by H_2 in the preceding reaction steps to obtain a fairly complete picture of the mechanism of the latter reaction at high temperature.

The author wishes to express his gratitude to Professor G. B. Kistiakowsky for his invaluable advice and assistance, and to Professor H. S. Taylor for his helpful criticism.

Summary

1. The photochemical oxidation of carbon monoxide has been investigated at room temperature in a flow system and at high temperature in a static system.

2. The room temperature investigation shows that oxygen atoms react with oxygen molecules to form ozone at least 150 times more rapidly than they react with carbon monoxide to form carbon dioxide.

3. The high temperature investigation indicates that the dry oxidation is practically independent of temperature and total pressure. When water is present, however, the reaction rate is no longer independent of pressure and shows a large temperature coefficient.

4. A mechanism involving hydrogen atoms and hydroxyl radicals has been suggested to explain the effect of water.

PRINCETON, NEW JERSEY RECEIVED OCTOBER 9, 1934

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 42] .

NO_3F, An Explosive Compound

BY GEORGE HAMILTON CADY

When the reactions of fluorine with nitric acid at about 2° were studied by the method previously used for sulfuric acid[1] surprising results were obtained. In addition to a dissolved oxidizing agent the fluorine produced a large yield of a gas of great oxidizing strength. Rough calculations indicated that this substance had a volume equal to that of the fluorine from which it was prepared. The yields of gaseous and of dissolved oxidizing agents which were obtained from different concentrations of acid are shown in Fig. 1. The measurements were made by iodimetry, the strongly acid solutions being diluted enough to keep nitric acid from liberating iodine.

A careful survey of the literature failed to reveal a complete explanation for the results, but a statement, by Moissan,[2] was found that the passage of bubbles of fluorine through concentrated nitric acid produced explosions. That the acid did not need to be concentrated was suddenly discovered, during this research, when a two-liter flask, in which fluorine was reacting with cold four normal nitric acid, exploded. Afterward precautions were taken. As the work progressed it became evident that the gaseous oxidizing agent exploded only when heated or when it was being prepared. Perhaps localized heating during the reaction caused the trouble.

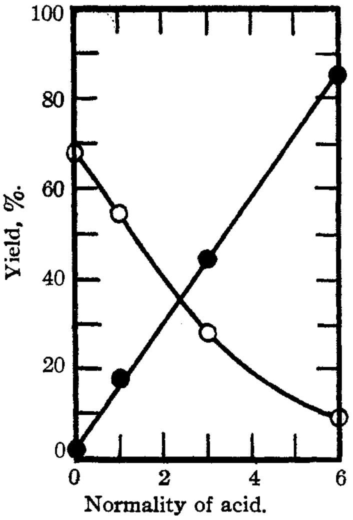

Fig. 1.—Yields of powerful oxidizing agents produced by the reaction of fluorine with an excess of cold nitric acid. ●, gaseous oxidizing agent; ○, dissolved oxidizing agent.

Preparation

The active gas was produced successfully in the reaction chamber shown in Fig. 2. A nickel tube, 1.5 cm. in diameter and 25 cm. in length, constituted the main body of the chamber, and to this were attached, by silver solder,

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[1] The procedure is described by the author in a paper which has not yet been published. A known volume of fluorine was allowed to react completely with an excess of the acid, and the gas and liquid phases were afterward separated and tested for their oxidizing strengths.

[2] H. Moissan, *Ann. chim. phys.*, [6] **24**, 224 (1891); "Le Fluor," Paris, 1900.

smaller tubes of monel metal. The end of the tube, from which fluorine bubbled into nitric acid, was of platinum. A metal disk at the top of the vessel was attached by means of the ordinary laboratory cement made from beeswax, rosin and ferric oxide. This weak adhesive allowed the disk to be blown off by explosions which occurred during the reaction. The lower part of the chamber was surrounded by chopped ice, and cold three normal nitric acid was allowed to flow through the vessel at a rate of about one liter per hour. Fluorine was generated at a rate of about three liters per hour and was considerably diluted with dry air before it entered the chamber, for it was found that the mixture of gases produced fewer and less violent explosions than pure fluorine. The gas stream from the chamber was led through a glass trap, cooled by boiling oxygen, where an increasing amount of a white solid collected on the walls.

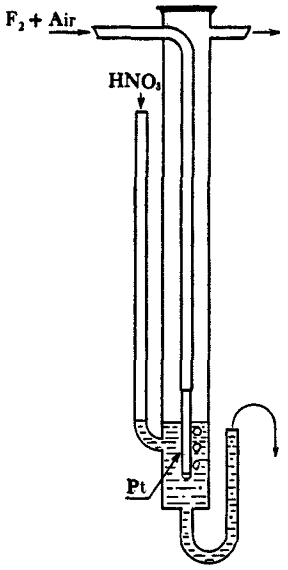

Fig. 2.—Apparatus used for the preparation of NO_3F.

When the tube was allowed to warm slowly, first in cold air and then in an alcohol bath, a small quantity of a gas having the odor of oxygen fluoride emerged. The white solid melted to form a clear effervescent liquid which had a slightly blue coloration. As the effervescence continued, the liquid became colorless.

Boiling Point.—After the temperature of the alcohol bath surrounding the trap rose to about −42°, the liquid commenced to boil, and it all evaporated within a small temperature range. This suggested that it was either a pure compound or a constant boiling mixture. The latter state of affairs seems unlikely, especially since it was found that the gas could be bubbled through water at about 25° without producing any pronounced change in its properties.

Vapor Density.—By using a modification of the apparatus described by H. P. Cady[3] at the Twelfth Midwest Regional Meeting of the American Chemical Society, it has been possible to determine the density of the vapor at about 25°. As a description of the apparatus will, no doubt, soon appear in the literature, no details need be given at this time. In one case the first fraction of vapor from a sample of the boiling liquid had a density of 81.6 and the last fraction 82.1, the middle fraction being 81.8. Values obtained by three other determinations were 81.7, 82.2 and 82.3. These results were obtained by using samples of liquid which were too small for accurate work, and the author feels that the correct vapor density will eventually be found to be somewhat less than 82.0. The fact that different fractions of the vapor had about the same density constitutes further evidence that the liquid was a nearly pure compound. The material used for the analyses which are to be described was further purified by fractional distillation.

Odor.—The gas had a pungent but characteristic odor which resembled that of oxygen fluoride. When a small amount was inhaled, it irritated the bronchial tubes and lungs and produced continued coughing.

Chemical Reactions and Analysis.—When a test-tube, which had been partially filled with the gas by the displacement of water, was heated with a small flame, an explosion occurred which shattered the glass. However, a mixture of the gas with air exploded less violently, and after the detonation, nitrogen dioxide could be observed in the test-tube.

The compound dissolved appreciably in water, yielding a solution which had the odor characteristic of the gas itself, was able to liberate iodine from potassium iodide but did not give a positive test for hydrogen peroxide with either titanium sulfate or Jorissen's reagent. Although this evidence indicates that the gas dissolved without rapid decomposition, there did appear to be a slow reaction which resulted in the liberation of oxygen. On this account, the substance could not be kept over water for a long period of time.

The gas was absorbed rapidly and completely by a solution of potassium iodide, iodine being set free. In Table I are given the results which were obtained when known volumes of gas were allowed to react, and, after the addition of sulfuric acid, the iodine was titrated with 0.1034 normal sodium thiosulfate. The calculation of the number of moles of iodine set free by one mole of the gas involves the assumption that the substance obeys the perfect gas laws. The samples were collected over water and were different fractions of the vapor coming from a portion of the boiling liquid.

TABLE I

DETERMINATION OF IODINE LIBERATED BY THE GAS

Volume of gas, cc.	25.8	29.4	27.7	27.1
Vol. of thiosulfate, cc.	20.10	22.52	21.10	21.23
Moles I_2 per mole of gas	1.02	1.00	1.00	1.03

From a solution of potassium hydroxide, one volume of the gas liberated one-half volume of oxygen. In two cases the experimentally determined values were 0.503 and 0.488. Although all of the compound was used up within a short time, the reaction did not go to completion at once. For a short time the oxygen was contaminated with a powerful oxidizing agent which had the odor of oxygen fluoride. The alkaline solution, also, contained an oxidizing agent which gave a positive test for hydrogen peroxide. Both of these oxidizing substances eventually decomposed in the presence of the alkali.

The analysis of the compound was accomplished by allowing a measured sample to react with an excess of 10% potassium hydroxide. Qualitative tests indicated the presence of fluoride in the solution. The fact that ammonia was not liberated from the alkaline solution showed the absence of ammonium ion. However, the characteristic ring test obtained by adding dilute sulfuric acid and ferrous sulfate, and subsequently pouring concentrated sulfuric acid under the solution, revealed the presence of nitrogen as nitrate ion but not as nitrite. For this reason it was easy to determine the nitrogen by precipitating the

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[3] H. P. Cady, *Ind. Eng. Chem., News Edition*, **12**, 137 (1934).

nitrate with nitron.[4] Fluorine was determined by precipitation as lead chlorofluoride. In order that the percentage of both nitrogen and fluorine could be calculated, the vapor density of the gas was taken as 82.0. The results are shown in Table II. The letter A represents the number of gram atoms of nitrogen in 22.4 liters of the gas at standard conditions, and B is the corresponding quantity of fluorine.

TABLE II

ANALYSIS OF THE GAS

N, %	F, %	A	B
16.8	23.15	0.984	0.999
17.0	23.13	.996	.998

In addition to one atom of nitrogen and one of fluorine, found by the analyses, each molecule of the gas must have contained three oxygen atoms. This conclusion may be reached by considering the properties of the possible compounds of the elements which could have been present: nitrogen, fluorine, oxygen, hydrogen. A reaction such as that observed in the case of sodium hydroxide could have resulted only from the action of NO_3F or one of its hydrates. However, the vapor density of the gas, about 82.0, permits one to decide that the substance was not hydrated and that its formula was NO_3F, a compound of which the molecular weight is 81.0.

The selection of a good name for this compound is not an easy task. Most of the chemists who have been consulted agree that a correct but not very descriptive name would be nitrogen trioxyfluoride.

Two substances which are related to NO_3F; namely, nitrosyl fluoride[5] and nitryl fluoride,[6] have been known for some time.

The author wishes to thank Professor W. C. Schumb and Dr. N. A. Milas for their interest and helpful advice.

Summary and Conclusions

The reaction of fluorine with moderately dilute nitric acid produces a gaseous compound which has the formula NO_3F. When heated, the gas explodes, but it may be handled without difficulty at room temperatures. The substance has an irritating odor, is colorless and boils at about −42°. It is moderately soluble in water, with which it reacts slowly, liberating oxygen. With solutions of potassium iodide and of potassium hydroxide, it reacts according to the equations

$$NO_3F + 3I^- \longrightarrow I_3^- + F^- + NO_3^- \quad (1)$$

$$NO_3F + 2OH^- \longrightarrow {}^1/_2O_2 + F^- + NO_3^- + H_2O \quad (2)$$

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[4] Busch, *Ber.*, **38**, 861 (1905).

[5] G. Gore, *J. Chem. Soc.*, **22**, 391 (1869).

[6] H. Moissan and P. Lebeau, *Compt. rend.*, **140**, 1576 and 1621 (1905).

CAMBRIDGE, MASS. RECEIVED OCTOBER 13, 1934

[CONTRIBUTION 292 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Integral Heats of Dilution, Relative Partial Molal Heat Contents and Heat Capacities of Dilute Aqueous Sodium Chloride Solutions[1]

BY E. A. GULBRANSEN AND A. L. ROBINSON

I. Introduction

The thermochemical properties of aqueous sodium chloride solutions have been studied extensively recently[2] over rather wide temperature and concentration ranges but except at 25°[3] there are no reliable measurements of heat contents or heat capacities at concentrations below 0.05 *m*. It is in this dilute region that measurements are particularly important for extrapolation to infinite dilution and for comparison with the predictions of current theories of strong electrolytes. In this paper are reported measurements of intermediate heats of dilution of aqueous sodium chloride solutions at 25, 20, 15 and 10° from 0.8 *m* (0.4 *m* at 15 and 10°) to 0.00016 *m* (0.00032 *m* at 10°). From these results integral heats of dilution (ΔH_∞),[4] relative partial molal heat contents ($\bar{L}_1$ and $\bar{L}_2$)[5] and relative partial molal heat capacities ($\bar{c}_{p_2} - \bar{c}^0_{p_2}$) have been calculated for the temperature and concentration ranges of the measurements.

II. Apparatus and Experimental Procedure

A differential adiabatic calorimeter similar to the one

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[1] From the thesis of E. A. Gulbransen presented to the Graduate School of the University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, August, 1934.

[2] Randall and Bisson, THIS JOURNAL, **42**, 347 (1920); Richards and Gucker, *ibid.*, **51**, 712 (1929); and other references.

[3] Robinson, *ibid.*, **54**, 1311 (1932).

[4] The integral heat of dilution is the heat absorbed when a solution containing one mole of solute is diluted to $m = 0$. $\Delta H_\infty = -n_1\bar{L}_1 - \bar{L}_2$ (n_1 is the number of moles of water associated with one mole of solute).

[5] Where possible the nomenclature of Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York City, 1923, is used.