PSBr3 8.0 Fax | | [RhCle[Na3-12]12@ \$5888 74(5) |
| PSBr3-H2O 536 PSCI3 532 | RbCs 685 311 . Mat | [Rh(NO2)6](NH als H5000 |
| . 0013 332 | rtho8 And | |

| No2O3 1 No2O3 1 | 15-441,20 1589 13-1541,20 1589 190 1597 120 1597 199 |
|--|---|
| s | |
| S 341 $S_2B_{22} 37$ $S_3B_{22} 37$ $S_5B_{22} 37$ $S_5B_{22} 37$ $S_5B_{22} 37$ $S_5B_{22} 37$ $S_5B_{22} 37$ $S_5B_{22} 370$ $SC1_2 370$ $SC1_2 370$ $S_2C1_2 37$ $S_5C1_2 37$ S_5C | 79 79 79 79 79 79 79 79 79 79 79 79 79 7 |

| 903-1 | 810: Vol. 2 | |
|-------|--|-----|
| | SOC12 382 | |
| 89 | SO ₂ Cl ₂ 383 | |
| 589 | S205Cl2 386 | |
| | SOCIF 174 | |
| | SO2CIF 175 | |
| | SOF ₂ 170, 179 | |
| | SOF ₂ 170, 179 SOF ₄ 171 | |
| | SO ₂ F ₂ 179 | |
| | S308F2 174 | |
| | (SO2N)3Ag3-3H2O | 463 |
| | SONH 480 | - |
| | (SO ₂ NH) ₃ 483 | |
| | SO ₂ (NH ₂) ₂ 482 | |
| | $SO_2(NHA_g)_2$ 483 | |
| | Sb 606 | |
| | | |
| | SbBr ₃ 613 | |
| | SbCi ₃ 608 | |
| | SbCl ₅ 610 | |
| | SbCl ₅ -H ₂ O 610 | |
| | SbCl5-4H2O 610 | |
| | SbCl ₂ F ₃ 200 | |
| | SbF3 199 | |
| | 5bl's 143, 200 | |
| | SbH ₃ 606 | |
| | Sbl3 614 | |
| | Sb ₂ O ₃ 615 | |
| | Sb ₂ O ₄ 618 Sb ₂ O ₅ 616 | |
| | Sb ₂ O ₅ 616 | |
| | Sb2O5-(H2O), 617 | |
| | SbOC1 611 | |
| | Sb4O5Cl2 611 | |
| | (SbO)2SO4 619 | |
| | Sb ₂ (SO ₄) ₃ 618 | |
| | SeF ₃ 245 | |
| | Se 415 | |
| | SeBr ₄ 427 | |
| | Se28r2 425 | |
| | SeCl4 423 | |
| | Se2Cl2 422 | |
| | SeF4 180 | |
| | SeF ₆ 179 | |
| | Se4N4 435 | |
| | SeO2 428 | |
| | SeOCl ₂ 429 | |
| | SeO(OC ₂ H ₅) ₂ 435 | |
| | SeSO3 435 | |
| | 440 | |

Si 676 SiBr₂ 687 SiBr4 686, 688 Si2Bre 688 Si(CH₃COO)₄ 701 SiCH₃Cl₃ 695 Si(CH₃)₂Cl₂ 694, 695 SiCl₄ 680, 682 Si2Cl6 680 SiaCla 684 Si4Cl10 684 SisCl12 684 Si6Cl14 684 Si10Cl22 684 Si10Cl20H2 685 SiF₄ 212 (SiH)* 681 (SiH₂)_x 681 SiH₄ 679, 680 Si2H6 679 Si₃H₈ 679 SiHBr3 692 SiH2Br2 694 SiHCl₃ 691 SiH₂Cl₂ 691 SiH₃Cl 691 SiHF₃ 214 SiI4 689 Si2I6 690 Si(N3)4 476 Si(NCO)4 702 SiO 696 Si2O3 700 Si(OCH3)4 702 Si(OC2H5)4 702 Si(OCN)4 702 Si2OCl6 696 Si3O2Cia 696 Si4O3Cl10 696 Si4O4Cl8 695 Si5O4Cl12 696 Si6O5Cl14 696 Si7O6Cl16 696 5iO2-12WO3-eq 1718 SiS 700 SiS₂ 700

| 14/164 | • |
|--------|---|
| | |

ł

| pp 1-992: Vol. 1; pp 1003-1 | 810: Vol. 2 | |
|--|--|---|
| SmBr ₂ 1150 | T | TiBr4 1201 |
| SmC) ₂ 1135 | TaBr ₂ 1311 | |
| SmI ₂ 1149 | TaBr3 1311 | TiC 1245 |
| Sp 727 | TaBr4 1310 | TiCl ₂ 1185 South |
| SnBr ₂ 732 | TaBrs 1311 | TiCl ₃ 1187 |
| SnBr4 733 | TaC 1331 | TiCl3-6H2O 1187, 1193 |
| Sn(CH ₃) ₄ 744 | TaCl ₄ 1301 | TiCl ₄ 1195 |
| Sn(C2H5)4 746 | TaC15 1302, 1305 | TiF3 248 |
| Sn(CH ₃ COO) ₄ 747 | $TaF_5 255$ | TiF4 250 |
| | | Ti-H 1184 |
| SnCl ₂ 728 | Ta-H 1296 | TiH2 114 |
| SnCl ₄ 729 | Tals 1316 | Til ₂ 1185 |
| SaF_2 217 | Ta-N 1328 | Til ₃ 1187, 1192 |
| SnF ₄ 217 | Te ₂ O ₅ 1318 | Til4 1205 |
| Sn1 ₂ 734 | [Ta5016 aq]Na7 1708 | TiN 1233 |
| $S_n I_4$ 735 | [Ta5O19-aq]Nag 1708 | Ti(NO ₃) ₄ 1237 |
| SnO 736 | TaP 1330 | TiO 1214 |
| SnO ₂ 738 | TaP ₂ 1330 | TiO ₂ 1216 |
| SnO2.nH2O 737 | Ta-5 1328 | TiO2.nH2O 1218 |
| [Sn(OH)3]Na 1687 | TaSi ₂ 1792, 1797 | Ti ₂ O ₃ 1214 |
| [Sn(OH)6]Na2 1694 | Te 437 | TiOC1 1209 |
| SnS 739 | TaBr4 445 | TiOCl ₂ 1209 |
| SnS ₂ 741 | TeCl ₄ 442 | TiO(NO ₃) ₂ 1241 |
| Sn(SO ₄) ₂ .2H ₂ O 744 | TeF ₆ 180 | TiOSO4 1228 |
| a | Tel4 447 | TiOSO4 2H20 1229 |
| Sr 922 S-P- 020 | TeO ₂ 447 | |
| SrBr ₂ 930 | | |
| SrCO ₃ 931 | TeO3 450 | |
| SrCi ₂ 930 | $Te_2O_3(OH)NO_3$ 437, 447 | |
| Sr(ClO ₄) ₂ 320 | TeSO ₃ 455 | TiS ₃ 1222 |
| Sr(ClO ₄) ₂ ,4H ₂ O | ገጉ 1174 | Ti ₂ (SO ₄) ₃ 1226 |
| 320 | ThBr ₄ 1203 | TiSi ₂ 1249 |
| SrF ₂ 234 | ThC 1248 | T1 867 |
| SrH ₂ 929 | TbC ₂ 1248 | TIBr 869 |
| SrJ ₂ 930 | ThCi4 1203 | TiBr3-4H2O 874 |
| $Sr(N_3)_2$ 941 | ThCl4-8H2O 1204 | Tl ₂ CO ₃ 884 |
| Sr3N2 940 | ТьН 1185 | TICI 869 |
| Sr ₂ [Ni(OH) ₆] 1686 | ThI ₄ 1205 | TIC13 870 |
| SrO 932 | Th ₃ N ₄ 1236 | TiCl ₃ -4H ₂ O 870 1 957 |
| SrO ₂ 936 | Th(NO ₃) ₄ 1240 | TIF 230 |
| SrO2-8H2O 935 | Th(NO ₃) ₄ -aH ₂ O 1238 | TIF3 230 |
| Se(OH)- AU-O OPE | | TH 869 |
| Sr(OH) ₂ .8H ₂ O 935 SrS 039 | ThO ₂ 1221 | TH-I2 876 |
| SrS 938 | Th ₃ P ₄ 1241 The: 1940 1799 1797 | |
| SrSe 939 SrS-O coo | ThSi ₂ 1249, 1792, 1797 | TI3N 883 |
| SrSeO ₃ 939 | Ti 1161 TiBr ₂ 1185 | 1TNO- 883 |
| SrSeO ₄ 939 | TiBr ₂ 1185 | T1-0 877 |
| SrSi 947 | TiBr3 1187, 1192 | TI-0- 879 635/ 4 |
| SrTe 940 | TiBr3.6H2O 1187, 1195 | an the second |

ep 1-092: Vol. 1; pp 1003-1810: Vol. 2 Tl₂Oy•xfl₂O 879 TIOH 877 TKOH)SO4+2H2O 882 T12(OOC)2CH2 684 THOOCH 884 TI25 \$50 Ti25 Ti253 880 71₂SO₄ 881 Ti₂Se Ti₂Se₃ 881 TI2TeCl6 444 TI(TIBr4) 875 Tl₃(TlBr6) 875 TI(TICI4) 872 Tig(T(C)6) 873 Ų U 1431 UBr4 1440 U(C2O4)2-61120 1449 UCI3 1435 UCI4 1436 UCI 1439 UD3 123 UF4 261 UF₆ 262 UH3 113, 1484 UO2 1442 UO3 1442 U(OC2H3)5 1451 U(OC2H3)8 1452 UO2(C15H11O2)2 1458 UO2CI2 1439

UO4-2H2O 1446 US2 1446 U(SO4)2-4H2O 1447 U(SO4)2-8H2O 1447 U(SO4)2-8H2O 1447 US12 1792

٧

V 1252 VBr: 1960 VBr: 1260

VC 1298 V₂C 1286 V(CH_COO)3 1283 V(C6H6)2 1289 VCI2 1255 VCI; 1256 VCI1-6H2O 1256 VCI4 1259 VF, 252 VF4 252 VF 3 253 V-H 1296 VI₂ 1261 Vij 1262 VN 1286 V₂N 1287 YO 1268 VO₂ 1267 V₂O₃ 1267 ¥205 1270 V6013 1266 Y_nO_{2n J} 1267 VOCI 1262 VOC12 1263 VOCI3 1264 VO2C3 1265 V(OH) 1268 YOSO4 1285 VOSO4-3H20 1285 VP<1 1267 VP 1287 VP2 1207 VS 1274 VS4 1275 V₂S₃ 1275 V₂(SO₄)₃ 1283 VSO4-6H20 1977 VSi2 1792

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W 14)7, 1622 W(CO)6 1741 WCls 1419 WCls 1419 $\begin{array}{c} & \psi_2 C t_6 P_{Y3} & 1429 \\ & \psi_6 & 260 \\ & \psi_0 & 1421 \\ & \psi_0 & 1423 \\ & \psi_{03-16q} & 1728 \\ & \psi_{18} O_{49} & 1422 \\ & \psi_{16} O_{49} & 1422 \\ & \psi_{16} O_{6} H_{516} & 1426 \\ & \psi_{0C14} & 1425 \\ & \psi_{0C14} & 1425 \\ & \psi_{2} & 1425 \\ & \psi_{2} & 1792 & 1797 \\ \end{array}$

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YF3 246 YbBv2 1150 YbCl2 1150 YbC2 1150 YbJ2 1150 YbSO4 1138

Z

Zn 1067 ZaAag 1083 ZajAuj 594, 1083 Z=8v2 1072 Zn(CH3COO)2 1007 Za(C2H3)2 1084 Zs(CN)2 1087 ZnCO3 1086 ZaCl₂ 1070 Z4F2 342 ZaFe204 1090 ZaH; 1069 Zal₂ 1073 Za3N2 1080 Za(NH2)2 1079 (Za(NH₃)4**MaO**g 1484 ZeO 1664 Za(OfD_ 1974 **Z_(CHOCI 1971** (2e(OR)_Na 1681 (Za(OB)4)Ney 1985 202(OH)PO4 1002 S20-13703-04 1713-

| pp 1-992: Val. 1, pp 1003- | Mill: Val. 2 |
|----------------------------|--------------|
| ZepPg 1080 | Ze 1172 |
| Za3(PO4)2-4820 1981 | ZiBra 128 |
| ZaS 1075 | Z-C 1245 |
| Za5204 394 | Z-Ci4 130 |
| ZeiSO2-CH2O(0)2 1026 | Z.F. 251 |
| Za ji Sh5 4) 2 1083 | Zr-# 1145 |
| ZaSe 1078 | 244 1205 |
| ZahiFa-6H2O 1090 | Z-N 1233 |
| Za 25104 1089 | 2.02 1230 |

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p 1-992: Vol. 1; pp 1003-1810: Vol. 2

This index is arranged alphabetically in terms of the major element, group or unit constituting the compound. Numerical prefixes such as mono, di, tri, etc., as well as poly are disregarded for purposes of arrangement (except that, for example, hexaphosphates follow pentaphosphates). The same applies to ortho, meta, para and pyro but not to per, sub, hypo and oxo.

Prefixes occurring at the beginning of the first word are not underlined. They are underlined within the word to help distinguish the key roots.

А

Acetates-see parent cation Acerylacetonate, aluminum 836 chromlum 1383 Active metals 1613 Active metal oxides 1656 a-Aleminate, chromium 1383 Alkali aluminates 1692 Alkali ammine graphite compounds 637 Alkali graphite compounds 635 Aikali hydrides 971 Alkali metal antimonides 985 arsenides 985 bismuthides 985 carbides 987 carbonates 987 germanides 989 niobates 1323 oxides 974 dloxides 980 phosphides 985 silicides 989 tantalates 1323 uranates (V) 1445 uranates (VI) 1445 Alicali metals, free 956 Alkyl ester of silicic soid 702 Alum, ammonium galitum (III) 854 ammonium vanadium 1284 cestum 956 cealum manganese 1468 cesium vanadium (III) 1284 potassium vanadium (ili) 1284 robidium vanadium (III) 1284 Alemiane, anmonium tetrafluoro-227 hexailuoro-226 cobair 1525 TRACIONALINA OXONYOROXO- 1693

Aluminate, sodium tetrachloro- 816 monosodium oxohydroxo-(1) 1693 oxohydroxo-(II) 1693 tetrasodium heptahydroxo- 1692 835 Aluminum acetate 836 acetylacetonate amalgam 1807 arsenide 831 azide 476, 829 boride 772 bromide 813 bromide-hydrogen sulfide adduct 819 celcium hydride 806 carbide 832 chloride 812 chloride ammoniate 817 chloride graphite 644 chloride hydrate 815 chloride-phosphorus pentachloride ad-818 duct chloride-sulfur dioxide adduct 817 chloride-thionyl chloride adduct 818 tetrachlorosluminic acid dietherate 816 chlorohydride 808 piethanolaminate 835 triethyl- 810 diethyl-, bromide 809 trictbyl-, etherate 811 diethyl-, hydride 811 ethoxide 834 fluoride 225 hydride trimethylaminate 809 hydride, polymeric 807 hydroxide 820 hydroxide gel 1652 iodide 814 iodide-hexaammoniate 819 lithium cyanide 833 lithium bydride 805

pp 1-992: Vol. 1; pp 1003-1810: Vol. 2 Aluminum lithium nitride 828 lithium phosphide 830 methoxide 833 nitride 827 oxide 822, 1660 orthophosphate 831 phosphide 829 selenide 825 sulfide 823 basic 824 neutral 824 telluride 826 Amalgams 1801 Amalgam, aluminum 1807 barium 1805, 1806 bismuth 1806 cadmium 1806 calcium 1804 lead 1806 potassium 1803 rare earth 1807 sodium 1802 strondum 1805 tin 1806 zinc 1806 Amide, Uthlum 463 sodium 465 tetreAmide, pyrophosphoryi 588 triAmide, phosphoryl 584 thiophosphoryl 587 monoAmidophosphate, <u>di</u>sodium 581 diAmidophosphoric acid 582 monoAmldophosphoric acid 579 Amidosulfonate, potassium 507 Amidosulfonic acid 508 Aminate, borine trimethyl- 778 trans-diAmminedichioroplatinum (II) 1578 hexaAmminechromium (III) chloride 1351 nitrate 1351 triAmminechromium tetroxide 1392 hexeAmminecobalt (II) chloride 1516 (ill) chioride 1516 (III) nitrate 1526 Ammine complexes of platinum (II) 1577 decaAmmine-µ-peroxocobalt (III) cobait (IV) suffate 1540 tetraAmminecopper (II) sulfate 1021 diAmminemercury (ii) dichloride 1114 1545 hexaAmminenickel (II) chloride diAmminepalledium (il) salts 1585 tetreAmminezinc tetreperoxomolybdate (V!) 1414 Ammonia 460 from labeled NH4Cl 461 solutions of 463 Ammoniate, boron trifluoride 785 Ammoniated mercuric chlaride 1114 Ammonium aluminum fluoride 226 orthoerseaste 602 hexabromoanzimonate 615

carnaliite 908, 951

Ammonium chlorate 313 hexachloroiridate (IV) 1594 -osmate (IV) 1603 tetrachioropalladate (II) 1584 chloroplatinate 1570 bexachloroplatinate (IV) 1\$70 -plumbate 751 -rhodate (iii) 1588 -ruthenate (IV) 1599 -selenate 425 -stennate 731 -tellurate 444 -titanete 1199 tetrachlorozincate 1072 cryolite 226 hexacyanoferrate (II) 1509 fluoride 183 tetrafluoroeluminate 227 hexafluoroaluminate 226 terrafluoroberyllate 232 baxafluorogallate 228 bexafluoroindate 229 diffuorophosphate 196 hexaficorophosphate 195 gailium alum 854 gallium (III) sulfate 854 hydrogen fluoride 183 hydrogen suäfide 357 iodide 289 iridium (IV) chloride 1594 lead (IV) chloride 751 luteophosphorungsmate 1723 hexanitrorhodate (iii) 1586 heptanitrosyltrichioferrate 1764 exopentschloromolybdate (V) 1413 palladium (IV) chloride 1584 palladochloride 1584 pentaperoxodichromate 1392 peroxydigulfate 390 perrhenate 1484 persulfate 390 platinichloride 1570 plumbic chlorida 751 rhodanijate 1378 ruthenium (IV) chloride 1599 selt of rhodualite acid 1978 diAmmonium <u>penta</u>sulfane 369 Ammonium disulfatovanadate (III) 1288. pentasulfide 369 ٤. - en A thicarsenate 604 1 trithiocarbonate 674 terrathiocyanatodiamminechtomate (III) . 4 1576 -diamilinochromstes(III) 1378 terrathiomolybdate 1416 14.5 paratungstate 1713 uranyi carbonata 1449 metayanadate 1272 5 6A vanadium (III) alum 1284

zine sulfate 1077

. . . See **1888**

Ĵ

te 1-352: Vel. 1: pp 1003-1810: Vol. 2 Anhydrous sodium tetraborate 793 Automorate, emmondum bezabromo- 615 3000 mm thio- 619 Antimonic sold, herechlaro- 631 Antimenide, gellium 857 Jadživan 867 Hehtern 985 potessituen 986 sediture 986 Antimogy 606 explosive 1638 Amimony bromide (ill) 618 chleride (III) 608 chioride (V) 610 gchloride trifluoride 200 fluoride (III) 199 fluncide (V) 200 hydrated oxide (V) 617 hydride (stibine) 606 lodide (III) 614 (UI) oxide 615 (V) oxide 616 diAntimony terroxide 618 Antimony (III) axide chloride 611 oride sulfate 619 (III) sulface 618 Aquopenteamminecobait (III) oxaiste 1533 diAquotetraamminecobalt (III) sulfate 1537 bexaAquochromium (III) acetate 1371 (III) chloride 1348 orthoArgentite, sodium 1039 Argentous sulfide 1039 Arsenste, ammonium ortho- 602 baran 797 bydraxylammonium 501 sodium dibydrogen ortho- 602 miArsenate, sodium hydrogen 1709 Arsenates, Isopoly- 1709 1-Arecostes, 12-molybdic acid- 1734 12-tungstic acid- 1724 2-Arsenates, 6-molybdic acid- 1736 18 molytrdic ecid- 1734 18-tungstic acid- 1725 Argenic 591 yellow 592 orthoArpenic acid 601 Arsenic prihromide 597 trichloride 596 Georide (III) 197 financide (V) 198 dilodide 598 <u>etiodide</u> 597 diArecuic pentarulfide 603 griezide 600 ietraAnsenic setresulfide 603 Aryenide, gallium 857 indian 967 hidian 985 **91**7 ndiano 786 No 986

Arsenide, sodium dihydrogen 595 Arsine 593 Aurate (III), hydrogen tatrachloro-1057 Aurere, potassium 1061 potassium tetrachloro- 1058 Aurate (I), potassium dicyano- 1065 Auric chloride 1056 hydroxide 1060 oxide 1059 potassium chioride 1058 Aurochlorohydric acid 1057 Aurous chioride 1055 s-triAzaborane 779 Azide 474, 959 aluminum 829 barium 942 beryllium 899 lead 763 magnesium 917 Azodisulfonate, potassium 510

8

Barium 922, 928 amalgam 1805, 1806 azide 942 bromide 930 chlorate 314 chloride 930 chromate 316 chromate (V) 1394 orthochromate (IV) 1393 tetracyanoplatinate (II) 1576 fluoride 234 hydride 929 dihydrogen hypophosphite 562 hexshydroxocuprate (HO 1685 hexabydroxoferrate (III) 1690 heptahydroxoferrate (III) 1690 hypophosphite 557 iodide 930 manganate (Vil) 1462 nitride 941 oxohydroxostannate (II) 1696 oxide 933 perchlorate 320 periodate 326 permanganate 1462 percodde 937 peroxide octahydrate 937 perrhenate 1487 mesopermenate 1487 pladnocyanide 1576 rhenate (VI) 1485 purification of salts of 933 selenide 939 disilicate 706 metasilicate 706 silicide 947 sulfare-potassium permanganate solid solution 1463

pp 1-992: Vol. 1: pp 1003-1810: Vol. 2 Barium sulfide 938 telluride 940 trithiocarbonate 674 dithionate 397 dithiophosphate 571 Bayerits 821 diffenzenechromium (0) 1395 iodide 1397 diBenzenemolybdenum (0) 1402 di Senzenevanadium (0) 1289 (Berthellet's) fulminating or detonating süver 1046 Beryllate, ammonium tetrafiuoro- 232 sodium 895 Beryllium 887 acetate 901 acetate, basic 901 azide 899 bromide 891 carbide 899 carbonate 893 chloride 889 formate, basic 902 fluoride 231 hydroxide 894 iodide 892 nitride 898 oxide 893 propionate, basic 902 selenide 897 sulfide 895 telluride 897 Bismuth 620 amalgam 1806 borate 627 (III) bromide 623 chioride 621 dichloride 622 fluoride 201 (V) fluoride 202 (III) todide 524 diBismuth <u>terroxi</u>de 629 Bismuth oxide bromide 624 oxide chioride 622 oxide lodide 625 oxide nitrite 626 (III) phosphate 626 Bismuthate, potassium 628 sodium 627 anhydrous 627 hydrous 628 Bismuthide, lithium 985 potassium 986 sodium 986 Bisulfide, carbon 652 Boehmine 821 diBorane 773 Borate Mamuth 627 796 lithium aluminum nitrosyl fluoro- 224 potassium fluoro- 223

Borate, potassium hydroxyfluoro- 224 metaBorate, sodium 791 orthoBorate, sodium 790 790 tetraBorate, sodium 793 pentaBorate, sodium 795 Borate, sodium fluoro- 222 sodium tetraphenyl- 803 1-Borstes, 12-tungstic acid-1716 Borax 793 Borazole 779 s-<u>qri</u>chloro-779 metaBoric acid 791 Borides 1798 aluminum 772 Borine trimethylaminate 778 Borofluoride, sodium 222 Borohydride, lithium 775 sodium 776 sodium grimethoxy 777 Boron 770 tetragonal 772 Boron trialkyls 600 arsenate 797 azide 476 tribromide 781 <u>tri</u>chloride 780 triethyl- 799 trifluoride 219 trifiuoride ammoniate 785 etherate 786 difluoride, n-butyl- 802 trifluoride dihydrate 784 triodide 782 methoxide 797 trimethyl-798 nitride 759 oxide 787 phosphate 796 (III) sulfide 788 801 Boronic acid, n-butyl-Boroxine, trimethyl- 800 tri-n-buty)- 801 monoBromamine 480 Bromate, barium 316 237 potassium terrafiuoro (ill)-Bromic seid 315 Bromide-See parent cation - A. Bromine 275 - - - - i .e purification of 275 2.1216 Bromine trifluoride 156 pentafluoride 158 graphize 643 hydrate 276 defant 🕈 (ill) altrate 328 dioxide 306 diBromine monoxide 307 Bromofluorophosgene 210 diBromolodide, cestum 297 1 1 2 1 2 1 2 potassium 296 1468 triBromotripyridinemolybdenuse

In I-Stit: Vol. 1; pp 1003-1810: Vol. 2 willrumodiana 692 diffromodianifana 377 -gionifana 379 -picrosulfana 379 -picrosulfana 379 -picrosulfana 379 -picrosulfana 379 -picrosulfana 379 -giosulfana 379 -giosulfana 379 -stronothallate (III), rubidium 876 thallium (I) 875 mcrafiromothallate (III), thallium (I) 875

С

Cedman, potessium terracyano- 1106 Cadmium (needles) 1092 Cadmium acetate 1105 amalgam 1806 amade 1100 arsenide 1103 bromide 1096 carbonate 1104 chioride 1093 chloride hydraxide 1094 cyanide 1105 diethyl- 1103 fermite (III) 1107 fluoride 243 bydroxide 1097 hydroxychloride 1094 ladide 1096 aitride 1100 phosphides 1101 potassium chloride 1095 cyanide 1106 rhodanide 1106 selezide 1099 silicate 1107 ernhosilicate 1107 sulfide 1098 delocyanate 1106 Calcium 922 aluminum hydride 806 amaigam 1601 faronalde 930 carbide 943 chiloride 930 cyanomide 946 Daoride 233 germanide 948 ydride 929 **hydroxide** 934 Jodide 930 maride 940 milde 931 precisionale 320 provide 936 termide bydrate 937 angelde \$27, 942

Calcium orthoplumbate 760 Calcium salts, purification of 931 sejenide 939 silicide 946 sutfide 938 telluride 940 Carbide, aluminum 832 beryllium 899 calcium 943 lithium 987 magnesium 920 sođium 987 Carbon 630 adsorptive (activated) 633 black, graphitized 631 lustrous 632 monoxide black 631 oxygen compounds reacting as acids 634 oxygen compounds reacting as bases 634 preparations, special 631 sulfur compounds 634 surface compounds of 633 Carbon monofiuoride 640 tetrafluoride 203 tetraCarbon monofluoride 641 Carbon monoxide 645 purification of tank CO 646 Carbon dioxide 647 purification of tank CO₂ 647 triCarbon dioxide 648 Carbon selenide 656 diselenide 656 suboxide 648 subsulfide 653 disulfide 652 triCarbon disulfide 653 Carbonate-see under parent cation Carbonatotetraamminecobalt (III) sulfate 1535 Carbonyl bromofluoride 210 chloride 650 chlorofluoride 209 fluoride 206 difluoride 206 iodofluoride 211 iron 1636 selenide 655 suifide 654 Caro's acid 389 Cementite 1503 Cerium metal, solid 1142, 1145 Cerium monochalcogenide 1155 compounds, pure 1132 earths, purification of 1131 (III) fluoride 247 (IV) fluoride 247 (ill) oxide 1151 Cestum 957 alum 956 azide 959

pp 1-992: Vol. 1; pp 1003-1810; Vol. 2 Cesium dibromoiodide 297 carbonate 988 chloride 961 from carnallite 951 from dollucite 955 dichlorobromide 294 dichiorolodide 296 bexachioroselenate 425 hexachlorotellurate 444 nonachlorodithaliate (iii) 874 chromate 1389 dichromete 1389 dioxide 981 germanide 989 graphite 635 hydride 971 hvdrodde 983 manganese alum 1468 manganese (III) suifate 1468 oxide 978 silicide 989 vanadium (Iil) alum 1284 Cesium, purification by vacuum distillation 963 Chalcogenides, europium (II) 1185 monoChalcogenides, cerium 1155 lanthanum 1155 neodymium 1155 preseodymium 1155 Chinese red 1112 monoChioramine 477 Chlorate-see parent cation Chloric acid 312 Chlorides—see parent cation Chlorine 272 azide 476 <u>monofluoride</u> <u>tri</u>fluoride 155 bydrate 274 nitrate 326 dioxide 301 diChlorine oxide 299 hexoxide 303 heptoxide 304 Chlorine dioxide fluoride 165 trioxide fluoride 166 terroxide fluoride 167 Chiorite, sodium 312 tetraChiorosiuminate, sodium 816 terraChloroaluminic acid dietherate 816 triChlorotriamminechromium 1381 -pyridinechromium 1381 Chioropentaamminecobalt (III) chioride 1532 -chromium (III) chloride 1352 diChlorotetreamminecobalt (iii) chloride 15361,2-diChlorotetraamminecobalt (lil) chloride (cis) 1536 1,6-diChlorotetraamminecobalt (III) chioride (trans) 1537

chioride 1590 nitrate 1590 Chloreantimonate (V), sicrosyl 612 hexaChloroantimonic acid (V) 611 diChiorcaquotriamminechromium (III) chloride 1358 triChlorotriaquochromium 1380 Chloropentaaquochromium (III) chloride 1350 suffate 1350 pentaChioroaquothaliste (III), potassium 674 tetraChlorcaurate (lil), potassium 1050 Chlorosuric acid 1057 s-triChloroborazole 779 Chlorochromate, potassium 1390 triChiorodiaiane 808 triChlorotriethanolochromium 1380 cis-diChlorodiethylenediaminechromium (III) chloride 1356 trans-diChlorodiethylenediaminechromium (UI) chloride 1857 diChlorotetrafluoroethane 205 triChiorodifluoroethane 205 -trifluoroethane 205 205 monoChlorotriffuoromethane diChlorodifiuoromethane 205 Chlorofiuorophosgene 208 diChlorofluorophosphine 191 triChlorogermane 721 Chlorohydride, aluminum 808 Chioraimidosulfonate, potassium -508 --tetraChloroiodic acid 299 diChlorolodide, cesium 296 potassium 295 tetraChlorolodide, potassium 298... hexaChloroiridate (IV), ammonium 1594-(III), potaseium 1595 . . (IV), potassium 1593 hexaChloroiridium (IV) acid 1593-2000 -manganate (IV), potassium 4464 -molybdate (III), popassium-1408 -osmate (IV), ammonium 1608. sodium 1602 tetraChioropalladate (II), ammonium 1586 . Cate potassium 1584 ್ಷ ನ ಭಾಷ sodium 1584 hexaChloropalladate (IV), ammonium 458 potas sium 1584 N8.790 Chlorophosgens 209 2011 (Sec. 10) (Sec. 10) (Sec. 10) tetraChiorophosphonium hexafluorophos phate(()) Chloropletinate (IV), ammonium 1570. terraChloroplatinate (II), potassium 1572 hexeChloropletinate (IV), ammoulum 1579 1. 1 A **#** potassium 1573 1999 A. 97 sodium 1571 Chloroplatinic scid 1569 tetraChloroplatinic (21) acid 1520 hexaChloroplatinic (IV) acid 1569

7. 6

1003-1810: Vol. 1: pp 1003-1810: Vol. 2 hem Chlercelumbere, anamonium 751 Propression 753 Pergeressocobelt chiaride 1597 Chieroperpercecebalt chloride 1593 errChiorogripyridinechromium 1382 bene Chloroprinyridiaeditungstate (III) 1425 bene Chlorophodate (III), ammonium 1588 1429 polessitile 1588 sections 1587 1599 aun Chierorusbenate (IV), ammonium hexaChicrosolenates 425 amatemium 425 cesium, 425 patassian 425 ruhidium, 425 thelium 425 Chierosilane 691 diChlorosilanc, dimethyl 694 Chlorosilozanes 695 bezaChiorostamate, ammonium 731 potassium 731 bezaChlocostamic acid 730 diChloromonosulfane 370 -disulfane 371 -trisulfane 372 -tetrasulfane 372 pentasulfane 372 exasultane 372 -beptasulfane 372 -octasulfane 372 Chlorosulfonic acid 385 bent Chierotellurates 444 ADDOSIUM 444 cesium 444 potassisso 444 rahkium 444 thallium 444 etraChlorothallate (III), thallium (l) 872 henaChlurothallate (III), potassium 873 thalling (1) 873 nensChlorodithallate (III), cesium 874 etraChlorothallium (fil) acid 872 casesChlorodiungstate (III), potassium 1427 Chlorovioleocobalt chloride 1537 Chicryl fluoride 165 oxyfinoride 166 diChloryiphosphoric sold anhydride 536 Chromete, cestum 1389 potassium chloro- 1390 potassium fluoro- 1390 F10445400 1388 Chromate (II), potassium hexathiocyaneto-1374 Chromote (10), annonium teurathiocyanato-<u>diamilino...</u> 1378 Continue Lettracyanatoritammine-1376 Similar happenyl- 1375 testan trioxeleto- 1372 E constitucyanatodipyridino-1379

Chromate (III), sodium <u>hexa</u>hydroxo- 1688 Chromate (IV), barium ortho- 1393 Chromate (V), barium 1394 potassium <u>tetrap</u>eroxo- 1391 diChromete, ammonium peataperoxo- 1392 cesium 1389 rubidium 1388 triChromate, potassium 1709 terraChromate, potassium 1710 Chromates, isopoly- 1709 Chromic (III) acid, tetrathiocyanatodiammine- 1377 chloride, luteo- 1351 nitrate, luteo- 1351 -2-Chromites, 12-molybdic scid- 1737 Chromite, sodium thio- 1394 Chromium 1334 Chromium (II) acetate 1368 (III) acetate, hexeaquo- 1371 triChromium (III) acetate, <u>di</u>hydroxo<u>hexa</u> acetato-1371 Chromium (III) acetylacetonate 1383 (0) dibenzene- 1395 (II) bromide 1340 (III) bromide 1341 carbonyl 1741 tricarbonyl, tripyridine 1749 tetracarbonyl, dipyridine 1749 (II) chloride 1336 (III) chioride 1338 bexsammine- 1351 hexaaquo- 1348 chloropentaammine- 1352 chloropentaaquo- 1350 dichlorosquotrismmine-1358 chioride, erythro- 1360 (iii) chioride, cis-dichlorodiethylenediamine- 1356 trans-dichlorodiethylenediamine- 1357 triethylenediamine 1354 triChromium (III) chloride, dihydroxohexaacetato-1371 Chromium (III) chloride, hexaures- 1359 trichlorotriammine- 1381 -triaquo- 1380 -triethanolo- 1380 -<u>tripyridino</u>-1381 (II) fluoride 256 (iii) fluoride 257 (IV) fluoride 258 (III) glycinate 1382 (ill) hydroxide 1345 (II) lodide 1344 (ill) iodide 1344 (I) iodide, <u>dibenzene</u>-1397 bis(diphenyl)- 1397 diphenyi)(benzene). 1398 (III) nitrate, hexaammine- 1351 uitride 1347 (II) oxalate 1370 tetroxide triammine 1392

SUBJECT INDEX

pp 1—992: Vol. 1; pp 1003—1810: Vol. 2 Chromium (lii) oxide, copper 1672 oxide gel, hydrated 1648 trioxide-pyridine 1385 perchlorate, tris(2,2 -dipyridyl)- 1362 (II) perchlorate, tris(2,2 dipyridyi)- 1361 (IV) diperoxotriammine-1392 (0) <u>bis(diphenyl)</u> 1396 (0) hexaphenylisonitrilo-1363 orthophosphate 1364 (0) <u>tris</u> (2,2'-dipyridyl)- 1363 (11) sulfate 1363 (III) sulfate, <u>tri</u>ethylenediamine 1354 sulfides 1346 (III) thiocyanate, triethylenediamine-1354 wans-dithiocyanatodi(ethylenediamine)-1357 (ili) xanthate 1383 Chromium (II) sait solutions 1366 Chromyl chioride 1384 fluoride 258 nitrate 1384 perchiorate 1387 Cinnabar 1112 Cinnebar green 1092 Cinnebarite 1112 Clerici's solution 884 Cobalt, metallic 1513 pyrophoric 1615 very pure 1513 Cobair aluminate 1525 (III) amide 1526 (II) bromide 1517 (III) bromide, triethylenediamine- 1538 bromide, <u>di</u>nitrosyl 1761 (ill) bromide tartrate, d-triethylenediamine- 1539 diCobalt carbide 1531 Cobalt carbonyls 1746 tetracarbonyl hydride 1753 carbonyl mercury 1755 (il) chloride 1515 hexaammine 1516 (III) chloride, hexsammine- 1531 chloropentaammine- 1532 1.2-dichlorotetreammine- 1536 1.6-dichlorotetraammine- 1537 nitritopentasmmine- 1535 nitropentasmmine- 1534 chloride, <u>di</u>nitrosyl 1761 (III) hexacyanide, potassium 1541 (II) fluoride 267 (III) fluoride 268 green 1092 (II) hydroxide 1521 (III) bydroxide - 1520 (II) fodide 1518 iodide, <u>di</u>nitrosyl 1761 (III) altrate, <u>bexaammine-</u> 1526 nitride 1529 diCobelt nitride 1529

Cobalt nicrosvi cricarbouvi 1761 1.1.1.16 dinitrosvi balides 1761 (III) exalate, aque<u>pentaammine-</u> 1538 (II) oxide 1519 (II, III) oxide 1520 (III) oxide 1675 phosphide 1530 (III) sulfate 1524 (IV) sulfate, decaammine-u-peroxocobalt (11) 1540 (III) sulfate, disquotetreammine- 1537 (III) suifate, carbonatotetraammine- 1535 sulfides 1523 sulfoxylate 393 Cobaltate (III), potassium hexacyano- 1541 (IV), potassium beptafluoro- 269 (III) sodium hexanitrito- 1541 Cobaltic (ill) acid, hexacyano- 1542 Copper, pure metal 1003 active 1633 colloidal 1003 Copper acetoarsenite 1027 (i) acetylide 1026 (ii) azide 1022 . bromide 1006 (II) bromide 1009 carbonates (basic) 1024 (I) chloride 1005 (II) chloride 1008 chromium oxide 1672 (II) fluoride 238 hydride 1004 (il) hydroxide 1013 (I) iodide 1007 (I) nitride 1021 (l) oxide 1011 (II) oxide 1012 oxychloride 1010 11.00 phosphide 1023 1.103 diphosphice 1024 (I) selenide 1019 (I) sulfate 1020 1. 1.1.2 11 (II) sulfate, tetraammine- 1021 : (1) sulfate 1016 (II) sulfide 1017 (I) telluride 1019 Cornandiam 822 Cuprate (III), potassium bezafluoro- 269 A STARREE Cupric bromide 1009 carbonate, blue 1025 - 10 **- 10 - 10** chloride 1008 hydroxide 1913 al barrette. oxide 1012 sulfide 1017 1.00 Suifice 1047 Cuprous szide 1022 bromide 1006 chloride 1005 tadda 1007 1 × 1 + 28.7 1994 - 1995 - 1995 - 1995 - 1995 - 1995 - 1995 - 1995 - 1995 - 1995 - 1995 - 1995 - 1995 - 1995 - 1995 - 1995 iodide 1007 nitride 1021 oxide 1011

1003-1810: Vol. 1: pp 1003-1810: Vol. 2 Cuprens salanide 1019 Suiture 1030 1016 mitericit 2019 Cyanamide, calcium 946 stiver 1047 peners, silicon 702 Cyanic acid 607 с, nida, kydrogen 658 Mehtum aturningn 833 Cyanoamminoferrate (II), sodium penta-**IS11** (III), sodium penta- 1512 Cyanoanrate (1), potassium di-1065 mere Cyanocedmete, potassium 1106 1373 Oyanochromate (Ui), potassium hexa-Cresocobeltare (III), potassium hexa-1541 herraCyanocobaltic (III) acid 1542 bers Cyanoferrate (II), ammonium 1509 sodium carbonyl 1769 sodium nitrosyl 1768 hexeCyanoferric acid, (ii) 1509 (11) 1510 Cymrogen 660 diCyanogen 660 Cyanogen bromide 665 chloride 662 iodide 666 Cranomanganate (I), potassium hexa- 1472 Europium (II) hromide (II), potassium hexa- 1473 (III), potassium bexa-1474 pocassium nitrosyl 1767 Cyanomercurate (II), potassium tetra-1122 Cyanamolybdate (IV), potassium octa-1416 potassium nitrosyl 1766 Cyanonickelate (II), potassium tetra-1559 Cyanoplatizate (II), barium tetra-1576 pression tetra- 1576 Cyanotong state (IV), potassium octa- 1429 (V), potassium <u>oct</u>a- 1430 Cymozin-ate, potassium terra- 1088 Cyanactic acid 668

D

Demeride, hydrogen 126 Desterios 121 Democratic incomide 131 chieride 129 mide 177 felide 133 والا ملط interesta 137 -phospheric acid 138 ric selé 135 ogi) (caree) chromium (l) lodide 1398

E

Erythrochromium chloride 1360 criEthanolaminate, aluminum 835 Etherate, boron trifluoride 766 Ethiop's mineral 1111 Ethoxide, aluminum 834 tetraEthoxygermane 725 -silane 702 miEthylaluminum 810 diEthylaluminum bromide 809 triEthylaluminum etherate 811 diEthylaluminum hydride 811 diEthylcadmium 1103 triEthylenediaminecobalt (III) bromide 1538 optical antipodes of 1538 triEthylenediaminechromium (iii) chloride 1354 sulfate 1354 thiocyanate 1354 Ethylenediamine iron carbonyl 1756 miEthylenedlamine iron (ll) octacarbonyl diferrate (II) 1756 diEthylmercury 1118 Ethyl dinitrosyl thioferrate 1765 diEthylzinc 1084 Europium compounds, pure 1136 1150 (II) carbonate 1137 (ii) chloride 1136 (11) Eusride 248 (II) todide 1150 (ii) oxide 1156 (iii) oxide 1156 (II) selenide 1155 (ii) sulfate 1137 (II) sulfide – 1155

F

(II) telluride 1155

Fehling's solution 1027 Ferrate (II), ammonium hexacyano- 1509 Ferrate, ammonium heptanitrosyl trithio-CETTE-1764 Ferrate (III), harium hexahydroxo- 1691 (III), barium heptahydroxo- 1691 (III), lithium 1504 (VI), potessium 1504 (IV), potassium <u>hexafiuoro</u>- 269 potassium nitrosyi <u>tri</u>carbonyi 1759 potassium dinitrosyl thiosulfato- 1766 sodium carbonyl cyano- 1769 (II), sodium pentecyanoammino 1511 (III), sodium pentacyanoammino 1512 (il), sodium pentacyanoaquo- 1769 (1), sodium terrahydroxo- 1686 (III), sodium heptahydroxo- 1689 (III), sodium octahydroxo- 1690

pp 1-992: Vol. 1; pp 1003-1810: Vol. 2 Ferrate (III), sodium nitrosyl cyano-1768 (ill), sodium hexathiocyano- 1511 Ferric (II) acid, <u>hexa</u>cyano-1509 (III) acid, <u>hexa</u>cyano-1510 Ferric bromide 1494 chloride 1492 Ferricyanic acid 1510 Ferrocyanic acid 1509 Ferrous bromide 1493 chloride 1491 iodide 1495 oxide 1497 sulfide 1502 Fluorides-see parent carions Fluorine 143 Fluorine nitrate 187 hexa Fluoroaluminate, ammonium 226 tetra Fluoroaluminate, ammonium 227 tetra Fluoroberyllate, ammonium 232 Fluoroborate, nitrosyl 224 potassium 223 potessium hydroxy-223 sodium 222 Fluorochromete, potassium 1390 Fluoroboric acid 221 Fluoroboric acid. dihydroxy- 784 tetraFluorobromate (III), potassium 237 Fluoroform 204 Fluoroformyl fluoride 206 hexaFluorogallate, ammonium 228 -germanate, potassium 216 -indate, ammonium 229 hoptaFluorocobaltate (IV), potassium 269 hexaFluoroiodate (V), potassium 238 tri Fluoroiodomethane 205 hexaFluoromanganate (IV), potassium 264 triFluoromethane 204 hexaFiuoronickelate (IV), potassium 269 255 hepta Fluoroniobate (V), potassium 196 diFluorophosphate (V), ammonium hexa Fluorophosphate (V), ammonium 195 tetrachiorophosphonium 193 potassium 196 triFluorosilane 214 tetra Fluorosilane 212 Fluorosilicate, zinc 1090 Pluorosilicic acid 214 hexaFiuorosilicic acid 214 Fluorosulfinate, potassium 178 Fluorosuifonic acid 177 heptaFluorotantalate, potassium 256 penta Piuorothorate, potassium 1177 hexaFluorotitanate, potassium 1163 sodium 1163 Fluosificic acid 214 Formyl nitrile 658 Free alkali metais 956 Fremys salt S04

Ģ

Gadolinite, treatment of 1129 diGallane 840 tetramethyl 840 Galiate, ammonium hexafiuoro- 228 iithium <u>tetra</u>hydro- 842 Callum 837 dissolving in acids 839 electrolytic separation of 837 Galifum alum, ammonium 854 antimonide 857 ersenide 857 azide 476 (ii) bromide 647 (III) bromide 845 (II) chloride 846 (III) chioride 843 (III) fluoride 227 hydroxide 847 <u>mets</u>hydroxide 847 (III) [odide 846 trimethyl- 840 nitrate 856 nitaride 855 (1) oxide 549 (III) oxide 848 839 (III) perchiorate phosphide 857 selenide 854 (III) suifate, ammonium 854 (1) sulfide 852 (II) suifide – 851 (III) suifide 850 telluride 855 Gel, aluminum hydroxida 1652 hydrated chromium oxide 1648 hydrated oxide 1646 sillca 1648 Germanate, potassium hexafiuoro-216 Germane, trichtoro-721 tetraethoxy- 725 Germanide, calcium 948 cesium 989 magnesium 922 potassium 989 rubidium 989 sodium 989 110 Germanium 706 metallic 712 Germanium tetraacetate 726 (IV) bromide 718 (IV) chloride 715 1.139.23 dichloride 716 <u>tetrafiuoride</u> 215 hydrides 713 (IV) iodide 719 . . . ditodide 720 ÷ triiodide, methyl-722 nicride 722 151.25 (U) oxide 711

SUBJECT INDEX

- 1-398 Yol. 1: pp 1003-1810: Vol. 2 Garmentum (IV) oxide 706 million of 709 via acid decomposition 706 a altabase decomposition 708 suitte 723 selfice 724 Glycinete chromium 1382 Geld, very pure 1052 colloidel 1053 Brom residues 1054 (1) aceryitide 1063 (I) objeciće 1055 (01) chileride 1056 monochtoride 1055 crichloride 1056 trichloride acid 1057 (I) cynnaide 933 (III) hydroxide 1060 (111) oocide 1059 sesquioxide 1059 triande 1059 (1) suitlide 1061 (Ü) saltikle 1062 (III) suffide 1063 Gold perassium cyanide 1065 See also aurous, auric, etc. Greham's sait 550 Graphite, alkali compounds 635 See also carbon Graphite, aikali ammine compounds 637 eluminum chloride 644 bisulfate 642 brandine 643 cestum 635 finoride 640 fails and films 632 trea (III) chloride 644 metal balides 644 minuale 643 onside 638 endde black 631 anylayda udde 638 perchlorate 643 petassium 637 rubidium 637 miles 642 stellinen 637 Graphitic acid 638

н

Hefinina 1172 Meparation from zirconium 1179 (V) irconide 1203 curitide 1245 (V) chloride 1203 mirride 1233, 1236 (V) oxide 1223 rightine 1244 Middan, <u>origin</u> 293

Heavy hydrogen and compounds-see Deuterium Hereropoly acids 1698 Reteropoly compounds 1699, 1716 Hittori's phosphorus 520 Hopkslite (Hopcslite) 1674 Hydrargillite 820 Hydrate, bromine 276 chlorine 274 diHydrate, boron trifluoride 784 octaHydrates of alkaline earth metal peroxides 937 Hydrated chromium oxide gel 1648 Hydramed oxide gels 1646 Hydrazine 469 hydrate 469 disulfonate, potassium 509 Hydrazinium sulfate 468 Hydrazoic acid 472 Hydrides-see parent metal Hydrochloroauric acid 1057 Hydrocyanic acid 658 Hydrogen 111 aluminum chloride 815 bromide 282 chloride 280 tetrachioroaurate (III) 1057 hexacyanocobaltate (III) 1542 hexa cyanoferrate (II) 1509 (III) 1510 deuteride 126 fluoride 145 fluoride, ammonium 183 potassium 237 diHydrogen hypophosphate, disodium 560 diHydrogen hypophosphite, harium 562 Hydrogen iodide 286 peroxida 140 dlHydrogen phosphate, sodium 544 Hydrogen phosphide (gaseous) 525 diffydrogen phosphide, sodium 530 Hydrogen selenide 416 selenide, sodium 419 disulfatovanadate (III) 1282 sulfide, ammonium 357 sulfide sodium 357 tetraHydrogentellurate, sodium 453 Hydrogen telluride 438 thiocyanate 669 Hydroxides—see parent metal diHydroxohexaacetatotrichromium (III) acetate 1371 chloride 1371 hexaHydroxochromate (III), sodium 1688 teuraliydroxocuprate (il), sodium 1684 hexaliydroxocuprate (il), barium 1685 Hydroxoferrates (III), barium 1690 aodium 1689 tetraHydroxoferrate (II), sodium 1686 tetraHydroxomsgnesate, sodium 1683 hexelydroxonickelate (II), strontium 1686 hexaliydroxopiumbate, sodium 1694

pp 1-992: Vol. 1; pp 1003-1810: Vol. 2 Hydroxo salts 1677 triHydroxostannate (il), sodium 1687 hexaHydroxostannate (iV), sodium 1694 Hydroxozincates, sodium 1681 Hydroxyapatite 545 Hydroxyfluoroborate, potassium 223 diHydroxyfluoroboric acid 784 Hydroxylamine 501 disulfonate, potassium 503 isomonosulfonic acid 510 Hydroxylammonium arsenate 501 chioride 498, 500 oxalate 501 phosphate 500 hexaHydroxyplatinates (IV) 1575 Hypersulfuric acid 388, 389 Hypobromite, potassium 311 sodium 310 Hypochlorite, sodium 309 Hypochlorous acid 308 Hyponitrates-see parent cation Hyponitrites-see parent cation Hyponitrous acid 492 Hypophosphate, disodium dihydrogen 560 tetrasodium 561 Hypophosphite, barium 557 harium dihydrogen 557 Hypophosphoric scid 558 Hypophosphorous acid 555

I

lmide, lithium 464 heptasulfur 411 thionyl 480 Imidophosphate, <u>tetra</u>sodium 589 Imidosulfonate, potassium 506 potassium chloro- 508 229 Indate, ammonium hexafiuoro-Indium 857 electrolytic refining of 858 prerefining of crude 857 antimonide 667 arsenide 867 (i) bromide 862 (ii) bromide 861 (III) bromide 859 (i) chloride 862 (ii) chioride 861 (III) chioride 858 (III) fluoride 228 hydroxide 862 (i) iodide 862 (II) iodide 861 (III) iodide 860 nitride 866 (I) oxide 863 (III) oxide 863 phosphide 867 selenides 365

sulfides 864 tellurides 865 Intermetallic compounds 1771 lodate, lodine (III) 331 fodic acid 316 tetrachioro-299 Iodine 277 recovery from laboratory waste solutions 276 lodine <u>mono</u>bromide 291 monochloride 290 crichtoride 292 pentafluoride 159 beptafluoride 160 (III) iodate 331 (III) ninrate 329 (III) perchlorate 330 (III) sulfate 329 iodine (I) perchlorate, dipyridine- 327 dilodine terroxide 333 pentoxide 307 lodine (III) sulfate, oxo-332 iodofluorophosgene 211 lodohydrargyrate, potassium 3110 lodoplumbite, potassium 754 trilodomercurste (II), potassium 1110 tetralodomercurate (il), copper (i) 1110 silver 1110 tridete (IV), ammonium hamchloro-1594 (III), potassium hexachloro- 1595 (IV), potassium <u>hexa</u>chloro- 1593 iridium, pure 1590 (IV) acid, <u>hexachloro</u>- 1593 (III) chloride 1592 (IV) chloride, ammonium 1594 (III) chloride, potassium 1595 (Vi) fluoride 27 (IV) oxide 1590 270 (III) oxide, hydrated 1592 (IV) oxide, hydrated 1591 iron, metallic 1490 carbonyl 1636 Iron (III) acetate, basic 1508 trilron (lil) hexaacetatodihydroxomono= ? acetate 1508 $\mathcal{M} = g_{1}^{2}$ iron (II) bremide 1493 (III) bromide 1494 - - e - 1 carbide 1503 ्रद्रेः terrecarbonyl 1745 1.12 pentacarbonyl 1743 carbonyi, ethylenediamine 756 tetracarbonyl halldes 1751 ेर्स व dinydride 1752 carbonyl mercury 1755 12.6.7 carbonyl, pyridine 1758 (ii) chioride 1491 (iii) chloride 1492 (III) chloride graphice 644 (11) fluoride 266 40 (III) fluorido 266 750.0 (II) hydroxide 1498

1.1

▶ 1-35\$ Vol. 1: № 1003-1810: Vol. 2 iron (III) hydroxide 1499 (II) tedide 1495 nigrides 1502 ninresyt dicerbonyi 1760 ninresyt halides 1762 **) azida** 1497 (E) ozide, e- 1061 (il. (il) oxide 1499 (iii) exide, "glimmering" hydrated 1654 (UI) azychloride 1501 (III) suitate, basic 1507 (il) sulfide 1502 (EII) sulfide, potassium 1507 (IB) this cyanate, sodium 1511 dires ennescarbonyl 1744 concarboayl 1744 critron dodeca carbonyl 1745 socyanate, silicon 702 Esopoly compounds 1702 arsenates 1709 chromates 1709 molybdates 1710 mobates 1705 sulfates 1714 manulates 1707 tongstates 1712 vanidates 1702

κ

Kernite, synthetic 794 Kurral's sodium polyphosphate 551

L

Lauchanium metal, powder 1141 solid 1144 Landramon <u>tri</u>bromide 1148 crichloride 1146 Cyclopestadienides 1159 fluoride 246 bydrozide 1152 griadides 1149 nitrate 1158 nitride 1157 magelende 1155 relevades 1154 **mif**ate 1156 manufide 1155 **mittide** 1153 magaciloride 1155 Lend 748 rest form 748 See also piembete, plumbous, etc. Lend (W) scetate 767 Stanootate 767 **EAM 1.80**6 artic 762

Lead carbonate 766 Lead chamber crystals 406 Lead (IV) chloride 750 terrechloride 750 terraethyl- 765 (II) fluoride 218 (IV) fluoride 219 tetramethyl- 763 (II, IV) oxide 755 (IV) oxide 757, 1668 dioxide 757 "superoxide" 757 red 755 metasilicate 705 (IV) sulface 761 disulfate 761 sulfide 760 thiocyanate 769 Lepidolite 950 Lindemana glass 796 Lithium 956 aluminum cyanide 833 aluminum hydride 805 aluminum nitride 828 aluminum phosphide 830 amide 463 andmonide 985 arsenide 985 azide 475 beryllium borate 796 bismuthide 985 borohydride 775 carbide 987 carbonate 950, 987 chromate 958 ferrate (III) 1504 fluoride 235 hydride 971 tetrahydrogaliate 842 hydroxide 982 imide 464 nitride 984 oxide 974 peroxide 979 triLithium hexaphenylchromate (III) 1375 Lithium phosphide 985 metasilicate 705 stlicide 991 Lastrous carbon 632 Luteochromic chloride 1351 nitrate 1351 Luteocobalt chloride 1531 Lateophosphomolybdic acid 1732 Luneophosphorungstic acid 1724

м

Madrell's salt, sodium <u>poly</u>phosphate 549 Magnesate, sodium <u>tetra</u>hydroxo- 1683 Magnesium 903

SUBJECT INDEX

pp 1-992: Vol. 1; pp 1003-1810: Vol. 2 Magnesium arsenide 917 azide 917 bromide 909 carbides 920 carbonate 232 chioride 905 fluoride 232 germanide 922 bydride 905 hydroxide 912 iodide 910 -nickel mixed oxalate catalyst 1615 nitride 912 oxide 911, 1663 perchiorate 320 phosphide 917 selenide 915 silicide 921 sulfide 913 telluride 915 Magnus's sait 1577 Malachite 1025 Manganate (VII), barium 1462 (VI), potassium 1461 (IV), potassium hexachloro- 1464 (I), potassium hexacyano- 1472 (II), potassium <u>hexacyano</u> 1473 (III), potassium hexacyano- 1474 (IV), potassium hexafiuoro- 264 potassium nitrosyl cyano- 1767 (III), potassium <u>tri</u>oxalato- 1470 (IV), potassium dioxalatodihydroxy-1471 (Vif), silver 1463 (V), sodium 1460 Manganese 1454 (III) acetate 1469 cesium alum 🛛 1468 (III) chloride, potassium 1464 (II) cyanide 1473 (III) cyanide 1474 (II) fluoride 262 (III) fluoride 263 hexafiuoride 264 (if) hydroxide 1456 nitride 1468 (II) oxide 1455 (ili) oxide 1457 (IV) oxide 1458 (VII) oxide 1459 dioxide 1458 heptoxide 1459 (III) sulfate 1467 (III) sulfate, cesium 1468 (II) sulfide 1465 1110 Mercurate (iI), copper (i) tetraiodo-(ii), potassium terracyano- 1122 (II), potassium trijodo- 1110 (iI), potassium tetrathiocyano- 1124 (II), silver tetrelodo- 1111 Mercuric acetate 1120

۰. Mercuric cyanide 1121 iminobromide 1115 ير د Ý oxychloride 1108 selenide 1113 sulfide, black 1111 sulfocyanate 1123 .1 thiocyanate 1123 thionitrosylate 1118 Mercuric precipitate (infusible), white -1114 (fusible), white 1114 Mercurous acetate 1120 thiocyanate 1122 thionitrosylate 1117 Mercury 27 acetate 1120 (III) acetate 1120 (II) amide chieride 1114 494 (II) bromide 1109 (ii) <u>dichloride, diammine-</u> 1114 cobalt carbonyi 1755 cyanide 1121 <u>di</u>ethyi- 1118 (i) fluoride 243 (il) fluoride 244 (11) Iminobromide 1115 iron carbonyl 1755 (II) oxychloride 1108 potașșium iodide 1110 (l) rhodanide 1122 (ll) selenide 1113 (li) suifide 1111 (1) thiocyanate 1122 (II) thiocyanate 1123 (I) thionitrosylate 1117 (II) thionitrosylate 1118 Methoxide, aluminum 833 boron 797 tetraMethoxysilane 702 triMethylboroxine 800 . : . diMethyldichlorosilane 694 tetraMethyldigallane 840 . s. 19 triMethylgallium 840 Methylgermanium triiodide 722 Millon's base 1116 bromide of 1117 Molybdate (VI), tetreamminezinc tetreper-OX0- 71414 (V), ammonium oxopentachloro- 4#18 ammonium tetrathio- 1416 part (B) (ill), potassium hexachioro- 1408.00+ potessium hydrogen diperoxo monose · ···· (+) be (624) potassium altrosyl cyano- 1766 6 . AG Molybdates, isopoly 1710 ammonium 1711 Sec. 2. 1944 Molybdemum 1401 Molybdemum (0), dibenzane : : : : : : Molybeanum blue 1411

SUBJECT INDEX

htybernam (ER) bromide 1407 conceripyration- 1408 carbonal 1741 Cohlantda 1403 til) chieride 1404 Nichleride 1405 (VI) Eventide 259 hydroxides, lower 1411 T-02100 1410 (VI) exide 1409 (VI) exide 1412 riezide 1412 ¥)swab£adae 1415 dissi20de 1415 Melybdic acid 1412 6-Matybelic acid-2-arsenates 1736 12-Molybdic acid-1-ersenates 1734 18-Molybdic acid-2-arsenates 1734 12-Molybdic acid-2-chromites 1737 5-Molybric acid-1-periodates 1738 12-Molybeic acid-1-phosphates 1730 18-Molybeic acid-2-phosphates 1732 12-Molybdic acid-1-silicates 1729 Malybdic anhydride 1412 Monazire sand, extraction of 1127 Mosaic gold 741

Ν

Neodymium monochalcogenides 1155 compounds from cerium earths 1131 Nichel 1543 (1) amide 1554 (U) bromide 1545 carbide 1556 (II) carbonate 1556 carboxy! 1747 dicarbonyl o-phenanthroline 1750 (II) chloride 1544 (II) chloride, <u>bexammine</u> 1545 (II) cyanide hydrate, potassium 1559 (**II**) **Descride** 269 fermato-paraffin catelyst 1631 (II) hydroxide 1549 (II, III) hydroxide 1551 (CB) hydroxide 1551 B- 1549 7- 1550 (II) iodide 1547 icial statide 1555 ginicride 1555 Michel (H) ender 1548 (II) millide 1551 CV) milline 1554 Read (V), d------benzoate)- 1558 Michel (II) Miecyanate 1558 ichters (I), petroders tetracyano-1559 (W), petaleten bezaltenro. 269

Nickeiste (II), strontium hexahydroxo 1686 Niobates, alkali 1323 (sopoly 1705 Niobate, potassium 1323 (V), potassium heptafiuoro-255 potassium peroxy-1325 sodium 1323 Nieble acid, peroxy- 1324 Nioblum 1292 (III) bromide 1309 (V) bromide 1311 carbides 1331 (II) chloride 1296 (III) chloride 1297 (IV) chloride 1299 (V) chlorides 1302 deuteride 1296 (V) fluoride 254 heptafluoride, potassium 255 hydride 1295 (II) iodide 1314 (III) iodide 1314 (IV) iodide 1314 (V) iodide 1315 nitrides 1328 (II) oxide 1317 (IV) oxide 1318 (V) oxide 1318 oxy<u>tri</u>bromide 1313 oxy<u>pri</u>chloride 1307 phosphides 1330 sulfides 1327 Nitramide 496 Nitrates-see under parent cation Nicrates, hypo-see hyponitrates Nitric acid 491 anhydrous 491 Nitric oxide 485 Nitride tetrahydride, sulfur 411 pentaNitride, triphosphorus 574 diNitride, <u>di</u>sulfur 409 <u>tetr</u>asulfur 408 terraNitride, terrasulfur 406 Nicrides-see parent metal Nitrilosulfonste, potassium 506 Nitrite, bismuth oxide 626 Nitritos, hypo-see Hyponitrites Nitritopentaammine cobalt (III) chloride 1535 -magnetaliana mined oxalate catalyst 1615 hexaNitritocobaltate (ill), sodium 1541 hexaNitritorhodiate (iii), ammonium 1586 Nitropentaamminecobalt (III) chloride 1534 cis-diNitrodiammineplatinum (ii) 1579 Nitrocarbamate, potassium 496 Nitrogen 457 from azides 457 purification of commercial 458 mibromide 480 <u>tri</u>chloride 479

pp 1-992: Vol. 1; pp 1003-1810: Vol. 2 Nicrogen trifluoride 181 triiodide 480 djoxide 468 trioxide 487 pentoxide 489 oxyfluoride 184 diNicrososuifide, potassium 504 Nitrosodisulfonate, potassium 504 Nitrososulfuryl fluoride 186 Nicrosyl compounds 1741 Nitrosyl bromide 513 chloride 511 chloroantimonate (V) 612 diNitrosyl cobalt halides 1761 Nitrosyi cyanoferrate, sodium 1768 cyanomanganate, potassium 1767 cyanomolybdate, potassium 1766 fluoride 184 fluoroborate 224 hydrogen sulfate 406 perchlorate 320 sodium 514 sulfuric acid 406 heptaNicrosyltrithiotetraferrate, ammonium 1764 diNitrosyl thioferrate, ethyl 1765 thioferrate, sodium 1763 thiosulfatocobaltite, potassium 1766 thiosulfatoferrate, potassium 1766 miosulfatonickelate, potessium 1766 Nitrous oxide 484 Nitroxylate, sodium 515 Nimyl chloride 513 fluoride 186 perchlorate 321 Noble gases 82

0

1603 Osmate (IV), ammonium hexachloro-(VI) potassium 1604 (IV), sodium <u>hexachloro-</u> 1602 Orthophosphates, condensed 546 Osmiamate, potassium 1605 Osmium 1601 (IV) chloride 1601 (IV) oxide 1603 (VUI) oxide 1603 1372 triOxalstochromate (iii), potassium -dihydroxymanganate (IV), potassium 1471 1470 -manganate (III), potassium 1450 tetraOxalatouranate (IV), potassium Oxalic acid dinitrite 660 Oxide-sec parent element Oxide chloride, antimony (III) 611 chioride, bismuth 622 Oxides in gases 1669 Oxohydroxostannate (II), barium 1696 Oxygen diffuoride 163

diOxygen difluoride 162 Oxyhydride, silicon 699 Ozone 337

₽

Palladate (II), ammonium tetrachiero-1584 (IV), ammonium hexechloro- 1584 (II), potassium tetrachioro- 1584 (IV), potassium hexechioro- 1564 (11), sodium mtrachloro- 1584 Pailadium, pure 1580 colloidal 1581 black 1581 Pailadium (II) tetraamminotetrahromopalladate (II) 1585 (II) tetrasmminetetrachloropalladate (II) (II) bromide, diammine- 1585 (ii) chioride 1582 chloride for detection of CO 4582 (II) chloride, diammine- 1585 (IV) chloride, ammonium 1384 (IV) chloride, potassium 1584 (II) oxide 1583 Pelladized asbestos 1582 Palladochloride, ammonium 1584 potassium 1584 sodium 1584 Paris green 1027 12153 Perborace, sodium 795 Perchlorate, alkaline earth 320 gallium (lil) 839 - - graphice 643 10.5 todine (III) 330 nicrosyl 320 nitryl 321 dipyridineiodine (1) 327 Perchloric acid 318 Periodate, barium 326 potassium 325 sodium 823 -16 1-Periodates, 6-molybdic acid- 1738;-1-Periodic scid 322 تعاقدون ورا Permanganete, barium 1462 1.14 $a_{ij} \in \mathcal{L}$ silver 1463 Permanganic acid anhydride 1452. 11 Peroxide, barium 936 a Lan M calcium 936 hydrogen 140 lithium 979 sodium 980 1. Star CO. SCHOOL stroatium 936 polysulfur 382 diPeroxorriamminechromium (IV) 1322penta Peroxodichromate, ammonium, 1892 tetra Peroxochromate (V), potessium, 1991

terraPeroxomolybdate (VI), terrarmerineri

4430-1444

4843

1.1.1.1.1.1.1.1

1. 1. 1. 1. 1.

2.144.23

10 1-393: Vol. 1: pp 1003-1810: Vol. 2 alterazione molybero, pomasium hydrogen 1414 Persymiabole, posssium 1325 matchic acid 1324 hosphan, pomssium 562 suttan ammonium 390 Suites, porassium 392 -monosulfuric acid 388 -disultaric acid 389 -manualate, potassium 1325 -pantalic acid 1324 -duanic acid 1219 Perrhosem, ammonium 1484 baritana 1485 asoPerchenate, barium 1487 Parruthenate, potassium 1600 Persetteric acid 389 Persulfate, ammonium 390 potassium 392 Peyrone's chloride 1578 Phenenthroline nickel djcarbonyl 1750 silver (II) persulfate 1050 tetraPhenyibarate, sodium 803 Phosgene 650 orthoPhosphane, aluminum 831 Phosphete, ammonium difluoro-196 ammonium hexafluoro- 195 barium dithio- 571 bismoch (III) 626 boros 796 pomessium 545 Crimeta Phosphate, sodium 552 terremetaPhosphare, sodium 553 triPhosphate, pentasodium 547 teuraPhosphare, bexasodium 548 Passphere, sodium dihydrogen 544 station monothio-569 sectiona distric- 570 sodium crithio- 571 oodium terrathio- 572 putyPhosphates, sodium 549 Greihaun's salt 550 Kurrel's sodiam polyphosphate 55t Madrell's salt 549 1-Phasphates, 12-molybdic acid-1730 2-Phosphate, 18-molybdic acid- 1732 I-Phosphate, 12-tungstic acid- 1720 2-Phosphate, 18-tungstic acid- 1723 22-respect acid-1722 24-wandle seid. 1739 44-vanadic acid-1739 ides-see parent element white \$25 whine 525 ٩.2 nolyblic acid, inteo-1732 mitrilic brouddes 578 tides \$75 14 171 - 14 🚾 529, 531 wic acid 543

diPhosphoric acid 546 orthoPhosphoric scid 543 pyroPhosphoric acid 546 Phosphoric acid, monoamido- 579 <u>di</u>amido 582 diPhosphoric acid tetrachloride 536 Phosphoric acid, deutero-138 orthoPhosphorous scid 544 Phosphorus, black 522 bright red 519, 521 colloidal 524 Hittorf's 520 red 519 white 518 dichloride fluoride 191 dichloride <u>urifi</u>uoride 192 ((II) fluoride 189 (V) fluoride 190 (III) iodide 540 Hodide 539 di Phosphorus terraiodide 539 riPhosphorus pentanicride 574 Phosphorus (V) oxide 541 oxide <u>trifluor</u>ide 193 tetrePhosphorus deceoxide - 541 triselenide 573 Phosphorus trisulfide 563 pentasulfide 565 neptasulfide 566 di Phosphorus pentasulfide 567 Phosphorus sulfochloride 532 Phosphoryl <u>mi</u>amide 584 (V) bromide 534 pyroPhosphoryl tetramide 588 chloride 536 Phosphotungstic acid, luteo- 1724 Pink salt 73) Platinate (IV), ammonium hexachloro-1570 (II), barium <u>terracyano-</u> 1576. (II), potassium tetrachioro-1572 (IV), potassium hexachloro- 1571 (II), potassium terracyano- 1576 (IV), potassium hexabydroxy-1575 (IV), sodium hexachioro- 1571 (IV), sodium hexahydroxy- 1575 Platinic (II) acid, tetrachloro-1570 (IV) acid, <u>hexa</u>chloro- 1569 Platinichioride, ammonium 1570 potassium 1571 sodium 1571 Platinic chloride 1569 salammoniae 1570 Platinized asbestos 1563 Platinocyanide, barlum 1576 potassium 1576 Platinum, pure 1560 reclaimed 1561 Platinum ammines 1577 Magnus's sale 1577 Reiset's first chloride 1577 second chioride 1578

pp 1-992: Vol. 1; pp 1003-1810: Vol. 2 Platinum ammines, Peyrone's chloride 1578 cis-dinitrodiammine platinum (II) 1579 Platinum black 1562 chlorides 1567 (II) chioride, diammine 1578 (II) chloride, <u>tetra</u>ammine- 1577 electroplating 1565 (II), cis-dinkrodiammine- 1579 (II) oxide 1573 (IV) oxiide 1574 sponge 1562 (İİ) sulfide 1575 (IV) suifide 1576 Plumbate, ammonium hexachloro-751 orthoPlumbate, calcium 760 Plumbate, potassium hexachloro-753 metaPlumbate, sodium 758 orthoPlumbate, sodium 759 Plumbate, plumbous 755 (IV), sodium hexshydroxo-1694 Plumbic acetate 767 chloride 750 chloride, ammonium 751 chloride, potassium 753 sulfate 761 Plumbite, potassium iodo-754 Plumbous plumbate 755 Potassium 958 amide 1043 amidosulfinate 507 antimonide 986 arsenide 986 aurate 1061 szide 475 azodisulfonate 510 bismuthate 628 bismuthide 986 dibromolodide 296 cadmium chtoride 1095 cyanide 1106 carbonate 987 chloroimidosulfonate 508 dichloroiodide 295 tetrachloroiodide 298 pentachloromonoaquochromata (III) 1334 pentachioroaquothaliate (III) 874 tetrachioroaurate (III) 1058 chlorochromate 1390 hexachloroiridate (III) 1595 (IV) 1593 hexachtoromanganate (IV) 1464 hexachloromolybdate (UI) 1408 tetrachioropaliadate (II) 1584 hexachioropalladate (IV) 1584 1572 tatrachloroplatinate (II) hexachioroplatinate (IV) - 1571 753 hexachioroplumbate 1558 hexachiororhodate (III) hexachioroselenate 425 hexachiorostannate 731

Potassium hexachlorotellurate 444 bexachiorothaliste (11) 873 enneschiorodinngstate (lil) 1427 nonachlorodiumgatate (Bil) 1427 trichromate 1709 terrachromate 1710 chromium exalate 1372 thioryanate 1374 cobait (III) <u>hexa</u>cyanide 1541 cuprate (III) 1014 dicyanoaurate (I) 1065 tetracyanocadmate 1106 hexacyanochromate (II) 1373 -cobaitate (lii) 1541 -manganate (I) 1472 (11) 1473 (III) 1474 tetracyanomercurate (ii) 1122 octacyanomolybdate (IV) 1416 tetracyanonickelate (II) 1559 -piatinate (II) 1576 octacyanolungstate (IV) 1429 (V) 1429 tetracyanozincate 1088 ferrate (VI) 1504 fluoride 236 bifluoride 237 fluoroborate 222 tetrafluorobromace (III) 237 fluorochromate 1390 hexafluorochromate (IV) 269 -cuprate (ill) 269 -ferrate 269 -germanate 216 -lodate (V) 238 -manganate (IV) 264 -nickelste (IV) 20 heptafluoroniobate (V) 255 269 hexafluorophosphate (V) 196 fluorosulfinate 178 heptafluorozentalate (V) 256 pentafluorothorate 1177 hexafluorotitanate 1163 -yanadate 270 germanide 989 bydrazine<u>di</u>sulfonate 509 hydride 971 dihydrogen arsezide 595 hydrogen fluoride 237 diperoxomonomelybdate 1414 hydroxide 525, 529 hydroxyfluoroborate 223 hydroxylamine disuifonate 503 hexahydroxyplatinate 1575 hypobromite 311 imidesulfenate 506 lodiđe 290 critodide 294 iodohydrargyrate 1110 triiodomercurate (II) 1110 · · . . · Jodoplumbite 754

23.0

pp 1-352: Vol. 1: pp 1003-1810: Vol. 2 Publicsion inidosulfonate 506 initian (UL) chlaride 1595 tron (81) switten 1507 had (IV) chloride 753 (N) toditide 754 unganen (VI) 1461 mangenese (III) chloride 1464 (II) cyanide 1473 (III) cynnide 1474 hexefluoride 264 mercuricyanide 1122 -indide 1110 -thiocyanate 1124 1559 nickel (II) cynnide hydrate sickets: 1323 michium heptafluoride 255 nurilosulfonate 506 aitrocarbamate 496 distrososulfite 504 nitrosodisulfonate 504 sitrosyl tricarbonyl ferrate 1759 cyazomanganate 1767 cyanomolybdate 1766 dinicrosyl thiosulfatocobeltate 1766 thiosulfatoferrate 1766 thiosulfatonickelate 1766 osmate (V?) 1604 osmiamate 1605 triozalatochromate (III) 1372 diozalatudihydroxymanganate (IV) 1471 mioxaletomanganate (Ш) 1470 terraoxalacouramate (IV) 1470 monourchydroxceluminate 1693 ozide 977 dioxide 981 pelladium (IV) chloride 1584 palladochloride 1584 periodate 325 permangenate-barium sulfate solid solution 1463 tetraperoxochromate (V) 1391 permayniobate 1325 -diphosphate 562 -disulfate 392 -tancelete 1325 persochenate 1600 persolfate 392 phosphate 545 phoophide 986 platinichioride 1571 platinocyanide 1576 plumbic chloride 753 plumbous lodice 754 rheatum (IV) chloride 1478 decesse 1600 scientide 421 **Hilds** 999 softwa siloy 1908 Gindian: 264 Cardina 366

diPotessium pentesulfane 367 hexesulfene 368 1714 Potessium trisulfate disulfatovanadate (iii) 1283 sulfide 360 <u>di</u>sulfide 363 urfsulfide 364 tetrasuifide 366 pentasulfide 367 hexesulfide 368 tantalum heptafluoride 256 telluride 441 hexathiocyanatochromate (II) 1374 tetrathiocyanatodipyridinochromate - (III) 1379 hexathiocyanatoyanadate (III) 1291 tetrathiocyanomercurate (II) 1124 trithionate 398 tetrathionate 399 pentathionate 401 hexathionate 403 vanadium (III) ahum 1284 zinc cyanide 1088 Praseodymium compounds from cerium earths 1131 1155 monochalcogenides (IV) exide 1155 Primary zinc oxymethenesulfinate 1076 Prussic acid 658 Purpureochromic chloride 1352 diPyridine chromium tetracarbonyl 1749 triPyridine chromium tricarbonyl 1749 diPyridine iodine (l) perchlorate 327 Pyridine Iron carbonyl 1758 hexaPyridine iron (il) <u>trideca</u>carbonyl <u>tetra</u> ferrate (II) 1758 Tris(2,2'-dipyridyi)chromium (0) 1363 (i) perchlorate 1362 (II) perchlorate 1361 Bis-a,a'-dipyridylsilver nitrate 1051 (ii) persulfate 1051 Tris- a,a'-dipyridylsilver (II) perchiorate 1050 nitrate 1051

Ř

Raney nickel 1625 Rare earths, metallic 1141 Rare earth amalgams 1807 tribromides 1148 monochalcogenides 1155 urichlorides 1146 cyclopentadienides 1159 dinalides 1150 hydroxides 1152 triiodides 1149 nitrates 1158 nitrides 1157 sulfates 1156

op 1-992: Vol. 1; pp 1003-1810: Vol. 2 Reinecke acid 1377 salt 1376 Reiset's first chloride 1577 second chloride 1578 Rhenate (VI), barium 1485 sodium 1483 Rhenite, sodium 1483 Rhenium metal 1476 residues, workup of 1488 Rhenium (III) chloride 1476 (V) chloride 1477 (IV) chioride, potassium 1478 (VI) fluoride 264 (JV) oxide 1480 (VI) oxide 1481 (VII) oxide 1482 (VI) oxychloride 1479 (VII) oxychloride 1480 (IV) sulfide 1486 (VII) suifide 1487 Rhodanilate, ammonium 1378 Rhodanilic acid, ammonium salt of 1378 Rhodate (ill), ammonium hexachioro-1588 (III), ammonium pentachloroaquo-1588 (III), potassium hexachloro- 1588 (III), potassium pentachlorosquo-1588 (III), sodium hexachloro- 1567 Rhodium 1585 (III) chioride 1587 (III) chioride, chioropentaammine- 1985. 1590 hydroxide 1588 (III) hitrate, chloropentaammine- 1586 1590 (III) oxide 1588 sulfate 1589 Rhodochromium chloride 1359 Rinmann's green 1092 Roseccobait oxalate 1533 Roussin's black ammonium salt 1764 red sodium sait 1763 Rubidium 957 azide 475 hexabromothallate (III) 876 carbonate 987 chloride 951, 961 hexachioroselenate 425 hexachlorotellurate 444 chromate 1388 dichromate 1388 germanide 989 graphice 637 hydride 971 hydroxide 983 oxide 977 dioxide 981 silicide 989 vanadium (III) alum 1284 Ruthenate (IV), ammonium hexachioro-1599 potessium 1600

Ruthenium 1595 (lit) chloride 1597 (IV) chloride, ammonium 1599 (IV) hydroxychioride 1597 (IV) oxide 1599 (Vili) oxide 1599

s

Samarium, pure compounds of 1135 purification of 1140 solid metal 1143 dibromide 1150 <u>Pri</u>bromide 1148 dichloride | 150 trichlaride 1146 diiodide 1150 triiodide 1149 Scandium compounds, pure 2125 fluoride 245 Schlippe's sait 619 Schweizer's reagent 1016 Selenate, ammonium hexachloro- 425 cesium hexechloro- 425 potassium <u>bexa</u>chloro- 425 rubidium <u>hexe</u>chloro- 425 sodium 433 thellium hexachloro- 425 Selenic acid 432 Selenide, aluminum 825 barium 939 beryillium 897 calcium 939 diSelenide, carbon 656 Selanide, gallium 854 hydrogen 418 Indium 865 magnesium 915 triSelenide, tetraphosphorus 573 Selenide, potassium 421 aodium 421 sodium hydrogen 419 diSelenide, sodium 421 1 K. M. K. Selenide, strossium 939 1. A. Selenite, sodium 431 Selenium, pure 415 12 emorphous 416 - C.A emorphous vitreous 416 colloidel 417 ಭಾಷ ವಿಶ್ವೇಶ hexagonal 417 小学院開 monoclinic α - and β - 416 5 344 Selenium monobromida 426 1. 1. 1402 diSelenium dibromide 426 1.22.0 Selenium <u>terra</u>bromide 427 monochloride 422 diSelanium dichloride 422 Selenium terrachioride 423 - - (c). terrafluoride 180 bexafluoride 179 1.14854 1 1. Sec. 14. hexafluoride nitride 435 11. **11. 1**44

143

1

1848

an 1-394: Vol. 1: pp 1003-1810: Vol. 2 Salanjum diaxida - 478 exychitoritie 429 puiller grioxide 455 mionere, sodium 434 denous acid (anhydrous) 430 bromide 436 chètotide 422 Saleegii chloride 429 Silano, tribromo- 692 merechoxy- 702 numericany- 702 dimethyldichtoro- 694 Silenes 679 chioro- 691 <u>poty</u>- 681 Splica gel 698, 1648 metaSilicate, harium 706 diSilicate, barium 706 metaSilicate, lead 705 lichium 705 silver 705 sodium 704 diSilicate, sodium 704 1-Silicanes, 12-molybdic acid- 1729 10-tengstic acid- 1719 12-tengstic acid- 1717 Silicic acids 697 aqueous malecular dispersions of 698 colloidet 698 rystalline disilicie acid 699 Silicides of alkali metals 989 Silicide, calcium 946 cestum 989 lithium 991 magnesium 921 potassium 989 rubidium 969 sodium 989 Silicides 1795 Silicochiaroform 691 SliceIuoric acid 214 Silicafluoroform 214 Silicou 676 tetrascetate 701 azide 476 (II) brumide 687 etrabromide 686 segrechioride 682 chierides, higher 684 cyanate 702 intraffmoride 212 etaziodkie 689 HCYMME 702 stematide 6% **Miride** 699 ide 700 **w, chiero**... 695 W. Wary pure 1028 active agent for reductors 1641 1014 na 102a

Silver, "molecular" 1623 from photographic solutions 1030 powder 1029 from residues 1029 (Berthollet's) fulminating or detonating 1046 acetylide 1047 amide 1043 orthoargentite 1039 azide 1045 carbonate 1048 chiorate 1037 cyanamide 1047 fluoride 240 (II) fluoride 241 subfluoride 239 hyponitrite 493 iodide 1035 manganate (VII) 1463 nitrate, bls- α,α'-dipyridyi-1051 (II) nitrate, tris- $\alpha_i \alpha'$ -dipyridyl 1051 nitride 1046 nitrite 1048 oxide 1037 (II) perchlorate, tris-αα'-dipyridy!-1050 permanganate 1463 peroxide 1038 (II) persulfate, bis-α,α'-dipyridyi-1051 (II) persulfate, o-phonanthroline-1050 (I) selenide 1041 metasilicate 705 sulfate 1042 sulfide 1039 trisulfimide 483 sulfite 1043 tartrate 1049 (l) telluride 1042 Sodium 957 dispersions of, in inert liquids 967 finely subdivided, on inert solids 969 Sodium amalgam 1802 amide 465 diSodium monoamidophosphate 581 Sodium entimonide 986 orthoargentite 1039 arsenide 986 azide 474 baryllates 895 bismuthate 627 bismuthide 986 metaborate 791 orthoborate 790 tetraborate 793 pentaborate 795 berofluoride 222 borobydride 776 carbide 987 carbonate 987 carbonyl cyanoferrate 1769 chlorite 312

pp 1-992: Vol. 1; pp 1003-1810; Vol. 2 Sodium tetrachloroaluminate 816 hexachloroosmate (IV) 1602 tetrachioropalladate (il) 1584 hexachioroplatinate (IV) 1571 -rhodate (III) 1587 cobaltinitrite 1541 pentacyanoamminoferrate (II) 1511 (((()))) 1512 fluoborate 222 fluoride 235 fluoroborate 222 hexaficorotitanate 1163 germanide 989 bydride 971 hydrogen triarsenate 1709 dihydrogen orthoarsenate 602 arsenide 595 phosphate 544 phosphide 530 hydrogen selenide 419 diSodium dihydrogen hypophosphate 560 Sodium hydrogen sulfide 357 tetrabydrogen tellurate (VI) 453 hydrosulfide 393 tetraSodium heptahydroxoaluminate 1692 Sodium <u>hexa</u>hydroxochromate (III) 1688 tetrahydroxocuprate (ii) 1684 -ferrate (11) 1686 heptahydroxoferrate (III) 1689 octahydroxoferrate (ill) 1690 <u>tetra</u>hydroxomagnesate 1683 hexahydroxoplumbate (IV) 1694 Tibydroxostannate (II) 1687 hexahydroxostannate (IV) 1694 trihydroxozincate 1681 <u>tetra</u>hydroxozincate 1682 hypobromite 310 hypochlorite 309 hyponitrate 517 hyponitrite 495 terraSodium hypophosphate 561 Sodium hyposulfite 393 tetraSodium imidodiphosphate 589 Sodium iron (III) thiocyanate 1511 manganace (V) 1460 <u>uri</u>methoxyborohydride 777 meremolybdate 1712 paramolybdate 1710 niobate 1323 hexanitritocobaltate (lil) 1541 nteroprusside 1768 nitrosyl 514 cyanoferrate 1768 dinitrosyl thioferrate 1763 thiosulfatoferrate 1766 nitroxylate 515 monoSodium oxohydroxosluminate (1) 1693 (11) 1693 Sodium oxide 975 <u>di</u>oxide 980 palladochioride 1584

Sodium perborate 795 periodates 323 peroxide 980 tetraphenylborate 803 trimetaphosphate 547 tetrametaphosphate 548 pentaSodium triphosphate 547 hexaSodium <u>setraphosphate</u> 548 Sodium tripolyphosphate 547 polyphosphates 549 phosphide 986 platinichloride 1571 metaplumbate 758 orthoplumbate 759 rhenate (IV) 1483 rhenite 1483 selenate 433 selenide 421 diselenide 421 selenite 431 setenopentsthionate 434 metasilicate 704 disilicate 704 silicide 989 orthostamate 739 diSodium <u>disujfane</u> 361 tetrasulfane 365 pentasulfane 367 Sodium sulfide 358 disulfide 361 tetrasulfide 365 pentasulfide 367 orthotellurate 453 telluride 441 ditelluride 442 tellurite 449 telluropentethionate 454 thicantimonate (V) 619 thioersenate 604 monothioorthearsenate 605 dithicorthoarsenate 605 ¢. thiochromite 1394 hexachiocyanoferrate (III) 1511 - $^{\circ}$ of dithionate 395 dithionite 393 1.04 monothiophosphate 569 w 1.00 dithiophosphate 570 والمربوب وا trithiophosphate 571 tetrathiophosphate 572 metathiostannate 742 · · · • • . *217* Z terrathiostennate 743 bit dinhiosulfatoaurate 1063 1.5 motatungstate 1727 1.5.500 **#**2 paratungstate 1712 metavanadate 1703 pyrovanadate 1702 Stannate, ammonium hexachloro- 731 (II) barium oxohydroxo- 1695 pomosium bezachlaro- 731 orthoStennate, sodium 739 Stannate (II), sodium trihydroxes 1687) r 1859

• 1-892: Wel. 1: pp 1003-1810: Vol. 2 Steambre (IV), sodium beaubydroxo Steambre acide, a- and 8- 737, 758 1694 Smanic acid, hexechloro- 730 amous axide 736 Subboo to05 Streament 926 Amalgam 1805 amido 941 Enoride 334 heitides 930 landerides 929 hydroxide 935 hembydrozonickelate (11) 1686 uturide 940 audde 932 perchlorate 320 peroxide 936 persuide octahydrate 937 selenide 939 stlicide 947 sattide 938 eellaride 940 Sulfamide 482 Salfane, crude – 346 Suttenes, pure 349 diSelfane 350 criSulface 350 tetraSulfane 353 pentaSolfane 353 bexaSulfane 353 heptaSulfane 353 octaSulfane 353 diSolface, dibromo- 377 triSulfane, dibromo- 379 cereSulfane, dibromo- 379 presaSulfane, dibromo- 379 heraSulfane, dibromo- 379 heptaSulface, dibromo-379 ocmSulfane, dibromo- 379 mounSulface, dichloro- 370 dSalfane, dichloro- 371 triSulfane, dichloro- 372 estraSulfane, dichloro- 372 pennaSulfane, dichloro- 372 hearSulface, dichloro- 372 heptaSuifane, dichloro- 372 actaSulfane, dichloro- 372 a Suffameric chloride 412 Sellare, ammonium gallium (iil) 854 2 (UI) 618 tent (IV) 761 619 streeyi byirogaa 406 de (IV) 744 Mates, tempity- 1714 Fullecomatic (III) acid 882 -wandle (E) acid 1282 inder-see parent element nickel (IV) 1558 all shadow

miSulfimide, sliver 483 Sulfite, aluminum 824 Suifocyanic acid 669 Sulfonate, potassium amido- 507 diSulfonate, potassium azo- 510 508 Sulfonate, potassium chloroimidodiSulfonate, potassium hydrazine-509 Sulfonate, potassium imido- 506 potassium nitrilo- 506 diSulfonate, potassium nitroso- 504 Sulfoxylate, cobalt 393 Sulfur, pure 341 colloidal solution 343 plastic 342 Sulfur monobromide 377 diSulfur dibromide 377 Sulfur monochioride 371 dichloride 370 diSulfur dichloride 371 Sulfur tetrachloride 376 <u>tetra</u>fluoride 168 bexafluoride 169 heptaSulfur imide 411 Sulfur nitrido tetrahydride 411 diSulfur dinteride 409 tetreSulfur dinitride 408 tetranitride 406 triSulfur dinitrogen dloxide 413 dinitrogen pentoxide 414 Lower sulfur oxides 379 diSulfur <u>tri</u>oxide 380 Sulfur <u>tri</u>oxide, selenium 435 tellurium 455 Sulfur peroxide, poly- 382 Sulfuric acid, deutero- 135 monoSulfuric acid, peroxy-388 Sulfurous bromide 377 chloride 371 Sulfuryl bromide fluoride 176 chloride 383 chloride fluoride 175 pyroSulfuryl chloride 386 Sulfuryl fluoride 173 triSulfuryl fluoride 174

T

Tantalates, alkali 1323 <u>isopoly</u>- 1707 Tantalate (V), potassium <u>heptafluoro</u>- 256 potassium peroxy- 1325 Peroxytantalic acid 1324 Tantalum metal 1292 (IV) bromide 1310 (V) bromide 1311 carbide 1331 (IV) chloride 1301 (II) chloride 1302 deuteride 1296 (V) fluoride 255

pp 1-992: Vol. 1; pp 1003-1810: Vol. 2 Tantalum heptafluoride, potassium 256 hydride 1295 (V) iodide 1316 nitride 1328 (V) oxide 1318 oxy<u>tri</u>bromide 1314 phosphide 1330 sulfides 1327 Tellurate, ammonium hexachioro- 444 cesium hexachloro- 444 potassium hexachioro- 444 rubidium hexachloro- 444 sodium tetrahydrogen 453 orthoTellurate, sodium 453 Tellurate, thallium hexachioro- 444 1-Tellurates, 6-tungstic acid- 1726 Telluric scid 451 Telluride, aluminum 826 beryllium 897 galijum 855 hydrogen 438 indium 865 magnesium 915 potassium 441 sodium 441 diTelluride, sodium 442 Tellurite, sodium 449 Tellurium 437 solution, colloidal 438 Tellurium tetrabromide 445 tetrachloride 442 hexafluoride 180 tetraiodide 447 dioxide 447 trioxide 450 sulfur trioxide 455 Telluropentathionate, sodium 454 Tellurous acid 449 874 diThaliate (III), cesium nonachloro-Thallate, potassium hexachioro- 873 potassium pentechiorosquo- 874 (III), rubidium hexabromo- 876 (III), thailium (I) tetrabromo- 875 hexabromo- 875 tetrschloro- 873 hexachloro- 872 Thaille (III) acid, disulfato- 882 Thailium 867 (III) acid, tetrachloro- 872 bromide 869 (ill) bromide 874 (I) tetrabromothallate (III) 875 (1) hexebromothaliste (III) 875 (I) carbonate 884 (i) chloride 869 (lli) chieride 870 hexachlorotellurate 444 (I) tetrachlorothallate (III) 872 (I) hexachlorothallate (III) 873 (I) fluoride 230

Thallium (III) fluoride 230 (I) formate 864 (l) hydroxide 887 (III) hydroxide sulfete 682 (I) locide 869 criticalide 876 () malonate 884 nitrate 883 (i) nioride 663 oxide 687 (13) oxide 879 (l, lll) selenide (l) sulfate 861 881 (III) Sulfate 681 (i) sulfide 860 (I, UI) suifide 860 Thenard's blue 1525 Thioantimonate, sodium 619 zinc 1083 Thioarsenate, ammonium 604 sodium 604 triThiocarbonate, ammonium 674 barium 674 diThiocarbonic anhydride 652 Thiochromite, sodium 1394 Thiocyanate, hydrogen 669 lead 769 tetraThiocyanatodiamminechromate (III), ammonium 1376 -diamminechromic (III) 1377 scid -dianilinochromate (IR), ammonium -1378 hexaThiocyanatochromets (II), potessium 1374 trans-di Thiocyanatodi (ethy) enediamine) 1957 chromium (III) thiocyanate tetra Thiocyanatodipyridinochromate (III), potessium 1379 hexaThiocyanatovanadate (III), potassium 1291 Thiocyanic acid 669 hexaThjocyanoferrate (III), sodium 1511 Thiocyenogen 671 terraThiocyanomercurate (il), potassium 4124 triThioferrate, ammonium heptanitrosyl 1764 1765 Thioferrate, ethyl dinitrosyl See. 6. 9 sodium dinitrosyi 1005 teura Thiomolybate, ammoasum 1446. di Thionate, barium 397 sodium dialtrosyi 1763 tri Thionate, potassium 398 1.00 tetra Thionate, potassium 399 penta Thionate, potassium 401 4. bexaThionate, potassium 403 11. 15.00 di Thionate, sodium 895 Thionic soids, poly- 405 diThionite, sodium 393 zinc 394 1. an 1. an 1. an 1. an 1. an 1. an 1. an 1. an 1. an 1. an 1. an 1. an 1. an 1. an 1. an 1. an 1. an 1. an 1.

1852

no 3-354: Vol. 1: no 1003-1810: Vol. 2 Theory broadle 387 chilorithe 352 chierède Electide 174 Eventes 170 merefueride 171 **inide** 480 teno Thioorthoarsenate, sodium 605 di Thioprosphare, sodium 605 di Thiophosphare, barium 571 menoThiophosphate, sodium 569 di Thiophosphere, sodium 570 tri Thiophosphate, sodium 571 tetra Thiphosphete, sodium 572 mono Thiophosphoric acid 568 Thiophosphory: <u>rri</u>amide 587 (V) bromide 535 chioride 532 meta Thiostangate, sodium 742 tetra Thiostannate, sodium 743 Thiosulfatoferrate, potassium dinitrosyl 1766 Thorium 1174 (IV) bromide 1203 carbides 1248 chloride 1204 (IV) chloride 1203 hydride 1184 (IV) iodide 1205 nitrate 1238 uttride 1236 (IV) oxide 1221 phosphide 1241, 1243 silicide 1249 sulfide 1222, 1226 Tia 727 gray, a . 727 powder 727 see also stannate, stannous, etc. Tin (IV) accessie 747 amaigam 1606 (II) brosnide 732 (IV) bromide 733 bronze 741 (II) chloride 728 (IV) chloride 729 erraethyl- 746 (H) Buoride 217 (IV) fimoride 217 (II) iodide 234 (TV) Lodide 735 tetralodide 735 tetranetivi-744 (B) ende 736 (IV) miliate 744 (III) militide 739 **(V) =484e** 741 Tagane (III), herechlorotripyridinedi-1429 the first gate chior odi- 1427 V), petnestam ognacysno- 1429 (V), petassium octacyano- 1430

Tungstates, isopoly- 1712 Tungsten 1417, 1622 blue 1423 carbonyl 1741 (V) chloride 1419 (VI) chloride 1420 (VI) fluoride 260 (IV) oxide 1421 (VI) oxide 1423 y-Tungsten oxide 1422 Tungsten oxytetrachloride 1425 hexaphenolate 1426 hexaphenoxide 1426 (IV) sulfide 1425 Titanate, ammonium hexachloro-1199 potassium hexafluoro- 1163 sodium hexafluoro- 1163 Titanic scid, peroxy- 1219 Titanium 1161 (II) bromide 1185 (III) bromide 1187 (IV) bromide 1201 carbide 1245 (II) chloride 1185 (III) chioride 1187 (IV) chioride 1195 (III) fluoride 248 (IV) fluoride 250 hydride 1184 (II) iodide 1185 (III) iodide 1187 (IV) iodide 1205 tetranitrate 1237 nitride 1233 (IV) oxide 1216 (IV) oxide hydrate 1218 oxides, lower 1214 <u>di</u>oxide 1216 (III) oxychloride 1209 (IV) oxychloride 1209 oxynitrate 1241 phosphide 1241 silicide 1249 (III) sulface 1226 sulfide 1222 Titenoxy sulfate 1228 Titanyl sulfate 1228 metaTungstates 1727 dodecaTungstates 1727 12-Tungstic acid-1-arsenates 1724 18-Tungstic acid-2-arsenates 1725 12-Tungstic acid-1-borates 1716 1-phosphates 1720 18-Tungstic acid-2-phosphates 1723 21-Tungstic acid-2-phosphares 1722 22-Tungstic acid-2-phosphates 1722 10-Tungstic acid-1-silicates 1719 12-Tungstic acid-1-silicates 1717 6-Tungstic acid-1-tellurates 1726 guanidinium salt 1726 Tungstic acid, yellow 1424 Turquoise green 1092

pp 1-992: Vol. 1; pp 1003-1810: Vol. 2

tı

Uranates (V), alkaii 1445 (VI), alkali 1445 (IV), potassium tetraoxalato- 1450 Uranium 1431 (IV) bromide 1440 (III) chioride 1435 (IV) chloride 1436 (V) chloride 1438 (V) echoxide 1451 (VI) ethoxide 1452 (V) ethylate 1451 (VI) ethylate 1452 (IV) fluoride 261 (VI) fluoride 262 hvåride 1434 (IV) oxalate 1449 (IV) oxide 1442 (VI) oxide 1442 peroxide 1446 (IV) sulfate 1447 (IV) sulfide 1446 Uranyldibenzoylmethane 1453 Uranyl carbonate, ammonium 1449 Uranyl chloride 1439 bexaUreachromium (III) chloride 1359

Vanadates, alkali 1273 metaVanadate, ammonium 1272 Vanadate, ammonium disulfeto- 1283 hydrogen disulfato- 1282 potassium <u>hexa</u>fluoro- 270 potassium disulfato- 1283 potassium hexathiocyanato- 1291 Vanadates, isopoly- 1702 24-Vanadic acid-2-phosphates 1739 48-Vanadic acid-2-phosphates 1739 Vanadic (III) acid, disulfato- 1282 Venedium 1252 acetate 1283 (lli) shum, ammonium 1284 (III) alum, cesium 1284 (III) alum, potassium 1284 (Ili) alum, rubidium 1284 (0), dibenzene - 1289 (II) bromide 1260 (III) bromide 1260 carbides 1288 (11) chloride 1255 (III) chloride 1256 (IV) chioride 1259 (111) fivoride 252 (IV) fluoride 252 (V) fluoride 253 bydride 1295 (III) hydroxide 1268 (II) iodide 1261

Vanadium (III) iedide 1262 muridea 1286 (V) oxide 1270 oxides, lower 1266 oxychloride 1262 oxydiichioride 1263 oxytrichloride 1264 dioxychloride 1265 (TV) corysulface 1285 phosphides 1287 selenidos 1276 (11) Sulfate 1277 sublides 1274 Vanadyl dichloride 1263 grichloride 1264 sulface 1285 Vermilion 1112

- - - **- -**

A. 8 - 3 - 24

ъ i

 $S_{1,0}$

. . 1

÷

1.1.4

Wackenroder liquid 405 Water, pure 117 "conductivity" 118 heavy 119 pH-pure 119 Wolfram--- 396 Tungsten

X

Xanthocobalt chlorida 1534

Υ

Ynerbium, pure compounds 1138 solid metal 1142 dibromide 1150 dichleride 1150 dilodide 1150 sulfate 1138 Yttrium fluoride 246

z

Zinc 1067 very pure 1067 Zinc acetate 1087 amalgam 1806 amide 1079 arsenides 1083 hromide 1072 carbonate 1086 chloride 1070 chloride bydroxide 1971 cyanide 1687 diethyl-1084 ferrate (III) 1090 fluoride 242

SUBJECT INDEX

- 1-510: Vol. 1; pp 1003-1810: Vol. 2. C Statesticate 1090 Recalificate 1090 makinayin sufferyiate 1076 Elin: formaldabyde sulfaxylate 1076 Aptrepairte 1069 kydraside 2074 Tesychiettes 1071 drugghoghan 1082 prodition 394 tedido 1073 mitzide 1080 emiño 1664 orgenerations of finate, primary 1076 photohoto 1081 (801 enadosphane 108) explaides 1080 penassium cyanide 1088 solonide 1078 silicate 1089 granulticate 1089 settine, arazonium 1077 subfide 1075 thiesatimonate 1083 dititionite 394

Zinc paratungstate [713] Zincate, ammonium terrschioro- 1070 potassium tetracyano- 1088 sodium trihydroxo- 1681 sodium tetrahydroxo- 1682 Zirconlum 957, 1172 salts, purification of 1232 separation of hafnium and 1179 Zirconium (IV) bromide 1203 carbide 1245 (IV) chloride 1203 (IV) fluoride 251 hydride 1184 (IV) iodide 1205 nitride 1233, 1236 (IV) oxide 1220 oxychioride 1210 oxynitrate 1241 phosphate 1244 phosphides 1241, 1243 silicide 1249 sulfate 1231 sulfide 1222, 1226 Zirconyl chloride 1210

1034

Index of Procedures, Materials and Devices

pp 1-992: Vol. 1; pp 1003-1810: Vol. 2

A

Active copper 458, 1633 metals 613 Agitation in the absence of air 1748 Air-sensitive substances, storage of 75 Alcohol, dehydration of 26 Alkali hydroxides, handling of concentrated 1679 A)loys 1771 Amaigams 1801 Ammonia, extraction with liquid 86, 1100, 1526, 1792 Ampoules, removal of contents of 119 for alloys 1782 breaking of, in the absence of air 120, 135 Anshütz flask 1271 Apiezon grease 29 Apparatus, assembly of 4 Arc furnace 42

B

Ball mill 1127, 1129, 1167, 1195 vacuum-type 76 Bodenstein valve 62, 481 Bomb mbe 1303, 1304, 1306 Break-seal valves 63, 133, 136, 137, 1168, 1197, 1206

С

Calcium fluoride lining 152 Carbon 13, 20 electrodes 181 tube furnaces 39 vessels made of 15 Catalyst carriers (supports) 1270, 1611 Catalysts 1270, 1563, 1574, 1580, 1583, 1609 Cathode, commercial, for electrolytic reduction 1277, 1366, 1427 Cements for glass tubes 10 glycerol-ittharge 31 phanol-formaidehyde 32 silver chieride 31 فيحتنى waterglass 31 zioc oxide 31 the second second second Ceramics 12, 1779

Cleaning of glassware 7, 9 1.14 Costing with silver 1031 28.7 Cold baths 45 Commercial electrodes 1277, 1366, 1427 Commercial gases, purification of 78, 111, 272, 334, 458, 460, 646, 647 Commination in the absence of air 74? 1786 Condensation traps 66 "Containerless" fusion 1786 Controller for power supply 47 Cooling 42 Copper cylinder, revolving 244 tower 459 Cristobalite 8 Crucible for westing of alloys 1774 Tammann 1214 Cryostats 42, 46 Crystal-growing processes 94, 1294 D a. 2617

5 - 2 **- 1** - 1 - 1

1.352

Dehydration of organic liquids Devirtification 8 Diaphragm valve 65 Differential manometers 65 Distillation, general discussion of In the absence of air 65, 1198 of metals 887, 903, 923, 960, 1 1455, 1789 10.000 of very pure water 117 vacuana 92, 1198 Dropping funnels for corresive f 131 - 10 X 🕮 🏙 Dry bag 70 box 70 ∿. X**⊛`i** 1000 [ce 43 7.000 Drying agents : The T pistol 1291 1.00 Electrical comminution (size I 524 Electrical discharge in gases 20. 265, 337 sputtering 524 Biectrode carboo, 19 sputtering Electrolysis cells 1269, 1557 and an of fused salts 143, 169, 1857 1143, 1170, 1177, 1250, 1498,

ap 2-392: Wel. 1: pp 1009-1810: Vol. 2 Eleczelysis gan evolution in 116, 123, 274, 394, 439, 607 and deposition (separation) from 837, 858, 867, 956, 1028, 1068, 1092, 1149, 1169, 1177, 1335, 1433, 1454, 1490, 1638, 1805 aration of substances by means of \$30, 1503, 1791 of very small quantities of liquids 224 Electrolytic exidation 390, 392, 562, 751, 761, 1556, 1694 reduction 239, 439, 498, 607, 1138, 1193, 1268, 1277, 1291, 1366, 1413, 1427, 1447 Boory resins 32 Eaher, dehydration of 27 Evaporation in vacuum 543, 559 Entraction with liquid ammonia 66, 1100, 1526, 1792 Faraday system (apparatus) 76, 1241, 1287, 1330 Fertneniation cap 1199 Filling (of vessels) in the absence of air 70, 74, 918, 960, 963, 966, 1280, 1304, 1343, 1786 Filtering in the absonce of air 72, 598, 1276, 1456, 1551, 1756 Pire cley 13, 18 Float valves 61 Fluidized bed 1616 Fluorine compounds, general 150 Fluorine-resistent vessels 143, 149 Pluorsper apparatus 152 Fractionation at low temperatures 66 Preczing baths 42 minures 42 Prit valves 61 Furnaces 32, 1764 arc and electronic radiation 42 Globar 38 induction 44 with internal heating colls 36 Nernst 39 aniybdemzn wire 37 **201.57** 42 Tamman 39, 1215 tebular pression 40 wire-wound 34 Foring glass to ceramics 10 gines to metals 11, 25 Protes in the absence of air 984, 1483, 1774 neiting) of alloys 1772, 1782, 1784, 1786 G Cas discharge, clacarical 90, 162, 265, 207 Hays 66

Gases, collector for 69 drying of 80 general discussion of 77 generators for 77 liquefaction of 86 liquid, as reaction media - 66 measuring the pressure of 55 purification of commercial 78, 111, 272, 334, 458, 460, 646, 647 rate of flow of (control and measuremeat) 84, 853 receivers for 69, 84 Gasometer 84 Gless 5 chemical 5 common types of 6 joints to ceramics 10 joints to metal 11, 25 Ругех б Vycor 6 Gold shield, movable 1483 Graded seals - 9 Graphite 13, 17, 22 clay-bonded 13 electrodes 181 retort 13 Gravity separation 97 Greases 28 Grignard reaction 744,763,1084,1103. 1118, 1398

H

Heat-induced synthesis of alloys 1772 Heating, combustion 32 electrical 32 High-surface materials 1609 High vacuum 53, 66 Hostafion 1265

1

Igniting cherry 1334, 1402 Induction furnaces 41 Ion exchangers 555, 1179, 1701 Ion-exchange resins 55, 1179, 1701 Isoteniscope 101

J

Joints, glass 9 glass to ceramics 10 glass to metal 11, 25 standard taper 9

κ

K-Mass 18 Kel-F 25 Kipp generator 77 рр 1—992: Vol. 1; pp 1003—1810: Vol. 2 L

Lead cathods for electrolytic reduction 1277, 1366, 1427 Leaks, testing for 69 Liquefied gases 65, 86 Liquid air, headiling of 44 Liquid ammonia as a reaction medium 66, 358, 360, 463, 585, 593, 1043, 1100, 1526, 1794 Liquid-filled thermometers 50 Low-melting alloys 1808 Lubricants 28

м

Manometers 55, 84 McLeod 39, 57, 1158 mercury 55 Moser 58 Null 56 with quartz spiral 56 Marquardt mass 18 McLeod gauge 39, 57, 1158 Melting point, determination of 69, 100 Melts, electrolysis of 143, 181, 956, 1144, 1170, 1177, 1250, 1433 Mercury, purification of 27 Metals, as materials for vessels 17, 1776 fusion to glass 11, 25 Microelectrolysis 124 Mirrors 1031, 1644 Movable gold shield 1483 Mullite 13

N

Nernst furnace 39 Null manometer 56

o

Observation port 75 Ovens 32, 1784 Ozonizer 337

P

Picein 30 Platinized asbestos 1565 Platinum coating, electrolytic 1565 by thermal means 1565 Platinum electrodes 1566 Platinum equipment, handling of 1564 Platinum, reclamation of 1564 Plexiglas 25 Pneumacolytic-hydrothermal synthesis 1089 Podbelniak distillation column 93 .-Polyethylene 25, 31 Polytrifluorochloroethylene 25 Polytetrafluoroethylene 25 Polyvinyl acetates 30 Polyvinyi chloride 25 Porcelain 12, 18 Ports, flat and parallel 73 Powder reactions 103 Precipitation in the absence of air 72, 1276, 1456, 1551, 1747, 1756 Pressure gauges 55, 84 measurement 55, 101 synthesis 76, 989, 1151, 1223, 1242; 1274, 1287, 1330, 1443, 1527, 1741, 2784. 1804 Protective melts for alloys 1774 Pyrex glass 5 Purification of substances 91 Purity, analysis of 100 Pyrometer, radiation 53 Pyrophoric tendency 1614 Pythegores mass 10, 1780

Q

Quartz, fused (glass) 5, 8, 18

R

Radiation pyrometer 53 Raschig rings 92 Resctions in arc furnaces 653, 1248, 1669 Reaction lamp 1332 Recrystallization 71, 94 Refining processes 1168, 1173, 1178, 1332 Residue methods for alloys 1791 Resistance thermometer 50 Rose's metal 31 Rometers 34, 853

S.

Schleak tube 75 Seals, graded 9 Sealing materials 28 wax 30 Shatter valves 63, 133, 136, 137, 116 1197, 1206 Silica gel 1648 Silicon carbide 22 gresse 30 Sillimenite 13, 18 Siffimantium 13, 18 Silver mirrors, deposition of 1031 Single crystals, growth of 94 Sintered alumina 13, 20 oxides 13, 18 Sintering 103, 1234, 1245, 1795, 1792

1492

an 1-303: Vol. 1: op 1003-1810: Vol. 2 Sinches 1009 Seiders for metals 24 Solvenis, organic 26 pure 25 Solash shield 1483 (electrical atomization) Southering 1035 Scandard reper and ball joints, glass Steel cylinders for gas storage 77 Stock's apparents for work in vacuum 66 Stock's mercury valve 61, 69 Stopcocks (see also valves) 59 for corrosive media 131 Sublimation (see also distillation) 92, 249, 903, 923, 1302 Synthesis under pressure 76, 989, 1151, 1223, 1242, 1274, 1287, 1330, 1443, 1527, 1741, 1784, 1804 Synthetic resins-Plastics 25

Т

Tablets 103, 1795, 1799 Tammann crucible 1214 Tammann furnace 39, 1215 Teflon 25, 149, 1266 Temperature, constant 45 gradient 76 high 32 low 42 measurement of 49 Thermocouples 51 Thermometers 49 Thermoplastic materials 25 Thermostats 46 Teepler pump 66 Tombac tube valve 65 Tungsten furnace, tubular 40 Two-arm nihe 1044

V

Universal reaction system 66

٧

Vecuum apparatus 65 ball mill 76 distillation 92, 1198 gauge 39, 57 systems, special 66 Vakuscope 58 Valves 61 Bodenstein 62, 481 diaphragm 65 float 61 frit 61 needle 64 shatter 63, 133, 136-7, 1168, 1197, 1206 Stock (mercury-filled) 61, 69 Vapor-deposition processes 1234. 1245, 1254, 1289, 1294, 1328, 1332, 1645, 1798, 1799 Vaporization of metals 18, 1643 Vapor pressure measurements 55, 101 eudlometer 102, 1100, 1115 thermometer 49, 67 Vessels resistant to fluorine 143, 149 Vitreasil 18 Vycor glass 5 rubes 1068, 1083, 1096, 1191, 1255, 1294, 1297, 1315, 1420 w Wash bottles, fritted-disk 79 Washing in the absence of air 1626 Wax 30

Welding of metals 24 Wordle matel 31 52 1900

Wacd's metal 31, 52, 1809 Work in the absence of air 53, 66, 119, 598, 916, 961, 1198, 1278, 1303, 1456, 1483, 1551, 1626, 1747, 1756, 1774, 1779, 1786

Z

Zone-melting process 97 Zinc reductor 1368 Zündgemisch 1334, 1402 Zündkirsche 1334, 1402

| Page | Line | Should read |
|------|---------------|---|
| 218 | 3 from bottom | b.p. 1293°C; d 8.24 |
| 505 | 1 | a drop of KI-starch solution, i.e., whether the desired large excess of nitrite is present. If this is not the case, one must either wait a while or add some more nitrite. Then 25 ml. of 10N |