error is 0.1 cal. per deg. per mole. It is reasonable to conclude that the values of C_{P_0} in Table III are correct to within 3% with perhaps a small systematic positive error due to the use of vibration frequencies determined with liquids. When these values are calculated to various finite pressures by use of the Berthelot equation in the thermodynamic expression, further error is introduced. It seems probable that no greater accuracy than 5% can be claimed at the present time for such values. Such accuracy, however, far exceeds that of most of the experimental determinations at present available.

The author wishes to express his appreciation to Professor W. F. Giauque for many helpful conversations during the course of this investigation.

Summary

1. The molal heat capacity over the temperature range 0 to 500° has been calculated for methane, methyl chloride, methylene chloride, chloroform and carbon tetrachloride from spectroscopic data.

2. It has been shown that the values obtained are probably good to 3% and are far more reliable than the fragmentary experimental thermal data.

BERKELEY, CALIF. RECEIVED APRIL 12, 1935

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 49]

Reactions of Zirconium Tetrabromide and Thorium Tetrabromide with Potassium and with Potassium Amide in Liquid Ammonia

BY RALPH C. YOUNG

Zirconium tetrabromide was found to be soluble in liquid ammonia, at least to the extent of 2 g. per 10 cc. of ammonia at −33.5°. It thus differs from zirconium tetraiodide[1] which is insoluble in this solvent, and from titanium tetrabromide[2] which ammonolyzes to give an insoluble product. Thorium tetrabromide,[3] as has been previously described, gives an insoluble ammine in liquid ammonia.

The procedure for carrying out reactions in ammonia as to the drying of the solvent, the introduction of the salt and the potassium, preparation of potassium amide, and the washing of the reaction product was in general that described in the numerous papers of Kraus and co-workers and of Franklin and co-workers on this subject.

The apparatus in which the reactions were carried out was constructed to allow a solution of potassium, or potassium amide, to be poured from one leg of 100 cc. capacity through a connecting tube packed with glass wool into another leg of the same volume. Both legs were provided with short tubes which were connected by pressure tubing to separate mercury manometers with mercury reservoirs by means of which the pressure in the apparatus could be regulated. Sealed also to each leg were tubes with ground glass joints which afforded a means of introducing the reactants and through which a solution could be decanted. A tube also extended to the bottom of each leg and these allowed the introduction of ammonia and afforded a method of stirring the contents with ammonia gas. The legs of the apparatus rested in separate Dewar tubes containing ammonia.

When into a solution of 2 g. (0.005 mole) of zirconium bromide in 10 cc. of ammonia there was poured 75 cc. of an ammonia solution containing 2 g. (0.05 mole) of potassium, there was formed a black precipitate and a red solution, neither of which was permanent. Secondary reactions began immediately which resulted in the precipitate becoming white, the solution slightly yellow, probably due to potassium amide, and an evolution of hydrogen gas. Burgess and Smoker[4] have reported observations somewhat similar to these for the reaction between manganese iodide and sodium in liquid ammonia. The anions of some metal compounds[5] are highly colored in this solvent, as are the solutions of certain salts.[6] Black precipitates are formed by finely divided metals, and may be formed by nitrides and ammonobasic salts.

After the solution was decanted and the precipitate washed with ammonia, the potassium bromide recovered was found to be equivalent to the zirconium bromide used. Since the white product was very reactive, and oxidized rapidly in the air, it was necessary, before analysis, to introduce it, in an atmosphere of ammonia, into an apparatus similar to that described by Franklin.[7] This afforded a means of obtaining the weight after all adsorbed ammonia had been pumped off, and allowed the product to be attacked by water vapor in the absence of air, after which it was readily analyzed.

Anal. Calcd. for $Zr(NK)_2 \cdot NH_3$: Zr, 42.54; K, 36.47; N, 19.58. Found: Zr, 41.22, 41.75; K, 36.45, 36.30; N, 18.14, 18.85.

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(1) Shähler and Denk, *Ber.*, **38**, 2615 (1905).

(2) Ruff and Eisner, *ibid.*, **41**, 2260 (1908).

(3) Moissan and Martinsen, *Compt. rend.*, **140**, 1514 (1905).

(4) Burgess and Smoker, *Chem. Reviews*, **8**, 269 (1931).

(5) Kraus and Kurtz, THIS JOURNAL, **47**, 43 (1925).

(6) Bergstrom, *ibid.*, **47**, 2317 (1925).

(7) Franklin, *J. Phys. Chem.*, **15**, 516 (1911).

The same product was obtained when the experiment was repeated with potassium amide instead of potassium metal, the amide being prepared in the apparatus.

Anal. Found: Zr, 42.75, 42.60; K, 36.43, 36.50; N, 18.80, 17.70.

When potassium amide was added in an equivalent amount to zirconium bromide, a mixture of zirconium imide and a monopotassium derivative of zirconium imide were formed.

Anal. Calcd. for an equimolal mixture of $Zr(NH)_2$ and ZrNHNK: Zr, 65.03; K, 13.93; N, 19.96. Found: Zr, 65.52, 65.02; K, 13.15, 13.33; N, 20.39, 20.65.

The first reaction product between potassium and zirconium bromide will be studied further in a solvent in which solvolysis is less than in ammonia.

Thorium bromide underwent no color change on being treated with potassium in liquid ammonia. There was, however, a slow reaction and potassium bromide was formed and hydrogen was evolved. It is possible that on account of the very slight solubility of the thorium salt, saturation of a very small amount of a reduction product by the NH_2 group, or NH group, would occur without any visible evidence of reduction. Another possibility is an initial formation of potassium amide and a subsequent metathesis with thorium bromide. If ammonolysis of the salt took place, potassium would then react with the ammonium bromide formed. In the course of the reaction between potassium and thorium bromide, which was very slow, there was, of course, a continually increasing reaction between the metal and the solvent to form the amide. Approximately the same molecular proportions of salt and metal were used as in the reaction with zirconium bromide and potassium, but in the majority of cases the composition of the product approached that represented by the formula $ThNKNH \cdot NH_3$.

Anal. Calcd. for $ThNHNK \cdot NH_3$: Th, 73.17; K, 12.32; N, 13.29. Found: Th, 72.73, 73.90; K, 15.35, 15.40; N, 9.25, 10.03.

A larger percentage of potassium could be introduced in the product by continued action, and analyses of samples were obtained which showed that the hydrogen of the second imide group was partially replaced by the metal. With excess potassium amide, however, the reaction was more nearly complete, the analysis of the final product pointing to a replacement of both imide hydrogen atoms by potassium and a molecular compound with the amide.

Anal. Calcd. for $Th(NK)_2 \cdot KNH_2$: Th, 59.00; K, 29.81; N, 10.67. Found: Th, 59.89, 60.11; K, 27.10, 26.70; N, 9.75, 10.41.

Summary

Zirconium tetrabromide was found to be soluble in liquid ammonia and was reduced in this solvent by potassium metal to form a black precipitate and red solution. The reduction product reacted further with evolution of hydrogen to form a compound $Zr(NK)_2 \cdot NH_3$ which was also formed by the reaction of zirconium bromide with potassium amide in excess. In equivalent proportions, however, the imide, together with a monopotassium derivative, was formed.

No reduction of thorium bromide was observed when it was treated with potassium in liquid ammonia. Reaction took place, however, with evolution of hydrogen and a product $ThNHNK \cdot NH_3$ was isolated. $Th(NK)_2 \cdot KNH_2$ was formed by reaction between thorium bromide and excess potassium amide.

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Solubility of Noble Gases in Aqueous Salt Solutions at 25°

BY GÖSTA ÅKERLÖF

Introduction

The influence of strong electrolytes on the thermodynamic properties of non-electrolytes in solution has been studied for a large number of different substances, mostly with a rather complicated structure, like ethyl acetate, phenyl thiourea, diacetone alcohol and others. Numerous measurements with simpler substances like hydrogen, oxygen and other gases have, however, also been carried out and the data available give on the whole, as shown in the exhaustive summary of Randall and Failey,[1] about the same picture as that of the behavior of more complicated substances. Therefore, at the suggestion of Professor H. S. Harned, it was considered to be worth while to make a study of the solubility changes in solutions of strong electrolytes of the simplest molecules known, those of the noble gases, which are mono-atomic, nonpolar and chemically inactive. As will be shown below, also in this case the general results of the measurements carried out do not differ from those obtained with non-electrolytes having a relatively very complicated structure.

Experimental Method

The principle of the method employed for the solubility measurements is extremely simple and consists in the direct

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(1) Randall and Failey, *Chem. Rev.*, **4**, 271, 285, 291 (1927).