adequate there has probably been a tendency to be satisfied with rather impure samples for heat of fusion determinations and it therefore seems important to point out its inadequacy and the consequent necessity for the use of highly pure samples in these measurements.

Summary

The magnitude of the errors in heat of fusion determinations due to the presence of impurities in the sample, have been calculated and it has been shown that the usual method for correcting for the effects of impurity in such data, namely, by neglecting the points on the heat content curve for the solid phase near the melting point, is quite inadequate and may lead to enormous errors.

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Reaction of Fluorine with Water and with Hydroxides

BY GEORGE HAMILTON CADY

This research is the direct result of a suggestion by Professor J. H. Hildebrand, of the University of California, that at low temperatures fluorine might be absorbed by ice or a solid hydroxide, due to the formation of an oxyacid or its salts. In 1929, he and the author allowed fluorine, contained in a closed system, to react with several different solids at a temperature somewhat above that of subliming carbon dioxide. In no case did the gas pressure, during the reaction, fall below half of its initial value. Since the formation of oxygen or oxygen fluoride, OF_2, would have just halved the pressure, and since both of these gases were produced, it appeared that there was no reason for concluding that a non-volatile salt of an oxyacid of fluorine had been formed.

The investigation was continued, and the experiments to be described were carried out at the Massachusetts Institute of Technology.

I. Reactions with Solid Hydroxides

From Moissan,[1] one learns that fluorine reacts vigorously with sodium and potassium hydroxides, but that the solid becomes coated with a layer of fluoride which decreases considerably the velocity of the process. It also appears that many oxides are not attacked at ordinary temperatures, and a difference between the behavior of oxides and hydroxides has been clearly demonstrated by Rengade,[2] who has found that sodium and potassium oxides are unreactive.

Experimental

A magnetically operated pump was used to circulate fluorine in a closed system consisting of a reservoir of capacity about twelve liters, a mercury manometer and a reaction chamber which contained a pulverized oxide or hydroxide. The chamber was immersed in a bath, at the desired temperature. The manometer permitted one to follow the reaction, and the apparatus in direct contact with the gas was entirely of metal, for the most part either nickel or Monel metal. After all, or nearly all, of the fluorine had been used up, a condition which could be recognized by the fact that the pressure remained constant at about half of its initial value, a sample of the gaseous reaction product was condensed and was analyzed by a fractional distillation method similar to that described by Podbielniak.[3] The different gases were collected and measured in separate flasks and, when sufficiently abundant, were later identified. Oxygen and oxygen fluoride were easily recognized by the vapor pressures, the vapor densities, the color of the liquids, the odor and the ability to react with a solution of potassium iodide.

Each distillation revealed a small amount of material which existed as a white solid at the temperature of liquid air, was less volatile than oxygen fluoride, but evaporated at low temperatures. The variable vapor densities, ranging between 60 and 98, which were obtained, as well as the fact that no sharp melting point was observed, indicated that a mixture had been encountered. The amount was never large enough to permit the separation and identification of the compounds by the methods readily available.

It is not necessary to conclude that this mixture was produced by the reaction with the oxide or hydroxide. The substances may have re-

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[1] Moissan, 'Le Fluor," Paris, 1900, p. 228.

[2] Rengade, *Compt. rend.*, **144**, 753 (1907).

[3] Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931).

sulted from impurities in the solids, which were of C. P. quality. They may have come directly from the fluorine generator, or from the sodium fluoride, which was used to remove hydrogen fluoride from the fluorine, or from impurities in the metal apparatus. Other experiments are needed to answer these questions.

The author is not the first[4,5,6] to encounter a mixture of this type.

Fluorine for these experiments was liberated from a nickel electrode by a method similar to that of Lebeau and Damiens.[7] When necessary, the supply of hydrogen fluoride in the electrolyte was replenished from a tank of the anhydrous acid, furnished by the Sterling Products Co. In the hands of the author, this procedure yielded a much purer gas than was obtained by the customary high temperature process, which uses a graphite anode. At least 98% of the gas was absorbable by mercury.

The oxides which were used for these experiments were well dehydrated by heating, but the hydroxides contained the water and carbon dioxide which had been absorbed during a brief exposure to the atmosphere.

It was found that fluorine did not react appreciably, at 0°, with mercuric oxide, cupric oxide, ferric oxide or freshly prepared calcium oxide. These observations are in agreement with those of Moissan[1] except for the case of calcium oxide. It is probable that his oxide had partially changed to the hydroxide, which does react.

Solid sodium hydroxide, or the octahydrate of barium hydroxide, reacted rapidly and uniformly, when the reaction chamber was placed in a bath at 0°. Much heat was liberated, and the actual temperature was far above 0°. The gaseous product formed was nearly all oxygen, but the odor of oxygen fluoride was present; and so was the unidentified mixture.

When lower temperatures, between -51 and $-78°$, were used, the reactions with the hydroxides of sodium, potassium or calcium were very erratic and were not controlled successfully. At a fresh surface, the fluorine reacted rapidly even at $-78°$. After the alkali became coated with the solid product of the reaction, the process became very slow. At times, when the chamber was vigorously shaken, the rate would suddenly increase very greatly, probably due to the exposure of a fresh surface. The experimental difficulties render the quantitative yields of little significance. The qualitative results are, however, of value. The only gases which were recognized definitely as reaction products were oxygen and oxygen fluoride. The latter substance sometimes constituted as much as 30% of the gas.

When the reaction chamber warmed to room temperature there was no surprising increase in the pressure within the apparatus. This indicated that no large amount of a non-volatile salt of an oxyacid had decomposed. That a considerable amount of such a compound was not present on the solid was also shown by the minute ability of the material to liberate iodine when dissolved in an acidified solution of potassium iodide.

II. Reactions with Water

It was found by Moissan[8] that the passage of bubbles of fluorine through a small quantity of water produced oxygen which was contaminated with a substance of great oxidizing strength. He[9] also observed that when a few drops of water fell into fluorine contained in a platinum tube equipped with fluorite windows, a fog was formed, which cleared away, leaving a beautiful blue gas with an odor like that of ozone. These experiments have given rise to the widespread belief that a major product of this reaction is ozone, although no one has described tests which definitely identify this substance.

In one of a series of interesting papers, Fichter and Bladergroen[10] have concluded that bubbles of fluorine which passed through water first produced hydrogen peroxide and that, subsequently, ozone was formed. They do not mention how they recognized these compounds.

By allowing fluorine to attack a mixture of water vapor and carbon dioxide at 100°, Ruff[4] obtained evidence indicating the formation of oxygen, oxygen fluoride, and a small amount of an unidentified fluorine compound of considerable oxidizing strength. With such knowledge at hand, it is not surprising to find that fluorine liberates oxygen fluoride from liquid water; but this makes one wonder whether the ozone of Moissan may have been, at least in part, oxygen fluoride. Some of the experiments to be described have been designed to answer this question.

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(4) Ruff, *Z. angew. Chem.*, **41**, 1291 (1928).

(5) Ruff and Menzel, *Z. anorg. Chem.*, **190**, 257 (1930).

(6) Ruff and Menzel, *ibid.*, **198**, 39 (1931).

(7) Lebeau and Damiens, *Bull. soc. encour. ind. nat.*, **139**, 15 (1927).

(8) Moissan, "Le Fluor," Paris, 1900, pp. 129–132.

(9) Moissan, Ref. 8, pp. 121–122.

(10) Fichter and Bladergroen, *Helv. Chim. Acta*, **10**, 549 (1927).

Experimental

A small flask with a narrow opening was filled with fluorine, by displacement, and was then inverted so that the neck extended into a beaker of ice water. When the flask was shaken vigorously the water soon rose until the remaining gas volume was about one-eighth that of the fluorine originally in the flask. The presence of hydrogen peroxide in the liquid was shown by the following qualitative tests: the yellow color produced with titanium sulfate solution, the blue color with chromic acid and ether, the precipitation of the oxidizing agent as a white solid by barium hydroxide. Since hydrogen and fluoride ions were also present, it appears quite evident that Fichter and Bladergroen[10] correctly wrote the equation: $F_2 + 2H_2O \longrightarrow H_2O_2 + 2HF$. Under certain circumstances most of the fluorine is used up by this process.

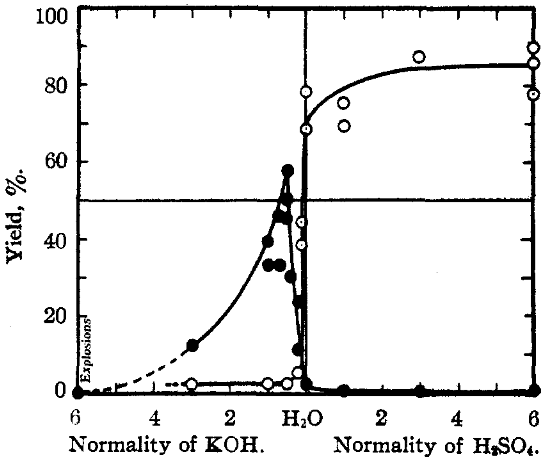

Fig. 1.—Yields of active oxidizing agents produced by the action of fluorine on aqueous solutions: ●, gaseous; ○, in solution.

The nature of the gaseous reaction product was determined by several experiments, the apparatus used in one case being a platinum vessel containing water through which fluorine was passed from a small platinum tube. The resulting mixture of gases then flowed through copper tubing to a trap, also of copper, kept at about −78°, where water and hydrogen fluoride vapors were condensed. The gas then passed through a glass trap cooled with liquid oxygen, the glass to copper attachment being made by Picein cement which did not come into direct contact with the gas stream.

In the first part of the experiment about 2 cc. of water was placed in the platinum vessel, this quantity failing to cover the end of the small platinum tube, and the device was then cooled with subliming carbon dioxide. During a thirty-minute period, about one liter of fluorine was passed over the cold ice, at such a rate that fluorine was always in sufficient excess to light a Bunsen burner, held at the exit from the glass trap.

The reaction vessel was then allowed to warm to about 0°, and the quantity of water in the crucible was increased to 7 cc. Another liter of fluorine was passed, this time through the liquid, and again fluorine was present in excess. During the first part of this experiment, a small drop of a yellow liquid collected in the glass trap, and this increased to a volume of about 0.5 cc., at the end of the second part. The color, odor and oxidizing strength of this compound, as well as the fact that its boiling point was above that of oxygen, sufficiently identified it as oxygen fluoride. As the liquid boiled away, no blue color typical of ozone was observed, and no odor other than that of oxygen fluoride was detected. When tested with tetramethyl base paper, instead of the violet typical of ozone, there appeared a blue color which changed to brown shortly before the paper burst into flame. When vessels containing both the middle and last fractions of the yellow liquid were inverted over mercury for two weeks, no marked change in the volume of the gas was observed. Although this experiment indicates that oxygen fluoride is formed, oxygen itself constitutes the major part of the gas produced by the reaction of fluorine with water. This latter fact has been well demonstrated by Moissan[8] and others and has again been confirmed by this research. However, since he specifies that ozone is formed by the action of an excess of fluorine on a small amount of water, it seems that experiments such as the one just described should have produced enough ozone to allow detection. We must conclude, therefore, that if ozone is produced, its importance as a product of this reaction has been considerably overemphasized.

III. Reactions with Alkaline Solutions

The only substances which have been shown definitely to be produced by the reaction of fluorine with a solution of the hydroxide of sodium or potassium are the following: the fluoride of the metal,[1] a derivative of hydrogen peroxide,[1,10,11] an unstable yellow compound[10] which may be potassium ozonate, oxygen,[1,10] oxygen fluoride.[5,6,12] Small amounts of other gases[6] have been found, but they may not have been formed in the alkaline solution. One of these compounds had some of the properties of ozone. It has not been shown that salts of oxyacids of fluorine are produced.[1,10,11,13]

Experimental

The effect of hydroxide-ion concentration on the yields of the gaseous and of the dissolved substances, capable of rapidly liberating iodine from a slightly acidified solution of potassium iodide, has been approximately determined by a simple method. The apparatus consisted of a 150-cc. separatory funnel bearing a stem about 4 cm. long, which was sealed to one of the tapered ends of a graduated glass cylinder. This was made from an ordinary 100-cc. graduate and terminated at the other end in a short length of tubing having an inside diameter of about 3 mm. To carry out an experiment, a few cc. of potassium iodide solution was poured into the funnel, and, after replacing the stopper, the device was partially evacuated, care being

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(11) Cady, This Journal, **56**, 1647 (1934).

(12) Lebeau and Damiens, *Compt. rend.*, **188**, 1253 (1929).

(13) Dennis and Rochow, This Journal, **54**, 832 (1932); **55**, 2431 (1933).

taken to keep the solution from entering the cylinder. After closing the stopcock, the cylinder was filled with fluorine by displacement of air. The open end was then immersed in a solution cooled to about 2°, and the apparatus was shaken until the reaction had become complete. This operation usually required about ninety seconds, and the position of the liquid in the tube was then observed. As soon as possible, the stopcock was opened and all of the gas was allowed to flow into the separatory funnel; but no liquid was permitted to enter. The liquid was then washed from the funnel into a flask, and the solution in the cylinder was placed in another flask. Enough sulfuric acid was added to each to give an acid reaction, and potassium iodide was added to the solution which had been removed from the cylinder. After waiting for several minutes, both were titrated with sodium thiosulfate.

From the values obtained and the volume of fluorine used, it was possible to calculate the yields of both the gaseous and the dissolved oxidizing agents which had liberated iodine. The results are shown with sufficient accuracy in Fig. 1. The diagram shows clearly that the production of the dissolved oxidizing agent, a derivative of hydrogen peroxide,[1,10,11,14] was influenced greatly by the hydrogen-ion concentration. It also illustrates that the maximum yield of active gaseous oxidizing agent, mostly, if not completely, oxygen fluoride,[5,6,12] was obtained from half normal potassium hydroxide. This is about the same hydroxide concentration as the 2% sodium hydroxide used by Lebeau and Damiens[12] for the preparation of oxygen fluoride.

In the past, the volume of a sample of fluorine frequently has been determined by allowing the element to react with water and subsequently measuring the volume of gas produced. It has been considered that this was equal to half of the volume of the fluorine. We see from the experiments just described that this is not strictly true, for the production of a peroxide results in the complete absorption of fluorine. When such a procedure is used, the quantity of oxidizing agent in the solution should be determined.

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Summary

1. Oxygen fluoride, OF_2, is produced by the reaction of fluorine with cold water or with a cold solid hydroxide of sodium, potassium or calcium.

2. If ozone is a reaction product, its importance as such has been overemphasized.

3. When cold aqueous solutions are allowed to react, the yields of powerful oxidizing agents, both gaseous and dissolved, vary considerably with the hydrogen-ion concentration.

4. These observations and those of others permit one to conclude that the substances which are listed below, in the order of their usual relative abundance, are formed, when fluorine reacts with the following: (a) with a cold solid hydroxide—the fluoride of the metal, water, oxygen, oxygen fluoride; (b) with cold water—hydrofluoric acid, hydrogen peroxide, oxygen, oxygen fluoride; (c) with alkaline solutions—the fluoride of the metal, water, oxygen, oxygen fluoride, a peroxide which in the presence of acid behaves as does hydrogen peroxide. With cold concentrated potassium hydroxide, an unstable yellow substance, probably potassium ozonate, is temporarily produced.

More work will be required to show definitely whether or not small yields of other substances such as ozone or oxyacids of fluorine are obtained.

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[14] Fichter and Humpert, *Helv. Chim. Acta*, **9**, 602–611 (1926).