Notes

The reliability of our method was controlled by a series of measurements on the solubility of nitrogen in ammonia. A very good agreement with the results obtained by WIEBE and TREMEARNE⁽¹⁾ has been found.

The ratio of the solubilities of argon and nitrogen in ammonia as calculated from our laboratory results agreed rather well with the statistical average obtained from measurements carried out previously in the working synthesis unit.⁽³⁾

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A new metal chloride synthesis

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WE wish to report that iron(III) chloride, niobium(V) chloride, and molybdenum(IV) chloride can be prepared in quantitative yields by refluxing excess hexachlorobutadiene saturated with chlorine over the appropriate metal oxide.

The quantities used by us are 2.0 g of metal oxide in 30 cc of hexachlorobutadiene-1,3, but we see no impediment to larger scale preparations. The amount of hexachlorobutadiene-1,3 is such that there is enough for refluxing, for reacting with the metal oxide, and for dissolving the metal chloride product. The apparatus consists of a 50 ml round-bottom flask fitted with a 300 mm water cooled condenser by means of a T 24/40 ground glass joint. A length of 2 mm capillary tubing enters the flask through a side tube and almost touches the bottom of the flask. A tube containing "Drierite" is fitted to the upper end of the condenser. The flask is heated by means of a Glas-col heating mantle.

The metal oxide is placed in the flask and the apparatus is purged with nitrogen at room temperature. Hexachlorobutadiene-1,3 is added, and chlorine is bubbled through the solution at such a rate that the liquid in the flask does not back up in the capillary tubing between bubbles by more than 3 mm. Refluxing is started and is continued until all of the metal oxide disappears, i.e. 18-24 hr. The apparatus is allowed to cool with chloride gas flowing. At room temperature the apparatus is purged with nitrogen to expel chlorine and phosgene. After replacing the side tube and the condenser with stoppers the flask is removed to an efficient dry box for opening. The metal chloride is filtered and washed with carbon tetrachloride.

Iron(III) *chloride*. After 24 hr of refluxing the flask contains a clear red solution. Upon cooling dichroic red and green platelets form leaving a light yellow solution. The losses in yield are manipulative in addition to that due to a very slight solubility in cold hexachlorobutadiene-1,3. (Found: Fe, 34.52; Cl, 65.51; Cl/Fe, 2.99. Calc. for FeCl₃: Fe, 34.43; Cl, 65.57.)

Niobium(V) *chloride.* After 18 hr of refluxing the flask contains a clear orange-red solution. Upon cooling lemon yellow crystals form leaving a light yellow solution. (Found: Nb, 34.26; Cl, 65.49; Cl/Nb, 5.01: Calc. for NbCl₅: Nb, 34.38; Cl, 65.62.)

Molybdenum(IV) *chloride*. Molybdenum(IV) oxide starting material was prepared by the reduction of molybdenum(VI) oxide with ammonia.⁽¹⁾ After 24 hr of refluxing the flask contains a clear blood red solution. Upon cooling dark crystals form, but the solution remains highly coloured. It is felt that the molybdenum(IV) chloride has a considerable solubility in both hexachlorobutadiene-1,3 and carbon tetrachloride. The wet crystals (wet with CCl₄) are brown-red; the dry crystals are steel blue. (Found: Mo, 40·23; Cl, 59·95; Cl/Mo, 4·03. Calc. for MoCl₄: Mo, 40·35; Cl, 59·65.)

The method offers a major advantage over the sealed tube method.⁽²⁾ The apparatus required is very simple, assembled of stock items available in any chemical laboratory. It suffers from the disadvantage of limited application. Attempts to apply the method to the oxides of beryllium, aluminium, chromium(III), zinc, zirconium, molybdenum(VI), lanthanum, tantalum, and tungsten (VI) result in partial or no conversion. However the obvious implications of potential metal separation procedures is of at least as much interest as the preparations themselves. The present experiments

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⁽²⁾ K. KNOX et al., J. Amer. Chem. Soc. 79, 3358 (1957).

Notes

cover a limited set of conditions only. Further studies are under way on the effect of the same and similar chlorocarbons upon various metal oxides.

The method is unique for pure molybdenum(IV) chloride. Previously reported preparations of molybdenum(IV) chloride were all sealed tube reactions, and there was always partial disproportionation of molybdenum(IV) chloride into molybdenum(III) chloride and molybdenum(V) chloride.^(3,4,5) The product of this method dissolves completely in water to give a clear, amber solution, indicating the absence of molybdenum(III) chloride inasmuch as the latter is a dark red crystalline powder, insoluble in water. It is surprising to us that what must be molybdenum(IV) chloride dissolved in hexachlorobutadiene-1,3 is not further oxidized by the stream of chlorine at the reflux temperature of the solvent (215°).

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Inorganic salts dissolved in non-aqueous and in mixed solvents-VI

Studies of two layer formation in the system: SnCl₄·5H₂O-methanol-carbon tetrachloride

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OPTICALLY transparent SnCl₄·5H₂O-methanol-carbon tetrachloride solutions become opaque, and then separate into two layers on the addition of carbon tetrachloride.^(1,2) The amount of carbon tetrachloride required to make a particular solution opaque depends on the initial salt and methanol concentrations for a fixed temperature.

Here are reported detailed studies at 15°C of the composition of SnCl₄·5H₂O-methanol-carbon tetrachloride solutions at the "Opaque Point" (where one drop more of carbon tetrachloride will yield an opaque solution) and at the stage where there are two clear layers due to the addition of more carbon tetrachloride. Conductance measurements at 25°C are reported for each solution obtained at 15°C by the method outlined. The addition of sufficient methanol will make a clear, single phase system of any "Opaque" or two phase system.

Results and Discussion

In Table 1 are given compositions for selected samples of solutions at the "Opaque Point" and of the two layers obtained on addition of a further 50 ml of carbon tetrachloride. Data for more than eighty samples of different concentrations have been recorded. In addition, a large number of these were checked with duplicate samples. Physical measurements were reproducible to within 1 per cent. Tin and chloride analysis (Lessens' Method as modified by BAKER⁽³⁾ and FAJAN's adsorption indicator method⁽³⁾ respectively) were done in duplicate for each solution. For carbon tetrachloriderich solutions the analysis values were reproducible to better than 2 per cent; and for the predominantly methanol solutions reproducibility was better than 0.5 per cent.

In computing the SnO₂ concentrations, we have assumed that all the chloride is present as stannic chloride and the "extra tin" is present as SnO₂. The presence of oxychlorides will fit into this scheme. With basic chlorides present the water concentrations in the methanol-rich solutions given in

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