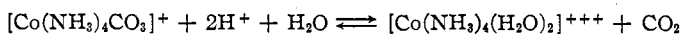


Summary

The kinetics of the decomposition of the carbonato-tetrammine-cobaltic ion



have been studied in glycolate and acetate buffer solutions at 25° and at different salt concentrations.

In the glycolate buffers the decomposition was practically complete. In some acetate buffers it could be shown that the reaction is balanced.

When the carbon dioxide pressure is low and the hydrogen-ion concentration not too small, the velocity may be expressed as the sum of two terms, one being independent of the hydrogen-ion concentration, the other being proportional to the hydrogen-ion concentration. No general acid catalysis was found.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE STATE UNIVERSITY OF IOWA]

SOLUBILITIES IN HYDROGEN FLUORIDE

BY P. A. BOND AND V. M. STOWE

RECEIVED JULY 28, 1930

PUBLISHED JANUARY 12, 1931

Solubility relations in non-aqueous inorganic systems have received attention in this Laboratory during several years. Sulfur monochloride, liquid nitrogen tetroxide, thionyl chloride and liquid sulfur dioxide have been employed as solvents.

As one branch of the general problem of solubilities in non-aqueous inorganic systems, the authors set out to develop a technique for the use of liquid anhydrous hydrogen fluoride as a solvent, and to determine some solubilities in this medium. Liquid hydrogen fluoride was chosen for this investigation because of its unusual properties.

The anomalous boiling point of liquid hydrogen fluoride indicates that it is an associated liquid. The anomaly is apparent if one compares the boiling points of the series HI (-35.7°), HBr (-68.7°), HCl (-83.1°) and HF (+19.0°). Water and ammonia show similar anomalous boiling points when compared with the appropriate series. The vapor pressure data of Simons¹ were examined by the use of Hildebrand's modification of the Trouton rule.² The value of the "constant" so determined is about the average of those for normal liquids.

The chemical relationships for hydrogen fluoride indicated that it would prove to be a good solvent. Polar liquids such as ammonia, water and,

¹ J. Simons, *THIS JOURNAL*, **46**, 2179 (1924).

² Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, 1924, p. 89.

to a less extent, alcohol, frequently form addition compounds with solutes. This appeared to be true also in the case of hydrofluoric acid.

Finally, the qualitative results of Gore³ and Franklin⁴ indicated that hydrogen fluoride is a vigorous reagent and a good solvent. The authors believe, however, that many of the solubilities in hydrogen fluoride previously reported were preceded by chemical reaction.

Recent publication by Cadenbach⁵ is quite in line with this statement. His results, while qualitative, or where quantitative, expressed in terms of molar solutions, are in quite close agreement with the results shown below.

Preparation of Hydrogen Fluoride

The liquid anhydrous hydrogen fluoride was prepared essentially according to the method of Gore,³ *i. e.*, by the distillation of dry potassium hydrogen fluoride, KHF_2 . For the preliminary work Baker and Adamson "C. P." potassium bifluoride was fused, electrolyzed by a direct current of 18 volts until arcing was no longer seen at the carbon pole, and the product was distilled from a platinum still described below. Later the potassium fluoride resulting from this distillation was treated with aqueous hydrogen fluoride, evaporated, fused and electrolyzed as above.

The acid salt is reported to be non-hygroscopic. However, electrolysis of the fused salt as carried out served to remove any trace of water which might have been present. The salt was then always preserved in a desiccator. The fused salt was poured into a clean platinum still which had been carefully dried. The still was then suspended by a nichrome wire so that the condensing tube was engaged. Heat was applied by means of a specially designed electric heating unit which supplied the heat in a ring about the still, and which could be moved up and down the still as desired. In this way the heat was applied above the acid salt and any frothing was checked by contact with the hot part of the still above. A light red heat was used. After three hours most of the acid had been distilled off from the salt. The vapor passed through a platinum tube 40 cm. long. This was surrounded by a water jacket which served to cool the gas to room temperature. The platinum tube was sealed with sulfur onto a spiral monel metal tube about three meters long and about 8 mm. in diameter. In the spiral, which was packed in an ice and salt freezing mixture, the hydrogen fluoride was condensed to a liquid. The liquid was collected directly in the solubility apparatus, which was sealed onto the still each time with ceresin wax, thus exposing only a very small amount of wax and that to the vapor only. Air pressure was equalized through a drying tube. The hydrogen fluoride obtained was clear, limpid and colorless. It carried less than 0.2% of non-volatile solid as shown by seven determinations made on amounts of hydrogen fluoride ranging from approximately 8 to 14 g.

Procedure for Determining Solubility.—The "bomb," or solubility apparatus, which was specially designed for this work, comprised the upper chamber (A, see Fig. 1) and the lower chamber (B). The piece (E) served as a partition and also formed the seat of the valve as shown. (E) was held in place by the union (D). Soft gaskets of 24 carat gold maintained an air-

³ Gore, *Phil. Trans.*, 159, 183 (1869).

⁴ Franklin, *Z. anorg. Chem.*, 46, 2 (1905).

⁵ Karl Fredenhagen and Gustav Cadenbach, *Z. physik. Chem.*, Abt. A, 146, 245 (1930).

tight joint. The valve stem was packed with ceresin wax or amorphous sulfur.

To operate the device it was assembled as shown. The plug (C) was removed and suction applied to form a moderate vacuum. The valve (E) was then closed tightly and the suction line was disconnected, leaving a vacuum in chamber (B). Dry air was blown through the chamber (A). The salt was next introduced into (A), and the solubility device was sealed onto the hydrogen fluoride delivery tube and the plug (C) was immediately inserted. This bore a gasket of wax or, at the higher temperatures, of 24 carat gold.

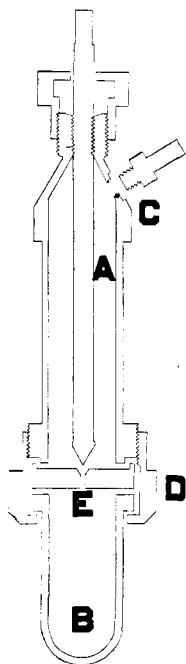


Fig. 1.—“Bomb” or solubility device.

The bomb was immediately placed in a constant temperature bath and shaken for two hours.

When time had been allowed for equilibrium to become established, the bomb was gently shaken in such a manner as to wash all the undissolved salt down into the corner of chamber (A) between the side and the bottom. The valve (N) was slowly opened two complete revolutions, then closed. The bomb was now removed from the thermostat. The plug (C) was removed, and the chamber (A) was washed out with concentrated hydrochloric acid followed by water, then dried by alcohol, ether and compressed air. The bomb and contents were now weighed on a large balance. The contents of B were washed into a platinum dish and evaporated. The bomb, platinum dish and contents were weighed. From these values the weight of the hydrogen fluoride and of the salt dissolved could be obtained by difference.

The bomb was made of monel metal. The absence of action on this material was shown by the failure to obtain tests for copper or nickel.

Potassium Iodide.—The salt was Mallinckrodt's “c. p.” grade. It was screened with wire gauze to yield crystals between 12 and 20 mesh.

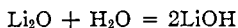
On treatment with liquid hydrogen fluoride in an open platinum crucible the solid apparently dissolved. However, when the solution was evaporated and the residue dissolved in water it was found that complete solvolysis had taken place. Only a slight turbidity resulted on treatment with silver nitrate, while a heavy precipitate followed the addition of calcium chloride solution to another portion of the solution. These tests indicate the absence of iodides and the presence of a fluoride. Gore³ states that this salt is soluble but the present work shows that a reaction has taken place.

Chromium Fluoride.—The salt used was J. T. Baker Co.'s “c. p.” grade. Concordant results could not be obtained with this salt even after weeks of experimentation, for unknown reasons. The material is plainly soluble.

Lithium Fluoride.—This salt was found to be quite soluble in liquid hydrogen fluoride. It reacts with the hydrogen fluoride as shown by the equation



This is a good analogy to the reaction of lithium oxide with water



Not only so, but the solubilities of the two compounds in the respective solvents are of the same order.

Solubility data for the salt lithium fluoride are given for several temperatures in Table I.

TABLE I
SOLUBILITY DATA FOR LITHIUM FLUORIDE

Temp., °C.	Weight of HF	Wt. of Li ₂ SO ₄	Moles LiF Moles HF
0	12.347	1.421	0.043
0	4.229	0.4838	.043
10	7.510	.6661	.033
10	10.341	1.144	.041
20	5.214	0.6069	.044
20	4.399	.5386	.046
30	4.908	.5520	.042
30	7.138	.8084	.042
40	5.913	.7386	.046
40	10.460	1.215	.043

Calcium Fluoride.—Native fluor spar was screened to yield crystals of about 1 mm. diameter. These were then carefully hand picked, washed with hydrofluoric acid and dried, and cloudy crystals were rejected. No action occurred after four hours. The solubility was less than 0.01% at 0°.

Zinc Fluoride.—The salt was of the stock previously prepared in this Laboratory by the action of hydrofluoric acid upon pure zinc carbonate; solubility: less than 0.01% from -20 to +25°.

Magnesium Fluoride.—Magnesium fluoride was prepared by the method of C. Poulenc,⁶ and that of F. Roder reported by Mellor.⁷ Five grams of magnesium chloride and four grams each of sodium chloride and sodium fluoride were fused in a crucible and then cooled slowly. The resulting crystals were digested with water and well washed; solubility: less than 0.01% at 0°.

Discussion

A critical study of previous work on the physical and chemical properties of anhydrous liquid hydrogen fluoride suggests that the material is highly polar, and therefore should prove to be a good solvent for polar salts. The present work shows that for the fluorides of several elements of the first two groups of the periodic table the liquid is quite comparable to water.

It is desired to point out very clearly, however, that comparisons are to be made only between corresponding compounds. Thus lithium fluoride although insoluble in water is soluble in hydrogen fluoride. This compares to the solubility of lithium oxide in water. When solubilities are thus compared, considerable correspondence between the two solvents can be traced for the salts tested. When so compared, however, the solubilities in

⁶ C. Poulenc, *Ann. chim. phys.*, [7] 2, 5 (1894).

⁷ Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IV, p. 296.

hydrogen fluoride appear to be somewhat less than corresponding salts in water. Thus calcium and magnesium fluorides are less soluble in hydrogen fluoride than are the oxides in water, etc. Chromium fluoride seems to be an exception to this conclusion.

Summary

1. The solubility of lithium hydrogen fluoride between 0 and 40° has been established, and zinc fluoride, magnesium fluoride and calcium fluoride have been shown to be very insoluble. Potassium iodide has been found to react with liquid hydrogen fluoride. Chromium fluoride was found quite soluble but to an undetermined extent. These solubilities refer to liquid hydrogen fluoride as a solvent.

2. Comparison of these results indicates a fair similarity in the solvent action of water and hydrogen fluoride for the salts tried.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
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A METHOD FOR THE DETERMINATION OF CRITICAL TEMPERATURES AND THE CRITICAL TEMPERATURE OF HYDROGEN FLUORIDE

BY P. A. BOND AND DELLA A. WILLIAMS

RECEIVED JULY 28, 1930

PUBLISHED JANUARY 12, 1931

Accurate determination of the critical temperature by the usual method is difficult for several reasons. In the first place, glass is a poor conductor of heat and slight differences in bath temperature are not readily transmitted to the substance through the necessarily thick walls. Also for the same reason one end of the tube may be of slightly different temperature than the other. The gas above the critical temperature is very dense, diffusion is relatively slow and equalization of conditions in the tube does not readily take place. Some substances such as hydrogen fluoride attack glass and some such as nitrogen peroxide are so intensely colored at the critical temperature that observation is exceedingly difficult. The liability of tubes exploding under high pressures has also been a real difficulty where greater pressures are encountered. The method noted below permits the determination to be made without danger to the operator and under conditions of greater accuracy than those obtainable when the glass tube is used. Monel metal was used in the determinations because of its resistance to the action of hydrofluoric acid. Other metals could be used in the construction if desired.

Description of Apparatus

The critical temperature apparatus was composed of a constant temperature oven (Z), an assay balance (Y) and a critical temperature tube (D)