$$Co(NH_3)_5(NO_2)Cl_2 \longrightarrow NH_3 + 2NH_4Cl + NH_4NO_2 + CoN;$$
$$NH_4NO_2 \longrightarrow N_2 + 2H_2O;$$
$$2CoN + 3H_2O \longrightarrow Co_2O_3 + 3NH_3;$$

or,

$$2Co(NH_3)_5(NO_2)Cl_2 \longrightarrow Co_2O_3 + 5NH_3 + 4NH_4Cl + 2N_2 + H_2O.$$

This case differs, therefore, from the preceding one in that the cobalt atom is not reduced, because of the interaction of 2 species of molecules both with subsidiary valence unions.

The results with trinitro-triammine cobalt are somewhat similar, but very interesting. Slight evolution of gas begins at 158°, but at 164° the decomposition takes place with almost explosive violence, forming pure nitrogen, water and cobaltic oxide, according to the following reactions.

$$2Co(NH_3)_3(NO_2)_3 \longrightarrow 2CoN + 2HNO_2 + 4NH_4NO_2;$$
$$4NH_4NO_2 \longrightarrow 4N_2 + 8H_2O;$$
$$2CoN + 2HNO_2 \longrightarrow Co_2O_3 + H_2O + 2N_2;$$

or,

$$2Co(NH_3)_3(NO_2)_3 \longrightarrow 6N_2 + 9H_2O + Co_2O_3.$$

The writers wish to express their indebtedness to the Gibbs Fund of the National Academy of Sciences for a grant of two hundred dollars made to W. D. Harkins, which was used in purchasing a very rapid vacuum apparatus, consisting of a mercury condensation pump, and a large supporting pump of the mechanical type, for use in this work.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN.]

THE PREPARATION OF SELENIUM OXYCHLORIDE.

BY VICTOR LENHER.

Received August 23, 1920.

The first record in the literature that we have of selenium oxychloride is its preparation by Weber[1] in 1859, who heated together in a kneé-shaped tube the vapors of selenium tetrachloride and selenium dioxide. Michaelis[2] prepared the oxychloride by the action of phosphorus pentachloride on selenium dioxide. Later, in 1889, in their work on selenic acid, Cameron and Macallan,[3] mention that selenium oxychloride is formed when common salt is distilled with selenium dioxide.

The methods used in this laboratory for the formation of selenium oxychloride may be grouped under 3 heads.

[1] Weber, *Pogg. Ann.*, **108**, 615 (1859).

[2] Michaelis, *Ann.*, **240**, 150 (1887).

[3] Cameron and Macallan, *Chem. News*, **59**, 267 (1889).

1. Direct Union of Selenium Tetrachloride and Selenium Dioxide at Room Temperatures.

When elementary selenium is suspended in carbon tetrachloride and chlorine gas is passed in, the chlorine first dissolves in the carbon tetrachloride, this being an excellent solvent for chlorine at low temperatures. The dissolved chlorine immediately attacks the selenium, forming selenium monochloride which also dissolves at once in the carbon tetrachlroide. Selenium monochloride, in turn, is an excellent solvent for elementary selenium. The solution and chlorination of the selenium is therefore, much expedited.

An alternate method of preparing the 2 chlorides of selenium which possesses interesting advantages with certain selenium containing materials is to suspend them in carbon tetrachloride, chloroform or similar solvent, and pass in chlorine. This converts the selenium first to the monochloride which is soluble in carbon tetrachloride while most of the metallic chlorides, being insoluble in carbon tetrachloride, can be at once removed by filtration or decantation, while the further chlorination of the selenium monochloride gives white selenium tetrachloride, which being sparingly soluble, separates out and if desired can be removed from the solvent by a second filtration.

To the suspended selenium tetrachloride in carbon tetrachloride it is convenient to add the calculated amount of selenium dioxide. Reaction takes place with formation of selenium oxychloride, which dissolves in the carbon tetrachloride. The liquid can then be distilled. Carbon tetrachloride distills at 76–77° and selenium oxychloride at 176.4°, hence they can be readily separated by distillation. Selenium oxychloride can be conveniently distilled under diminished pressure to a high degree of purity.

The carbon tetrachloride suggested in the above procedure can be replaced by chloroform or still better replaced by selenium oxychloride itself.

Inasmuch as selenium oxychloride is a solvent for elementary selenium the entire operation of its formation can be accomplished by mixing together selenium dioxide and elementary selenium, treating this mixture with selenium oxychloride and then chlorinating.

2. Partial Hydrolysis of Selenium Tetrachloride.—This can be readily accomplished by treatment with water according to the following reaction.

$$SeCl_4 + H_2O— = SeOCl_2 + 2HCl.$$

This reaction can be carried out with solid selenium tetrachloride or with the selenium tetrachloride suspended in carbon tetrachloride, chloroform, selenium oxychloride or other liquids.

3. Dehydration of the Compound $SeO_2.2HCl$.—This substance, first described by Ditte,[1] can be formed by bringing hydrogen chloride into contact with selenium dioxide. The 2 substances unite at moderately low temperatures to form an amber-colored liquid of the formula $SeO_2.2HCl$. It is possible to remove the elements of water from this compound by means of phosphorus pentoxide, calcium chloride, or a similar dehydrating agent. The reaction can be carried out in the laboratory in one of 2 ways.

Selenium dioxide can be treated with hydrogen chloride, the resulting liquid mixed with excess of the dehydrating agent and the oxychloride distilled off, or selenium dioxide can be first mixed with the dehydrating agent and this mixture treated with hydrogen chloride. The operation can be conducted by either first passing hydrogen chloride into the mixture of selenium dioxide and dehydrating agent in the cold and subsequently heating to drive off the selenium oxychloride formed, or the mixture can be heated, hydrogen chloride passed in, and selenium oxychloride distilled from the hot mixture as it forms.

The author takes this opportunity of acknowledging the valuable help rendered by his assistant, Mr. A. J. Snyder, for various preparations of material in the above processes.

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THE IONIZATION OF AQUEOUS SOLUTIONS OF AMMONIA IN THE PRESENCE OF UREA.

BY WINTHROP M. BURKE.

Received August 27, 1920.

Introduction.

According to the Nernst-Thomson hypothesis,[2] the dielectric constant of a solvent largely determines its power to ionize electrolytes dissolved in it. In cases which have been investigated[3] in solvents of lower dielectric constant than water, the ionization of the electrolyte has in general been found to be lower than in water. It has been found that aqueous solutions of urea have a dielectric constant higher than water; that of water is 78.83, while for a 2 *M* solution of urea it is 83.98 at 18.0°.[4] Consequently, according to the Nernst-Thomson hypothesis, we should expect to find a greater ionization constant for an electrolyte, which obeys the mass-action law, in an aqueous urea solution than in water alone. Assuming the mass-action law to be obeyed, the ionization constant for binary dissociation may be derived from the expression

$$\frac{(C\gamma)^2}{C(1-\gamma)} = K.$$

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[1] *Ann. chim. phys.* [5] **10,** 82 (1877).

[2] Thomson, *Phil. Mag.*, **38,** 320 (1893); Nernst, *Z. physik. Chem.*, **38,** 487 (1901).

[3] Kraus and Bray, THIS JOURNAL, **35,** 131 (1913).

[4] Harrington, *Phys. Rev.*, **8,** 581 (1916).