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THE PROPERTIES OF FLUORINE, OXYGEN BIFLUORIDE, AND CHLORINE TRIFLUORIDE

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CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA

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BASIC RESEARCH ON ROCKET PROPELLANTS

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CALIFORNIA INSTITUTE OF TECHNOLOGY, JET PROPULSION, LAB.,
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THE PROPERTIES OF FLUORINE, OXYGEN BIFLUORIDE, AND
CHLORINE TRIFLUORIDE

RUSSELL N. DOESCHER 6 SEPT'49 65PP. TABLES

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FUELS AND
LUBRICANTS (12)
FLUID PROPELLANTS (7)

FLOURINE - PROPELLANT PROPERTIES
FLOURINE COMPOUNDS

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September 6, 1949

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

TABLE OF CONTENTS (Cont'd)

LIST OF TABLES

LIST OF TABLES (Cont'd)

I. INTRODUCTION

During recent years, considerable interest has developed in fluorine and several fluorine compounds as rocket propellant oxidizers. The material presented here is a compilation of certain properties of fluorine, oxygen bifluoride, and of chlorine trifluoride described in the unclassified literature and in other unclassified writing. The properties selected for inclusion are those which might be of interest in connection with the operation of a rocket-motor test cell or propulsion equipment for aircraft or guided missiles employing one of these substances as the oxidizer. Decisions as to which properties should be included have necessarily been arbitrary, and other readers possibly would prefer different sets of properties. Methods of preparation and spectroscopic data have been omitted. The compilation has been limited to unclassified material with the purpose of making it generally available. Nevertheless, the compilation is believed to be fairly complete.

II. FLUORINE

A. Notes on Behavior of Electrolytic Cells for Producing Fluorine

The March 1947 issue of *Industrial and Engineering Chemistry* contains six articles on cells for producing fluorine. Five of these articles deal with the medium-temperature cell, and one deals with the high-temperature cell. The operating procedures are given in some detail, but since the exact procedure to be followed depends upon the design and would be furnished to the persons concerned by the manufacturer, these procedures will not be repeated here. However, several items of general interest in connection with these cells will be mentioned.

It is necessary at all times to maintain the electrolyte in the cell at a temperature above that at which solidification occurs. Thus an adequate heat source must be provided.

Polarization is a troublesome matter. Polarization of anode or cathode can occur, and carbon anode cells are more susceptible than nickel anode cells. Causes of polarization in the medium-temperature cell are nonwetting of carbon anodes (formation of gas film), water in the electrolyte, high current density, low or high hydrogen fluoride concentration, and low or high electrolyte temperature. Nonwetting of carbon anodes can be eliminated by adding a small amount of lithium fluoride. Sodium fluoride or aluminum fluoride can also be used, but these compounds are more easily precipitated than lithium fluoride. Water can be removed from the electrolyte by electrolysis with a nickel anode. Polarization in the high-temperature cell can be eliminated by raising the applied voltage until the current is brought up to its normal value, breaking the circuit when depolarization occurs (indicated by a sudden increase in the current), and connecting the cell with the voltage at the normal value.

Most of the cells described normally operate at 8.0 to 9.5 volts. The voltage tends to rise gradually during the life of the anode because of increasing contact resistance, an increase of about 2 volts indicating the end of the life of the anode in the case of one cell design. For the same case, a maximum contact resistance of approximately 0.04 ohm per blade can be accepted without breaking the carbon. The voltage is of importance in connection with the selection of a generator with the proper voltage range.

A very informative article by Neumark (Cf. Ref. 1) entitled "Electrolytic Fluorine Production in Germany," will be of interest to anyone concerned with the chemistry involved in the operation of fluorine cells.

In the preparation of fluorine in an electrolytic cell employing a graphite anode, CF_4 and other fluorides of carbon are present as contaminants (Cf. Refs. 2 through 5). When the electrolyte contains water, the product contains oxygen bifluoride in appreciable percentages (Cf. Ref. 6). If sulfate is present in the electrolyte, the fluorine is contaminated with SO_2F_2 (Cf. Ref. 3).

According to Ruff (Cf. Ref. 7) if the electrolyte of a fluorine cell contains H_2O, then OF_2 and O_3 occur with the fluorine produced. If the electrolyte contains H_2O, Cl^-, and $SO_4^=$, then a red compound containing oxygen, chlorine, and fluorine (perhaps ClOF) is given off, together with SO_2F_2. Besides, small amounts of colorless substances are produced which do not dissolve in liquid fluorine. These remain as a solid residue after the fluorine has boiled off and are likely to decompose with a shattering explosion if the temperature is raised rapidly.

B. Materials for Handling Hydrofluoric Acid

Anhydrous hydrogen fluoride is made by the fractional distillation of a hydrogen fluoride — water mixture containing 80 per cent HF. This mixture is stored in tanks of mild carbon steel; the column and reboiler are of copper. The anhydrous hydrogen fluoride leaving the still is condensed and cooled in a steel shell-and-tube condenser. The liquid flows through steel lines to mild-steel storage tanks. Monel valves are employed throughout the plant and have rendered good service. Copper is as satisfactory as any available material for the column and reboiler (Cf. Ref. 8).

Mild carbon steel is excellent for handling anhydrous hydrogen fluoride. It is used for storage tanks, pipes, fittings, valves, and pumps. The use of mild carbon steel for this purpose is justified by 12 years of experience. Steel tanks have been found in good condition after 10 years of use for the storage of anhydrous hydrogen fluoride. Apparently corrosion is inhibited by the formation of a protective coating on the surface of the steel. However, steel valves will freeze unless operated at fairly short intervals, apparently because the coating cements the moving parts together. This operating difficulty can be avoided by opening and closing the valves at least twice each shift. Double-valving is necessary. Steels of certain types are more resistant than others to anhydrous hydrogen fluoride. The ideal steel is a thoroughly deoxidized, dead-melted, or milled steel in which nonmetallic inclusions are positively at a minimum. Steel is not resistant to aqueous solutions of hydrogen fluoride containing less than 60 per cent HF (Cf. Ref. 8).

Steel is resistant to aqueous hydrofluoric acid over the HF concentration range 60 to 100 per cent at room temperatures and over the range 70 to 100 per cent at the boiling point (Cf. p. 10 of Ref. 9).

Of all metals, platinum is probably the most resistant to hydrogen fluoride, either anhydrous or in aqueous solution. Silver has excellent resistance when sulfides and appreciable quantities of sulfuric acid are absent (Cf. Ref. 8).

Of all the commercially available nonferrous metals, Monel appears to be the best for hydrogen fluoride, either anhydrous or in aqueous solution. Under certain conditions, copper is almost as good. However, copper is attacked when sulfur dioxide or oxygen is present with the hydrogen fluoride (Cf. Ref. 8).

Brown found that types 430, 347, 309-Cb, 310-Cb, and 304 stainless steel were badly attacked by anhydrous hydrogen fluoride at 1000°F. A high corrosion rate was observed in the case of type 347 stainless steel at 930°F. Nickel was only slightly attacked at 1100°F. Of six samples of Monel exposed to anhydrous hydrogen fluoride at temperatures between 930 and 1110°F, only one was appreciably attacked; the same was true of deoxidized copper. Inconel was found to be less resistant to corrosion than was nickel or Monel under the test conditions, and probably should not be used above 900°F. Aluminum (2S) gave results comparable to those with fluorine. Commercial anhydrous hydrogen fluoride sometimes contains sulfur compounds, and it has been found that if sulfur compounds are present, typical and severe sulfide attack can be expected in high-temperature operation with such metals as nickel, Monel, copper, and Inconel (Cf. Ref. 11).

Anhydrous hydrofluoric acid has no appreciable action on copper or nickel in the absence of oxygen or other oxidizing agent. Stainless steel and Monel are quite resistant. Brass, lead, or soft solder withstands the anhydrous acid, but each is rapidly attacked in the presence of water or oxygen. Steel pipes and valves are satisfactory for the anhydrous acid; in connecting them, threaded joints may be used. If flanges are employed, they should be of forged steel. Welded joints are excellent provided the welds are slag-free. Cast iron or any other material containing silica cannot be used. Numerous difficulties have been experienced in the use of cast-iron fittings. Glass, quartz, porcelain, or any other silica-containing material is rapidly attacked. In general, natural and synthetic resins, gums, plastics, etc. are attacked by the anhydrous acid (Cf. Ref. 10).

Among materials unsatisfactory for use in contact with anhydrous hydrogen fluoride are wood, rubber, most plastics, and materials containing silicon. Lead is serviceable for aqueous hydrogen fluoride solutions containing less than 65 per cent HF, but ordinarily it is unsatisfactory for more concentrated solutions or for anhydrous hydrogen fluoride. Cast iron is more resistant than lead, but it is not a generally satisfactory material. Cast-iron fittings last only a relatively short time (Cf. Ref. 8).

Myers and DeLong (Cf. Refs. 12 and 13) have reported corrosion data for a number of metals exposed to hydrogen fluoride gas at elevated temperatures and at a pressure of approximately 1 atmosphere. The data are given in Table I.

Myers and DeLong have also reported corrosion data for nickel and Monel exposed to equimolar mixtures of hydrogen fluoride and steam at temperatures up to 750°C and at pressure of approximately 1 atmosphere. The data are given in Table II.

C. Analytical Methods

Turnbull et al (Cf. Refs. 14 and 15) have developed a method for the analysis of mixtures of F_2, O_2, HF, and inerts (such as N_2) in which the fraction of F_2 is greater than 0.5. At first, the HF is absorbed in a copper or nickel tube containing sodium fluoride pellets. The gas is then passed into a tube containing anhydrous chemically pure sodium chloride, in which the F_2 is replaced by the equivalent amount of Cl_2. The gas issuing from this tube is passed into cold 2*N* NaOH, which reacts with the Cl_2 to form sodium hypochlorite, and the O_2 and inerts are discharged into the air.

After several minutes of sweeping out the gases present in the system before the start of the analysis, a sample of the gas issuing from the tube containing the sodium chloride is taken for the determination of Cl_2, O_2, and inerts. The Cl_2 is determined by absorption in caustic solution, and the O_2 is determined by passing the gas unabsorbed in the caustic solution into alkaline pyrogallol solution. The residual gas is composed of the inerts. The quantity of fluorine used in the analysis is found by measurement of the amount of chlorine absorbed as hypochlorite plus that taken in the gas sample. The former amount of chlorine is found by titration with sodium thiosulfate of the iodine liberated by the action of potassium iodide and acetic acid on the hypochlorite solution. The HF is determined by maceration of the sodium fluoride pellets in a nickel or platinum dish in the presence of cold neutralized potassium nitrate, which is employed to eliminate any error that would follow from the presence of sodium fluosilicate, and titration with silicate-free sodium hydroxide solution.

TABLE I

CORROSION OF VARIOUS METALS BY ANHYDROUS HYDROGEN FLUORIDE AT ELEVATED TEMPERATURES

Metal	Temperature (°C)	Penetration Rate of Corrosion (in./month)
Steel		
SAE 1020	500	0.051
Type 430 stainless steel	500	0.005
	550	0.030
	600	0.038
Type 347 stainless steel	500	0.6
	550	1.5
	600	0.58
Type 309-Cb stainless steel	500	0.019
	550	0.14
	600	0.55
Type 310 stainless steel	500	0.040
	550	0.33
	600	1.0
Type 304 stainless steel	600	0.044
Nickel and alloys		
Nickel	500	0.003
	600	0.003
Monel	500	0.004
	550	0.004
	600	0.006
Inconel	500	0.005
	600	0.005
Aluminum (2S)	500	0.016
	600	0.048
Copper	500	0.005
	600	0.004
Magnesium (Dow metal G)	500	0.042

Kimball and Tufts (Cf. Ref. 16) have developed a method for the analysis of fluorine gas. The parts of the apparatus coming in contact with fluorine are chiefly of brass, copper, nickel, and Monel. The valves are packed with Teflon. The authors describe methods for sampling at high pressures and at low or "negative" pressures.

The sample is passed through a tube containing anhydrous sodium fluoride to absorb the hydrogen fluoride, and the hydrogen fluoride is determined by titration. Then, by passing the gas over dry sodium chloride, the amount of Cl_2 equivalent to the F_2 in the original sample is produced. A routine analysis and a precision analysis are described. The routine analysis gives the percentages of F_2, HF, O_2, and inerts; the precision analysis gives the percentages of F_2, HF, O_2, CO_2, CO, H_2, and inerts. In the routine analysis, inaccuracies are introduced from various sources. Kimball and Tufts state that they have never found either CO or H_2 in analyzing fluorine.

TABLE II

CORROSION OF NICKEL AND MONEL BY EQUIMOLAR MIXTURES OF HYDROGEN FLUORIDE AND STEAM AT ELEVATED TEMPERATURES

Metal	Temperature (°C)	Penetration Rate of Corrosion (in./month)
Nickel	550	0.0026
	600	0.006
	650	0.009
	700	0.012
	750	0.010
Monel	600	0.002
	650	0.005
	700	0.013
	750	0.017

In the precision analysis, the Cl_2 is determined by absorption of a large sample in an alkaline arsenite solution and determination of the chloride by the Volhard method. The sample is made large in order that a sample of the residual gases adequate for the determination of the minor impurities can be collected. Any CO_2 present is also absorbed in the alkaline solution, and it is determined by an evolution method. The application of this method to samples containing known amounts of CO_2 gave the following results:

Weight of CO_2 Present (mg)	Weight of CO_2 Found (mg)
27.0	27.2
44.7	45.1

In the case of the precision analysis, the residual gases are analyzed in any standard gas analysis apparatus. In the case of the routine analysis, the Orsat apparatus is used for the analysis of the residual gases.

D. Products of Reaction of Fluorine with Water and With Certain Solutions

Brunner (Cf. Ref. 17) states that fluorine reacts with water, forming oxygen and ozone. Fichter and Humpert (Cf. Ref. 18) report that the treating of a sulfate solution or a bisulfate solution with fluorine leads to the formation of persulfate with the vigorous evolution of ozonized oxygen, and hydrogen peroxide never results; however, fluorine with pure water produces largely hydrogen peroxide with a relatively small evolution of gas when the water is between 0°C and room temperatures.

Fichter and Bladergroen (Cf. Ref. 19) studied the reaction between fluorine gas and liquid water. In an experiment in which the water was stirred in a platinum dish cooled with ice, they found that hydrogen peroxide was present in a varying concentration, dependent upon the fluorination time. The concentration reached a maximum at about 20 minutes after the start of the fluorination and declined afterward. Ozone was present, and the quantity increased after this maximum had been reached. Fichter and Bladergroen attributed these variations to the following reaction:

$$H_2O_2 + O_3 \rightarrow H_2O + 2O_2$$

Cady (Cf. Ref. 20) reports that hydrofluoric acid, hydrogen peroxide, oxygen, and oxygen fluoride are formed in the reaction of fluorine with cold water. He concludes, however, that if ozone is a product, its importance as such has been overstressed.

In the preparation of potassium persulfate by the oxidation of potassium bisulfate in a cold saturated aqueous solution with fluorine, the solution evolves ozone rapidly, according to Fichter and Humpert (Cf. Ref. 21). They state that they observed the copious evolution of ozonized oxygen during the oxidation of ammonium bisulfate to ammonium persulfate in a saturated solution with fluorine (Cf. Ref. 22). Later, Fichter and Bladergroen (Cf. Ref. 23) reported that treating solutions of sulfates or of bisulfates with fluorine results in the formation of persulfate and ozone. Jones (Cf. Ref. 24) found that when fluorine acts upon a cold saturated aqueous solution of potassium bisulfate or of ammonium bisulfate, the corresponding persulfate is formed together with some ozone and other products.

Fichter and Goldach (Cf. Ref. 25) found that the introduction of fluorine into silver nitrate solutions results in the formation of oxygen, ozone, and silver peroxynitrate.

Briner and Tolun (Cf. Ref. 26) report that when fluorine was allowed to react with water at 0°C, no ozone could be detected in the gases produced. They report also that, when fluorine was allowed to react with aqueous potassium hydroxide solutions at -5°C, the gases produced contained about 1 per cent ozone. A solution of hydrogen fluoride, sulfuric acid, or potassium nitrate cooled below 0°C did not give ozone.

E. Purification

Froning et al (Cf. Ref. 27) have developed a process for the reduction of the hydrogen fluoride content of the impure fluorine from a cell, in which the gas mixture was first cooled to -70°C at atmospheric pressure and then passed through a tower containing sodium fluoride pellets. Sodium fluoride has been employed for hydrogen fluoride absorption since the days of Moissan. Before a plant method was developed, the vapor pressure characteristics of such a system were investigated by determining the vapor pressure of sodium acid fluoride in the presence of nitrogen. These data are summarized in Table III.

TABLE III
VAPOR PRESSURE OF SODIUM ACID FLUORIDE

Temperature (°C)	Vapor Pressure of Hydrogen Fluoride over NaF·HF (mm)	Hydrogen Fluoride in Nitrogen (vol %)
25*	0.01	0.001
100*	1.4	0.18
200	87	11.5
250	422	55.6
275	706	93.0
278*	760	100.0

**Value obtained by extrapolation.*

The data indicated that hydrogen fluoride could be largely removed from a fluorine stream by sodium fluoride at 100°C. Pilot plant performance confirmed this fact. Temperatures below 100 C were not employed, because semifluid polyacid fluorides tended to form and plug the reaction bed.

It was found that sodium fluoride pellets absorbed up to 1 mol of HF per mol of NaF with practically 100 per cent efficiency. The partial pressure of hydrogen fluoride in the exit gas rose only very slightly before this quantity had been absorbed.

A tower containing 1/8-inch sodium acid fluoride pellets (obtained from Harshaw Chemical Co.), 3 inches in diameter and 4 feet high, was swept with nitrogen at temperatures between 275 and 300°C, to remove all of the hydrogen fluoride except about 0.02 per cent. The sodium fluoride formed was used to treat fluorine containing 4 volume per cent of hydrogen fluoride at the rate of 1.5 lb/hr. Such a tower was taken through five 60-hour cycles of alternate absorbing and regenerating approximately 12 weight per cent of hydrogen fluoride; deterioration of the pellets was not sufficient to increase resistance to gas flow.

Copper oxide wire may be used to remove ozone from the fluorine delivered from an electrolytic cell, since it is not affected by the fluorine but decomposes quantitatively any ozone present (Cf. Ref. 5).

F. Liquefaction

Fluorine can be fairly easily liquefied at low temperatures, and it can then be placed in containers under pressure by re-evaporation. A large quantity of liquid nitrogen is required, however, and the cost of the labor is high. This method has been employed on a considerable scale for packaging fluorine in small cylinders under pressures of several hundred pounds per square inch (particularly by the du Pont Co.), but so far it has been considered safe to liquefy only a few pounds at one time, and the procedure is slow (Cf. Ref. 28).

In one series of experiments in which fluorine was condensed in a nickel container holding 6.75 pounds of the liquid, 7 pounds of liquid nitrogen was required per pound of fluorine, on the average (Cf. Ref. 27).

In describing the liquefaction of fluorine from an electrolytic cell, Neumark (Cf. Ref. 1) states that the fluorine gas from the cell was passed through a nickel coil at 300°C in order to destroy such "potentially explodable" substances as O_3 and O_2F_2. The gas was then passed through a cooler and through a trap cooled with liquid oxygen in order to remove hydrogen fluoride. Finally the fluorine was condensed in a glass flask cooled with liquid nitrogen. There was a sulfuric acid pressure regulator at the end of the train; by raising or lowering the liquid nitrogen Dewar flask, a pressure a little above that of the atmosphere was maintained in the system. Thus no air could enter the system through leaks.

Steel cylinders were charged with fluorine by distillation from the glass flask to the cylinder. The cylinder was evacuated after being carefully cleaned of all traces of moisture, scale, and organic matter. It was then placed in a Dewar container with liquid nitrogen. A copper tube and ground joints were used to connect the flask with the cylinder. A metal gage and a diaphragm valve were used. The distillation was controlled by slowly removing a Dewar flask from the flask containing the fluorine. Cylinders charged in the manner described were shipped and were used for more than 3 years in Germany without trouble.

G. Characteristics of Reactions Between Fluorine and Certain Substances

Simons (Cf. Ref. 29) points out that, although the fluorine molecule is very stable, it is extremely reactive under the proper conditions. For this reason reactions of the element are difficult to control, and catalysts are important in these reactions. The reaction between fluorine and hydrogen involves a relatively large amount of energy, but this reaction is difficult to control. In measuring the heat of this reaction, it was found necessary to use an electric discharge at the site of the flame in order to prevent flame extinction and subsequent explosion.

Aoyama and Kanda (Cf. Ref. 30) investigated experimentally the reaction between solid fluorine and liquid hydrogen. A violent explosion occurred in one experiment, and only a mild explosion if any, in the others. All of the experiments were conducted outdoors, and light was allowed to reach the elements in contact with each other. No explosion occurred when the gaseous elements were mixed in a large glass container at ordinary temperatures, even when the container was exposed to sunlight or to the light from a mercury lamp, except occasionally when the wall of the container was new. Fluorine fresh from the generator was found more likely to react than fluorine which had been first liquefied and then vaporized.

Bodenstein and Jockusch (Cf. Ref. 31) studied the reaction between fluorine and hydrogen in glass, quartz, and silver. In new glass at -190°C, the pressure decreased from 500 to 470 mm in 30 minutes. In used glass at -190°C, evacuated at -190°C, the pressure decreased from 500 to 485 mm in 30 minutes. In used glass at -190°C, evacuated when hot, the mixture exploded. In used glass at 20°C, the pressure decreased one half in about 100 minutes. In quartz at -80 and at -190°C, there was a shattering explosion within a few seconds, regardless of which element was introduced first. At 20°C, when the fluorine had stood for 20 minutes in the quartz and was removed, and the hydrogen introduced first, the reaction resembled that in glass. In silver with a film of silver fluoride (AgF) at 20°C, there was an explosive reaction; at -190°C the reaction was slow.

Mixtures of carefully dried hydrogen and fluorine are nonreactive, even under the influence of ultraviolet light (Cf. Refs. 32 and 33). Bodenstein, Jockusch, and Shing-Hou-Chang (Cf. Ref. 34) report that very little reaction occurred between fluorine and hydrogen in a magnesium vessel at room temperature and at a pressure less than atmospheric. Ultraviolet radiation caused no reaction in the magnesium vessel at -78°C. The addition of a moderate amount of chlorine to a mixture of fluorine and hydrogen in the magnesium vessel caused no reaction. The authors have not stated their conditions completely. Fluorine and hydrogen reacted with a measurable velocity at -78°C in a quartz vessel into which ultraviolet light was passed. In a platinum vessel at -78°C with no illumination, the reaction began slowly and gradually died out. The authors conclude that the reaction was wall-catalyzed. The velocity was increased by ultraviolet radiation, but the effect was weak. The reaction was irregular.

Eyring and Kassel (Cf. Ref. 35) describe experiments in which the reaction between hydrogen and fluorine was inhibited. Fluorine obtained from a generator of the usual type was conducted to the center of a 3-liter flask by means of copper tubing. Also hydrogen and nitrogen from tanks could be introduced near the center, and an exit tube was provided. The usual procedure was to flush the flask with nitrogen, admit one of the reactant gases, and then admit the other. Eyring and Kassel never observed a steady flame where the gases mixed. They sometimes observed flashes from the copper tubing. In some experiments, no reaction occurred for several minutes; then there was a mild explosion, sufficient only to blow the rubber stopper out of the flask. In one experiment, they admitted the hydrogen and then a quantity of fluorine much larger than usual, but there was no indication of reaction. They waited 1/2 hour and started a rapid flow of nitrogen with the intention of sweeping the mixture out of the flask. Immediately there was a very violent explosion. The flask was shattered, a towel which had enclosed the flask was cut into shreds, and a protective screen made from glass containing wire was cracked in many places. The experimenters presume that the explosion was started by sulfur, talc, or other catalytic material from the rubber tubing of the nitrogen supply line. They point out that for 1/2 hour before the explosion, there must have existed a mixture of hydrogen and fluorine varying in composition between 100 per cent hydrogen and 100 per cent fluorine without appreciable reaction.

No reliable catalyst for initiating the reaction between hydrogen and fluorine has been found (Cf. Refs. 14 and 15).

Generally, the reactions of elementary fluorine involve relatively large activation energies. On the other hand, it has strong affinities for most of the other elements. Consequently, after a reaction has started, it proceeds very rapidly. A mixture can be made up of fluorine and some substance with which it will react, and a small stimulus can cause the mixture to explode. For example, fluorine can be mixed with carbon tetrachloride vapor without an explosion occurring, but heating the mixture or an electrical spark causes a shattering explosion (Cf. Ref. 7).

In an experiment performed by Ruff and Keim (Cf. Ref. 36), fluorine was conducted through a glass tube into liquid carbon tetrachloride in a glass vessel fitted with a condenser. The gases escaping passed through the condenser (which kept back the carbon tetrachloride vapor) and were then condensed in two receivers, one at about -120°C and the other at about -190°C. No significant reaction was evident at room temperature or upon heating to 40 or 50°C. However, when the fluorine was conducted in while the carbon tetrachloride was being boiled, violent explosions occurred after some time, shattering the vessel.

Some of the reactions of fluorine often have erratic rates. Fluorine usually reacts vigorously with water, either as the vapor or the liquid, the products being hydrofluoric acid and oxygen, but an unexplained inhibition has been observed frequently. A mixture of water vapor and fluorine may be formed until an explosion occurs. Inhibition has been observed in reactions between fluorine and organic matter, particularly with fluorine at pressures near 1 atmosphere (Cf. Ref. 37).

The reaction between water and fluorine can occur in two ways: (1) a reaction at the gas-liquid interface, in which a purple flame is evolved, and (2) a reaction slower than the first, in which no flame is evolved. The second reaction is actually quite rapid, a hundred fold decrease in fluorine concentration occurring in a contact time of 4.5 seconds, and a thousand fold decrease occurring in a contact time of 6.9 seconds. This slow reaction can be replaced by the burning reaction through the addition of small amounts of volatile alcohols to the water. Violent explosions occur when the slow or nonburning reaction is suddenly replaced by the burning reaction (Cf. Refs. 14 and 15).

When fluorine at high pressure is suddenly released under such conditions that it reacts with neighboring substances or with water vapor, a flame similar to that of a high-current electrical flare is produced (Cf. Ref. 37).

Fichter and Goldach (Cf. Ref. 38) found that if fluorine gas is passed into a solution of ammonia or ammonium carbonate in small bubbles and is finely dispersed by means of a high-speed stirring device, some of the fluorine escapes unreacted.

According to Bancroft and Jones (Cf. Ref. 39), "when fluorine is brought in contact with benzene vapor there is an induction period, after which the reaction goes explosively." Delayed reaction has been observed with chloroform vapor and fluorine and with acetylene tetrachloride vapor and fluorine at room temperatures (Cf. Ref. 40).

Aoyama and Kanda (Cf. Ref. 41) state that the "solubility" of chlorine in liquid fluorine at -195°C is 1.04 per cent.

H. Materials for Various Purposes in Apparatus Handling Fluorine

Iron is not satisfactory as the material for the body of the high-temperature fluorine cell (Cf. Ref. 42), but Monel is suitable (Cf. Ref. 43). Fowler et al (Cf. Ref. 44) report that Monel was found to be the only satisfactory material for the skirt and riser tubes (in contact with fluorine) in the high-temperature cell. Copper was not satisfactory for parts exposed to the electrolyte.

Copper has been employed in fluorine cells, but it is attacked somewhat by the electrolyte (Cf. Ref. 24). Used for the pot and diaphragm, magnesium is said to resist very well the action of the hot electrolyte, even though the pot serves as the cathode. A thin adhering coat of magnesium fluoride forms on the surface and is insoluble in the hot electrolyte. Magnesium is considered superior to copper for this application. In the cell constructed by Bancroft and Jones, the magnesium showed no corrosion after use of more than a year (Cf. Refs. 24 and 39).

In experiments in Germany with various metals as fluorine cell cathode materials, it was found that nickel corroded considerably without current flow and that the corrosion deposit tended to blister. The electrolyte had approximately the composition expressed by $KF \cdot HF$, and the temperature was 250°C. The corrosion rate was 28 gm/sq m day, but with a current density of 45 amp/sq ft the rate was approximately 5.5 gm/sq m day (Cf. Ref. 1).

Magnesium corroded badly, expecially at the liquid level line, when the current was flowing, but a dense coating of magnesium fluoride protected the metal underneath when no current was flowing. Magnesium and an alloy containing 98 per cent magnesium and 2 per cent manganese proved to be the materials most resistant to attack under the conditions specified (Cf. Ref. 1).

In using cast nickel for the body of a fluorine generator, Miller and Bigelow found that this metal was almost unaffected by corrosion, even though the cell operated at temperatures between 250 and 300°C (Cf. Ref. 45).

It is reported that Moissan and Dewar liquefied fluorine in 1897, using liquid oxygen. Glass, silicon, finely divided carbon, sulfur, and powdered iron are said not to have reacted with fluorine at the boiling point (Cf. Ref. 28).

Fluorine can be safely handled in iron pipe at room temperatures and atmospheric pressure (Cf. Refs. 37 and 46). There is no appreciable attack except for the formation of scale and some corrosion at the exit end in case atmospheric moisture can come in contact with it. This statement applies to copper tubing also. The metal fluoride deposit which forms protects the metal underneath from attack, but in pipes subject to bending or vibration, the deposit may become dislodged and accumulate at points of restriction. Oxide scale, sometimes present in new iron pipe, forms a powdered fluoride, which may cause stoppages (Cf. Ref. 46). Where equipment is contaminated with organic material or water, combustion of this material in the fluorine can cause ignition of the metal. After the metal is ignited, it burns as long as the fluorine is supplied (Cf. Refs. 27, 37, and 46). If the fluorine is at a high pressure, bursting of the pipe creates a situation very dangerous to personnel, the fluorine, molten metal, and reaction products being spread over a relatively large region. Even if the metal does not ignite, difficulties result from fouling and plugging of the system (Cf. Ref. 27). Where the wall of the pipe is at least as heavy as that of standard pipe, spontaneous combustion will not occur in the absence of contaminants except in very unusual cases (Cf. Ref. 37).

Landau and Rosen (Cf. Ref. 37) report the results of experiments on the effects of fluorine on contaminated systems. These results are presented in Table IV.

TABLE IV

EFFECTS OF FLOWING FLUORINE ON A CONTAMINATED SYSTEM

Tube	Pure Fluorine at 50 psig		Gas Containing 20% Fluorine	
	Orifice 3/8 in.	Orifice 1/8 in.	Tank Pressure	Orifice 1/8 in.
Clean brass	no reaction	---	---	---
Clean copper	no reaction	---	---	---
Clean stainless steel	no reaction	---	---	---
Brass, 1/4 in. D, 1/16-in. wall, oil-covered	heated to red heat, no burning	---	---	---
Copper, 3/8 in. D, oil-covered	burning as long as gas flowed	burning as long as gas flowed	50 psig	no reaction
Stainless steel, 3/8 in. D, 1/16-in. wall, oil-covered	heated to red heat, no burning	heated to red heat, no burning	---	---

Nickel is known to be less reactive to fluorine than steel is at pressures near 1 atmosphere. Though pipes of steel, copper, and brass have been used successfully (Cf. Ref. 27), Monel or nickel is recommended for applications in which the formation of fluoride scale is objectionable or in which the temperature of the pipe may be elevated (Cf. Ref. 46). Of the metals which are useful for fluorine piping, those having the lower corrosion rates at atmospheric pressures have the higher kindling temperatures (Cf. Ref. 27). Brass is more resistant than steel (Cf. Ref. 27), and lead is unsafe even for gaskets (Cf. Refs. 27 and 46).

In an article which appeared in March 1947, Landau and Rosen (Cf. Ref. 37) wrote: "The use of Monel or nickel for piping is preferable for the handling of pure fluorine, particularly under pressure. Commercial large scale experience to date has not involved the extensive piping of fluorine at pressures above 30 pounds per square inch gage and the use of Monel pipe for this service has been very satisfactory. Present evidence is that Monel piping can be used safely at even higher pressures."

Experience has demonstrated that welded joints are better than joints made with flanges or by threading at any pressure, but in case joints must be capable of easy disassembly, as where provisions must be made for repairs or other operating procedures, flanges should be used. Only a few materials are suitable for gaskets. Soft copper or aluminum can be used, or Teflon in the case of low pressures. For mixtures of fluorine and inert gases containing less than 20 per cent fluorine, clean Butyl or Neoprene gaskets can be employed, provided the surface of contact between the gasket and the gas is relatively small and the joint is not frequently broken. Most rubbers lose strength rapidly upon exposure to fluorine; for this reason it is desirable to replace a rubber gasket (other than Butyl) each time the joint is formed. A copper-jacketed asbestos gasket also can be used for these mixtures (Cf. Ref. 37). Froning et al (Cf. Ref. 27) recommend annealed copper for gasketed joints. The seating surfaces should not have nicks and should be aligned carefully.

According to Froning et al (Cf. Ref. 27), the use of threads for joints at atmospheric pressure is practical, provided the minimum amount of lute for lubrication is used. The least reactive lute that has been applied is a paste made from powdered fluorspar and a fluorocarbon. Threaded joints for high pressure are back-welded as a routine matter, but steel-to-brass threaded joints have never required back-welding when the threads have been in good mechanical condition. The formation of a seal without a lute is supposed to result from the relationship between the resiliencies of these two metals. Landau and Rosen (Cf. Ref. 37) state that threaded joints are unsatisfactory. They add that if threaded joints must be used, lute should be applied sparingly and not to any parts of the thread which might be exposed to fluorine. They also recommend the paste made from powdered fluorspar and a fluorocarbon. Systems containing welded joints have been found almost as flexible as those containing flanges or threaded joints, since a good welder can cut and weld a pipe in a short time.

In one instance, it was observed that no leaks had occurred in certain standard-taper, pipe-thread joints between brass valves and steel cylinders which had been under pressure constantly for more than 2 years. However, it was necessary to devise a gasket-sealed joint for nickel cylinders, apparently because the resilience of nickel is less than that of steel (Cf. Ref. 27).

The desirability of welded joints is greater in the case of operations with fluorine at high pressures than in the case of operations at pressures near 1 atmosphere. Metal gaskets alone are satisfactory for flanges used at high pressures. Under these conditions, all joints should be of massive construction with ring-type copper or aluminum gaskets. A gasket should not be used again after the joint is disassembled. The use of nickel or Monel for retaining fluorine under high pressure is highly desirable, because these metals do not take fire easily. Containers for the storage of fluorine under high pressure should be isolated in concrete rooms which are adequately ventilated (Cf. Ref. 37).

Fluorine has been stored at room temperatures and pressures up to 20 atmospheres in nickel cylinders having capacities of 3, 5, and 12 liters. Upon opening these cylinders after a year of use, it was found that in each case the inside surface consisted of a thin uniform film of nickel fluoride, which evidently acted as a protective coating (Cf. Ref. 47).

In a patent, Priest and Grosse (Cf. Ref. 48) have described a tank for holding fluorine, made from copper, nickel, or a copper-nickel alloy with a copper content in excess of 60 per cent. The fluorine can be stored at pressures up to 200 psi in the tank. Charging may be accomplished by passing the fluorine through a trap in dry ice, causing it to condense in a trap immersed in liquid nitrogen, and distilling it from the latter trap into the tank. A helium atmosphere is used to prevent condensation of air in the liquid fluorine in the trap.

Froning et al (Cf. Ref. 27) give information with regard to protective barriers. It has been found that steel plate 1/4 inch thick is satisfactorily resistant to an impinging fluorine stream. If a line carrying fluorine at high pressures must be placed less than 6 inches from a wall, or if reservoirs containing more than 5 pounds of fluorine or pressures greater than 400 psi are to be employed without further field tests, a brick structure is recommended. Although fluorine readily attacks brick after ignition, penetration occurs slowly. Concrete loaded with fluorspar has been found much more resistant than brick.

Nickel and Monel have excellent resistance to fluorine at low and high temperatures. Aluminum and magnesium have good resistance. Iron and steel are much less resistant, particularly at 900°F and above. The excellence of nickel and Monel is due to the nature of the fluoride coating, which is adherent rather than powdery. The nickel fluoride coating is invisible, whereas the iron fluoride coating is green and powdery (Cf. Ref. 37). Mild steel in contact with fluorine begins to burn at about 500°C, but the temperature depends somewhat upon the thickness of the steel (Cf. Ref. 49).

Data on the corrosion of various metals by fluorine under many conditions are reported by Brown, by Landau and Rosen, and by Myers and DeLong. The data in Table V are given by Brown (Cf. Ref. 11). All the types of stainless steel tested by Brown were quite severely attacked by fluorine at temperatures above 400 to 500°F. Nickel appears to be quite resistant to corrosion up to 900°F and probably to about 1000°F, according to Brown. Corrosion rates for Monel were more erratic and generally higher than those for nickel, and the limiting temperature for useful service should probably be given as 50 to 100°F lower. Inconel is considerably less resistant, and it is definitely unsuitable at 750°F, the lowest temperature at which it was tested. Under the test conditions aluminum (2S) was essentially unaffected up to 850°F and could probably be used at somewhat higher temperatures, aside from mechanical limitations. Copper was found to be more resistant to fluorine than to chlorine and proved quite useful in service, although it was inferior to either nickel or Monel. Magnesium (Dow metal G) was unattacked up to about 575°F.

The fluorine used in the tests conducted by Brown was prepared in a laboratory generator and contained traces of oxygen. Prior to entering the heating tube, the fluorine was cooled to approximately -80°C. The fluorine pressure was approximately 1 atmosphere. Generally the period of exposure was 2 or 3 hours, but some tests were made of durations between 3 and 15 hours. Longer periods had no apparent influence upon the results.

In Brown's experiments, different lots of steel displayed great variations in the resistance to corrosion by fluorine. He traced these variations to the difference in silicon content. The ratio of the corrosion rate for fully killed steel, having a silicon content of the order of 0.20 per cent, to the rate for rimmed steel, normally containing less than 0.01 per cent silicon, can be as high as 100. Steel having a very low silicon content is satisfactorily resistant at temperatures up to approximately 700°F, whereas steel containing 0.22 per cent silicon used in the tests was quite badly attacked at 400°F. At 930°F, the silicon content was no longer a controlling factor, all steel samples being very severely attacked at this temperature.

TABLE V

CORROSION OF CARBON STEELS BY FLUORINE

Steel	Temperature (°C)	Penetration Rate of Corrosion (in./month)
Armco iron	200	0.0002
	350	0.0082
	400	0.236
	450	0.300
	500	11.6
SAE 1020 (0.22% Si)	200	0.0377
	250	0.480
	300	0.920
	350	0.145
	400	0.680
	450	1.52
	500	14.9
Mild steel (0.007% Si)	200	0.0000
	250	0.0161
	300	0.0044
	400	0.0114
	450	0.300
	500	7.4
0.27% C steel (trace of Si)	200	0.0006
	250	0.0079
	400	0.153
	450	0.540
	500	19.8

The corrosion rates obtained by Brown for copper were higher than those observed in practice, but the difference is believed to be due to traces of oxygen in the fluorine. It was observed that the coating formed on the copper was at least partly oxide.

The data presented in Table VI are given by Landau and Rosen (Cf. Ref. 37).

The data given in Table VII are taken from Myers and DeLong (Cf. Refs. 12 and 13). In the tests corresponding to these data the pressure of the fluorine was approximately 1 atmosphere. The duration of exposure was about 4 hours in most cases. The longest time was approximately 15 hours. No significant decrease of corrosion with time was observed.

The composition of the carbon steels used is given in Table VIII. An examination of the corrosion data together with the compositions indicates that the silicon content profoundly affects the corrosion behavior at temperatures up to about 400°C. Carbon steels having a silicon content less than 0.01 per cent resist fluorine well at these temperatures, whereas a silicon content of 0.07 per cent or greater increases the corrosion rate materially. The corrosion rates for carbon steels are so large above 400°C that these materials are useless for handling fluorine at such temperatures.

TABLE VI

CORROSION OF VARIOUS METALS BY FLUORINE

Metal	Time of Exposure (days)	Temp (°F)	Pressure of Fluorine (atm abs)	Corrosion Rate		Remarks
				(mg/sq ft day)	(in./month)	
Steel						
Armco iron	20	167	1	33		
		930	1		11	initial
SAE 1010	6	167	1	1.25	--	initial
				0.1	--	final
Low-silicon iron (0.004% Si)	1	392	0.5	187	--	
High-silicon iron (0.79% Si)	--	392	0.5	324	--	
Nickel and alloys						
Nickel foil	2	140	0.03	0.5	--	probably high
Monel weld	4	125	1	--	--	no evidence of corrosion or embrittlement
Monel tubing	10	250	1.3	--	--	no noticeable attack
Nickel sheet	--	930	1	--	0.006	weight gain
	--	1290	1	--	0.1	weight gain
Monel sheet	--	930	1	--	0.02 (max)	after cleaning
		1290	1	--	0.02	after cleaning

TABLE VI (Cont'd)

Metal	Time of Exposure (days)	Temp (°F)	Pressure of Fluorine (atm abs)	Corrosion Rate		Remarks
				(mg/sq ft day)	(in./month)	
Aluminum						
Foil	6	309	1	0.41	--	initial attack higher
Sheet	--	930	1	--	0.04	max of several values
	--	1110	1	--	0.06	max of several values
Copper and alloys						
Foil	2	140	0.03	0.6	--	probably high
Wool	--	200-250	1	--	--	caught fire
Sheet	--	930	1	--	0.02	
	--	1290	1	--	3	
Brass (70-30) sheet	2	140	0.03	1.3	--	probably high
Bronze	2	140	0.03	0.8	--	probably high
Cu-Ni (80-20)	2	140	0.03	1.0	--	probably high
Magnesium alloys (Revere sheet)						
MA (1.2% Mn)	2	140	0.03	0.7	--	
FS-1A (3% Al, 1% Zn, 0.2% Mn)	2	140	0.03	1.5	--	
J-1H (6% Al, 0.7% Zn, 0.2% Mn)	2	140	0.03	1.4	--	
Chromium						
Plate (0.03 in. on SAE 1020)	1	302	1	--	--	no visible sign of attack

TABLE VII

CORROSION OF VARIOUS METALS BY FLUORINE

Metal	Temperature (°C)	Penetration Rate of Corrosion (in./month)
Steel		
Armco iron	200	0.0000
	250	0.002
	300	0.009
	350	0.008
	400	0.024
	450	0.3
	500	11.6
SAE 1020 (0.22% Si)	200	0.038
	250	0.48
	300	0.66
	350	0.147
	400	0.54
	450	1.52
SAE 1030 (trace of Si)	200	0.002
	250	0.008
	300	0.009
	350	0.0000
	400	0.015
	450	0.54
	500	19.8
SAE 1030 (0.18% Si)	300	0.75
SAE 1015 (0.07% Si)	300	0.83
Sheet steel (0.007% Si)	200	0.0000
	250	0.016
	300	0.004
	350	0.0002
	400	0.012
	450	0.30
	500	7.4
Music wire (0.13% Si)	300	0.40
Type 430 Stainless steel	200	0.0007
	250	0.0000
	300	0.255
	350	0.078
	400	0.078
Type 347 stainless steel	200	0.0000
	250	0.145
	300	0.213
	350	0.517
	400	0.795

TABLE VII (Cont'd)

Metal	Temperature (°C)	Penetration Rate of Corrosion (in./month)
Steel		
Type 309-Cb stainless steel	200	0.0000
	250	0.0000
	300	0.075
	350	0.462
	400	0.665
Type 310 stainless steel	200	0.0000
	250	0.0000
	300	0.031
	350	0.354
	400	0.561
Nickel and alloys		
Nickel	400	0.0007
	450	0.0019
	500	0.0051
	600	0.029
	650	0.016
	700	0.034
Monel	400	0.0005
	450	0.0015
	500	0.002
	600	0.060
	650	0.080
	700	0.15
Inconel	400	0.038
	450	0.096
	500	0.062
	600	0.17
	650	0.13
	700	0.51
Aluminum (2S)	400	0.0000
	450	0.0000
	500	0.013
	600	0.018
Deoxidized copper	400	0.16
	500	0.12
	600	0.99
	700	2.9
Magnesium (Dow metal G)	200	0.0000
	250	0.0000
	300	0.0000

TABLE VIII

COMPOSITION OF CARBON STEELS USED

Steel	Composition (%)				
	Carbon	Manganese	Silicon	Sulfur	Phosphorus
Armco iron	--	--	--	--	--
SAE 1020	0.192	1.00	0.22	0.033	0.024
SAE 1030	0.27	0.50	trace	0.031	0.014
SAE 1030	0.27	0.62	0.18	0.025	0.018
SAE 1015	0.15	0.62	0.074	0.023	0.012
Sheet steel	0.042	0.30	0.007	0.055	0.020
Music wire	0.93	0.54	0.13	0.031	0.030

None of the stainless steels tested is satisfactory for handling fluorine at temperatures above 250°C. The corrosion rate of type 347 was high at even this temperature. Probably the presence of silicon is partly responsible for the poor resistance of the stainless steels. The wrought stainless alloys usually contain approximately 0.5 per cent silicon.

Fluorine from cells of the type employed contains some oxygen, and Myers and DeLong suspect that high rates in some cases, particularly in that of copper, were due to oxygen in the fluorine. The corrosion products formed on the copper specimens were black and friable, suggestive of cupric oxide.

Information regarding the behavior of nonmetallic substances in contact with fluorine is available from a number of sources. Landau and Rosen (Cf. Ref. 37) give the information presented in Table IX.

If lubricated with a fluorocarbon oil, vacuum pumps can be used on diluted fluorine. Laboratory pumps such as the Cenco have been so used. The F.J. Stokes Machine Company and the Beach-Russ Company have made pumps which handle diluted fluorine, with capacities up to 100 cu ft/min, for plant use (Cf. Ref. 37).

Teflon is unaffected by exposure to hydrogen fluoride at temperatures in the neighborhood of 100°C, but it may be severely corroded by fluorine gas at these temperatures, especially at points where good thermal release is not provided (Cf. Ref. 46). Myers and DeLong (Cf. Refs. 12 and 13) used Teflon gaskets and Teflon-packed valves in an apparatus in which corrosion rates of various metals in fluorine gas were measured. Apparently the Teflon was at or near room temperatures.

According to Landau and Rosen (Cf. Ref. 37), a material described as "fireproof neoprene on a fiber glass base", developed by the B.F. Goodrich Company for hangar curtains, has proved satisfactory in resisting fluorine blasts of 8 liters at 40 psig at zero distance. Similar materials produced by other companies failed under conditions similar to these. The B.F. Goodrich Company has designated the satisfactory material as ECC-11-128-44000 (misc.) fabric. All the cemented seams tested except one developed by the same company burned vigorously upon exposure to blasts of fluorine. The cement of the resistant seam was the original coating material of the ECC-11-128-44000 (misc.) fabric. For the best results, the final product should be cured after the seam has been made. In discussing industrial experience with fluorine in Germany, Neumark (Cf. Ref. 1) states that rubber was found to withstand fluorine gas very well in a dead space, being ignited in flow only.

TABLE IX

EFFECTS OF FLUORINE ON NONMETALLIC MATERIALS

Material	Conditions	Results
CCl_4	10% gas bubbled through 20% gas bubbled through	no reaction flames; mild explosion
β-alumina	3 hr at 392°F	no weight gain or surface effects
Activated alumina	various conditions	partial or nearly complete conversion to AlF_3
CaF_2 cement, baked dry (with Na_2SiO_3)	400°F, approx	no apparent attack
Amorphous carbon	212°F	no visible effect
Graphite	212°F	embrittlement
Glyptal	77°F	no burning if baked dry
Rubber (various kinds)	various conditions	erratic; may or may not burn; attacked to some extent in all cases, with increasing brittleness, cracking, surface hardening
Transite	various conditions	resistant if clean
Mixture containing 5% nitric acid (70%) and 95% sulfuric acid (96 to 98%)	100%, 1 atm, 4 hr	no noticeable change
100% sulfuric acid	100%, 1 atm, 100°F	little attack; may get warm if impurities are present
95% sulfuric acid	100%, 1 atm, 100°F, 1 hr	rapid temperature rise: some explosions as temperature rises
85% orthophosphoric acid	100%, 1 atm, 100°F, 0.1 hr	no temperature rise

An explosive substance is formed when fluorine reacts with carbon (Cf. Ref. 50). Ordinary Norit ignites in fluorine at 20°C and burns to a mixture of fluorides with the formation of an explosive residue corresponding to the formula CF. Oxygen-free Norit can be heated to 280°C in fluorine of about 25 mm pressure without igniting. Nevertheless, fluorination takes place and at 280°C continues until the composition corresponding to CF is reached. When the fluorination is carried out in a copper tube at about 400°C, explosions occur at regular intervals. However, above about 450°C, burning occurs quietly and completely (Cf. Ref. 51).

Graphite does not ignite in fluorine at ordinary temperatures. Moreover, it combines with fluorine or absorbs fluorine only slightly. For example, graphite absorbs about 15 per cent of its weight of fluorine in 5 to 6 hours at 20°C, and heating of the product causes no noticeable reaction. However, at about 420°C, it reacts to form CF. At about 500°C, powerful explosions occasionally occur under conditions similar to those for Norit, but these explosions disappear as the temperature is raised. At about 700°C, the fluorination takes place smoothly and without danger (Cf. Ref. 51).

In an article concerning industrial experience with fluorine in Germany, Neumark (Cf. Ref. 1) states that anhydrous hydrogen fluoride catalyzes the reaction between graphite and fluorine to form CF. Table X shows the results of experiments in which fluorine was conducted over a coarse S-40 graphite under various conditions of temperature and time. The fluorine — hydrogen fluoride mixture was obtained by passing the fluorine through a flask containing liquid anhydrous hydrogen fluoride maintained at 0°C. In the experiment at 300°C, the graphite lost its characteristic metallic appearance and became much blacker. In the experiment at 400°C, CF was formed, as was shown by an X-ray study. In the research discussed by Neumark, fluorine free of hydrogen fluoride had important effects upon graphite and caused the formation of CF at temperatures above 450°C only.

TABLE X

EFFECTS OF FLUORINE UPON GRAPHITE

Temperature (°C)	Time Interval (min)	Gain in Weight (%)	
		Fluorine Stream	Fluorine-Hydrogen Fluoride Stream
215	60	--	3
270	180	0	7.2
270	360	--	7.8
300	55	--	4.6
360	60	1.35	--
365	50	--	8.9
400	55	--	14.1
420	150	--	36.8
440	60	5.3	--
460	210	--	67.2
510	90	30	--

The results of a series of experiments in which the coarse S-40 graphite was compared with coke oven graphite with respect to the formation of CF are given in Table XI. The appearance of the coke oven graphite and its X-ray picture seemed to be unchanged.

Neumark discusses experiments with S-40 graphite which had been treated for 8 hours with a mixture of fluorine and hydrogen fluoride at 250°C and had been compressed at pressures of the order of 400 kg/sq cm.

Fluorine attacks ordinary glass only slowly in the absence of water at room temperatures and pressures near 1 atmosphere (Cf. Ref. 4). Pyrex glass is more resistant than ordinary glass. Quartz is a little more resistant than glass (Cf. Ref.

52). Fluorine attacks Pyrex glass only slowly, if at all, at room temperatures and at pressures up to 1 atmosphere, provided no water is present on the surface of the glass (Cf. Ref. 5).

That carbon dioxide does not react with fluorine at room temperatures and pressures near 1 atmosphere is shown by the fact that Bockemüller (Cf. Ref. 40) used carbon dioxide to dilute fluorine in studying the reaction of the latter with paraffin.

TABLE XI

COMPARISON OF EFFECTS OF FLUORINE UPON GRAPHITE SPECIMENS OF TWO TYPES

Temperature (°C)	Time Interval (hr)	Gain in Weight (%)			
		S-40 Graphite in Fluorine Stream	S-40 Graphite in Fluorine--Hydrogen Fluoride Stream	Coke Oven Graphite in Fluorine Stream	Coke Oven Graphite in Fluorine--Hydrogen Fluoride Stream
250	4	0.2	8.5	0.2	0.5
250	8	--	9.0	0.4	0.7
300	4	0.5	9.0	--	4.0
300	8	--	10.0	--	6.0
360	4	1.5	10.0	--	18.0
360	8	--	13.0	--	26.0

I. Valves for Handling Fluorine

The problem of valves is the most troublesome one in the industrial handling of fluorine. The principal difficulties are leakage across the stuffing box and leakage past the seat when the valve is shut. Packless valves can be used to avoid leakage across a stuffing box. Of the few such valves which are suitable for the industrial handling of fluorine at low pressures, one is the Kerotest diaphragm packless valve, in which the diaphragm is of copper. This valve can be used if the seat is replaced with one of Teflon or the equivalent. Another satisfactory packless valve is a bellows-seated valve made by the Crane Company. For diluted fluorine at low pressures, other industrial valves have been used with some success; all were packed with special corrosion-resistant substances, such as Teflon. In valves handling fluorine at low pressures, seat leakage can be largely overcome by proper designing, in which Teflon or its equivalent is used as the seat material, and Monel or nickel is used as the mating element. A much tighter seat results than in an all-metal valve. All-metal valves having Monel or aluminum bronze seat-and-disk units have been used also, but it is not safe to assume that the seat will continue tight indefinitely for any type of valves. Landau and Rosen recommend that double valving be installed where tightness is important, such as points at which fluorine is separated from the atmosphere or from equipment not handling fluorine. In some cases, the use of an inert gas at elevated pressure in the space between the two valves is desirable. The bellows-seated valve made by the Crane Company can be used at pressures below 100 psi in sizes 1 inch and larger. In March 1947, Landau and Rosen stated that no satisfactory packless valve for pressures above 100 psi was known. Hoke Monel needle valves, packed with Teflon or the equivalent, have been successfully used at pressures up to 400 psi. The Kerotest 440-A Chlorine Institute valve, packed with Teflon or the equivalent, has been used successfully on fluorine cylinders. Nonmetallic seats or disks are unsafe with fluorine under high pressure (Cf. Ref. 37).

Froning et al (Cf. Ref. 27), in describing their experience with fluorine valves, state that valves for use under high pressure were operated by means of extension handles. Some of the desirable valve features were rugged needle-valve form, the use of dissimilar metals (for example, mild steel and hardened steel) for seat and stem, turning action for seating, and true alignment of seat and stem. The true alignment was important, because the Teflon packing employed was not resilient enough to allow self-alignment in the case of a poorly constructed valve. Incorporation of these features resulted in valves which operated many months without significant leakage. However, these features rule out packless valves also.

The valve packing used by Froning (Cf. Ref. 27) consisted of machined Teflon annuli with an annulus of a mixture of Teflon and calcium fluoride (30% calcium fluoride) on the bottom. This packing gave excellent service for indefinite periods except where contaminated with reactive substances or where leaks occurred, through loose packing nuts or scored stems, for example. It was shown that a slow leak along the rings (easily detected by means of potassium iodide —starch paper) caused the bonnet of a Monel valve to catch fire and to be destroyed. An explanation involving a blanketing layer of gaseous reaction products can be given. According to this explanation, the reaction products, of which carbon tetrafluoride is an example, usually have a retarding influence, but they are removed by the fluorine sweeping over the surface at a leak. If the conditions are such that reaction heat can accumulate, the Teflon and the adjacent metal finally reach their ignition temperatures.

The abrading action occurring in the turning of a valve demands that stem and seat be made of materials which show the least scale formation. These materials are Monel and nickel. Because of the factor of scale formation, globe valves and needle valves are better than gate valves, and plug cocks are definitely unsatisfactory. Teflon packing performs well with fluorine at pressures near 1 atmosphere, where the relationships of volume to surface in the packing are such that the heat release under the conditions of incipient combustion is good. According to Gall and Miller, diaphragm, bellows, and other types of packless valves are serviceable if the operating mechanism in contact with the fluorine is not easily rendered inoperative by fluoride scale (Cf. Ref. 46).

Pressure relief valves for fluorine have been unsatisfactory because of seat leakage. It is difficult to maintain motor-operated and air-operated valves tight against pure fluorine, because sufficient torque for seating is not available. It has been found best to control fluorine under pressure by means of several valves in series with suitable alarms and by-passes. For very large pressure differences, additional stages of throttling may be preferable. Two controllers have been successfully used in throttling between 30 psig and a steady level of 1 psig. (Cf. Ref. 37).

J. Instrumentation in Apparatus Handling Fluorine

Blind multipliers or transmitters of bellows construction, either welded or silver-soldered, and employing an inert gas as a buffer, have been used successfully for flow recorders and controllers and for pressure recorders and controllers. These are manufactured by the Moore Company, the Taylor Instrument Company, and others. These multipliers or transmitters can be coupled with any of the usual instruments for recording, indicating, or controlling. All-welded gages of the Bourdon type are practical for simple pressure measurement (Cf. Ref. 37).

Temperatures should be measured with completely enclosed thermowells. Thermocouple elements are undependable when in direct contact with fluorine (Cf. Ref. 37).

K. Compression

Although many metals withstand attack by fluorine at low temperatures, and some metals withstand attack at fairly high temperatures, their resistance is due to a protective layer of fluoride. The nature of the resistance creates a problem in the mechanical compression of fluorine. If the protective layer is displaced by mechanical action, for example, by the action of the piston in a reciprocating pump, more fluoride will form, and serious damage will be done as the process continues. The problem of lubrication also is difficult, since fluorine reacts with carbon or graphite in finely divided form and with hydrocarbon oils. Fluorocarbon oils resist fluorine to a certain extent, but even these react at high pressure and temperature (Cf. Ref. 28).

According to Landau and Rosen (Cf. Ref. 37), writing prior to March 1947, experience in the use of mechanical compressors lubricated with fluorocarbon oils for fluorine has not been sufficient to establish the commercial applicability of such equipment. Leaking past the piston may be serious. Bellows-type pumps have not been satisfactory, because flexing of a bellows in fluorine under pressure causes intergranular corrosion or rupture, with bad leaks. The Wilson Pulsafeeder Company and the Hooker Electrochemical Company have built a successful diaphragm-type compressor, in which the stroke is relatively short. Pressures up to 40 psi can be produced by this compressor. Leakage occurs around the valves (metal-seated), but leakage occurring here is not highly important, since pumping efficiency is not the principal consideration involved. Centrifugal equipment, sealed at the shaft with rings of such materials as graphite or Teflon, has operated on pure fluorine at pressures near 1 atmosphere.

A standard single-acting, single-stage air compressor lubricated with a fluorocarbon oil has been operated on fluorine at 175 psi for periods of several hours. The oil blackened quickly and caught fire occasionally (Cf. Ref. 27).

L. Disposal

The matter of fluorine disposal is highly important in connection with processes in which fluorine is not completely consumed. Not only may operators suffer irritations from low concentrations of the gas, but their health may be affected. Vegetation at relatively great distances may be damaged through transportation of the gas by winds (Cf. Ref. 37).

Fluorine can be destroyed by conducting it into a hydrocarbon flame in which there is an excess of fuel. The reaction products include hydrogen fluoride and carbon fluorides. The latter are not objectionable, but the hydrogen fluoride should not be discharged into the atmosphere if moderate or large quantities of fluorine are destroyed in this way. It can be absorbed in water or alkaline solutions. The method has the disadvantage that fuel must be consumed over the entire period of readiness (Cf. Ref. 37).

The following disposal methods, drawn from the work of Landau and Rosen (Cf. Ref. 37), have been tried:

1. The fluorine is passed over sodium chloride or calcium chloride to produce chlorine, which is absorbed by soda lime, lime slurry, or some other suitable agent.
2. Solutions containing 5 to 10 weight per cent sodium hydroxide absorb fluorine satisfactorily provided the time of contact exceeds 1 minute. Oxygen bifluoride is formed at contact times of approximately 1 second.
3. A lime slurry can be used to remove fluorine, but care must be taken to allow sufficient contact time. The destruction of the intermediate

compound, oxygen bifluoride, occurs more slowly than in the case of sodium hydroxide, because much higher concentrations are possible with sodium hydroxide than with lime. Knowledge sufficient to establish a satisfactory quantitative basis for design had not been accumulated by March 1947.

4. Such inorganic fluorides as AgF, SbF_3, and CoF_2 react with fluorine. Hydrogen returns the metals from the higher valence states into which they were raised by the fluorine to the original valence states, with the formation of hydrogen fluoride. These reactions can be made the basis of a fluorine disposal method, but it is distinctly unsatisfactory for small installations; in the case of large installations, the necessity for a series of operations and the usual hazards of handling hydrogen are disadvantages.

Fluorine does not always react rapidly with water, for reasons which are unknown. Explosions occur in some cases, not in others (Cf. Ref. 37).

Landau and Rosen (Cf. Ref. 53) have designed and tested a system for the industrial disposal of fluorine. The fluorine-containing gas is introduced into a packed absorption tower and flows countercurrently to a stream of sodium hydroxide solution. The sodium fluoride produced reacts with calcium hydroxide introduced as a slurry into the effluent liquid from the tower. Thus the sodium hydroxide is regenerated, the fluorine being removed as calcium fluoride. The reasons for the use of calcium hydroxide are (1) that the sodium fluoride would be an objectionable contaminant in the effluent water from the system and (2) that sodium fluoride, having a low solubility in the hydroxide solution, would plug parts of the system, since the hydroxide solution is recycled, as explained herein. After the calcium fluoride has settled out in a tank, the hydroxide solution is returned to the tower. The temperature of the hydroxide solution entering the tower is kept between 100 and 150°F. The designers believe that the optimum sodium hydroxide concentration is between 5 and 10 per cent. Make-up sodium hydroxide is added as needed.

A 1-month test of the system was made. Fluorine was introduced into the system at approximately 60 lb/day. The basic operability of the chemical regeneration process was proved. Tests of the completeness of fluorine absorption showed that the concentration in the gas discharged did not exceed 3 ppm, even at the fluorine input rate of 500 lb/hr. Operation of the installation was continued for a long period of time following the 1-month test and proceeded smoothly.

The best fluorine disposal method found by Turnbull et al (Cf. Refs. 14 and 15) was based upon the reaction of fluorine with hydrocarbons such as propane and butane. The waste fluorine was conducted to the cone of a flame of the hydrocarbon burning with a deficiency of air in a conventional ring burner. The products of the reaction were inert fluorides (such as carbon tetrafluoride), hydrogen fluoride, carbon dioxide, and water. This disposal method does not involve the complications that arise when inhibited reactions are employed. A 4-inch ring burner was found to have a capacity of 4.5 lb/hr of fluorine. For large-scale operations, a system consisting of a 10-inch ring burner, a water scrubber tower, and a caustic scrubber tower, each packed with 2-inch carbon rings to a height of 30 feet, was fully satisfactory from the standpoint of engineering and operation. This system could dispose of fluorine at approximately 125 lb/hr.

M. Density of the Gas and of the Liquid

The densities of gaseous fluorine and liquid fluorine in equilibrium with each other at various temperatures (Cf. Ref. 54) are given in Table XII. Other data on the density of liquid fluorine (Cf. Ref. 55) are presented in Table XIII.

TABLE XII

ORTHOBARIC DENSITIES OF FLUORINE

Temperature (°K)	Pressure (mm)	Density (gm/cc)	
		Liquid Fluorine	Gaseous Fluorine
57.10	--	1.205	--
59.95	--	1.195	--
64.20	28.22	1.181	0.27×10^{-3}
72.11	129.90	1.155	1.10×10^{-3}
76.30	247.50	1.140	2.02×10^{-3}
84.91	733.50	1.112	5.76×10^{-3}

TABLE XIII

DENSITY OF LIQUID FLUORINE

Temperature (°K)	Density (gm/cc)
57.40	1.204
60.51	1.195
64.41	1.185
68.38	1.154
73.00	1.141
75.01	1.136
79.40	1.124
83.21	1.113

N. Viscosity of Gaseous Fluorine

The viscosity of gaseous fluorine under various conditions is given (Cf. Ref. 56) in Table XIV.

TABLE XIV

VISCOSITY OF GASEOUS FLUORINE

Temperature (°K)	Pressure (mm)	Viscosity (poises)
86.8	758	555×10^{-7}
118.9	758	875×10^{-7}
148.8	758	1080×10^{-7}
167.9	765	1201×10^{-7}
192.3	765	1379×10^{-7}
213.1	765	1492×10^{-7}
229.6	763	1611×10^{-7}
248.9	763	1727×10^{-7}
273.2	763	2093×10^{-7}

O. Surface Tension

The surface tension of fluorine is presented (Cf. Ref. 54) for a range of temperatures in Table XV. The inside radius of the capillary tube corresponding to the capillary height values given was 0.00805 cm. The assumption was made that the angle of contact was 0.

TABLE XV

SURFACE TENSION OF FLUORINE

Temperature (°K)	Pressure (mm)	Capillary Height (cm)	Surface Tension (dynes/cm)
57.10	--	3.068	14.61
59.95	--	3.002	14.16
61.41	--	—	13.85
64.20	28.22	2.884	13.46
65.30	--	--	13.17
71.00	--	--	12.20
72.11	129.90	2.654	12.10
76.30	247.50	2.536	11.40
81.50	--	--	10.41
84.91	733.50	2.254	9.85

P. Dielectric Constant of Liquid Fluorine

The dielectric constant data presented in Table XVI is derived from the work of Kanda (Cf. Ref. 55).

TABLE XVI

DIELECTRIC CONSTANT OF LIQUID FLUORINE

Temperature (°K)	Dielectric Constant
57.40	1.567
60.51	1.561
64.41	1.553
68.38	1.546
73.00	1.536
75.01	1.533
79.40	1.524
83.21	1.517

Q. Vapor Pressure

Vapor pressure data for fluorine are given by several scientists. Cady and Hildebrand (Cf. Ref. 57) report the values which are given in Table XVII. The values in the third column were obtained from the equation

$$\log_{10} p = 7.3317 - \frac{406.8}{T} - 0.007785\, T$$

in which p is the vapor pressure in centimeters of mercury and T is the temperature on the Kelvin scale.

TABLE XVII

VAPOR PRESSURE OF LIQUID FLUORINE

Temperature (°K)	Vapor Pressure (cm)	
	Observed	Calculated
72.53	14.54	14.41
72.53	14.57	14.41
75.18	21.53	21.65
75.18	21.54	21.65
75.18	21.53	21.65
75.18	21.50	21.65
75.45	22.25	22.50
75.53	22.53	22.78
75.59	22.69	22.99
75.88	23.83	23.99
75.93	24.01	24.16
76.70	27.10	26.97
76.72	27.20	27.03
76.72	26.90	27.03
76.74	27.09	27.11
78.96	36.68	36.76
79.01	36.78	36.99
79.02	36.87	37.01
79.18	37.88	37.80
79.18	37.87	37.80
80.09	43.00	42.58
80.09	43.00	42.58
80.96	48.03	47.48
80.98	48.23	47.59
81.19	49.32	48.85
81.20	49.34	48.92
81.22	49.53	49.04
83.09	61.53	61.55
83.11	61.57	61.67
83.45	64.24	64.20
83.48	64.48	64.38
84.13	68.64	69.35
84.65	73.40	73.50
84.68	74.18	73.78
84.68	73.93	73.78

TABLE XVII (Cont'd)

Temperature (°K)	Vapor Pressure (cm)	
	Observed	Calculated
84.73	74.02	74.19
84.77	73.84	74.55
84.81	74.14	74.85
85.25	78.55	78.62
85.27	79.40	78.85
85.28	78.02	78.95
85.32	79.36	79.35
85.40	79.77	79.87
85.81	84.11	83.56
85.99	85.50	85.20

Claussen (Cf. Ref. 58) obtained for liquid fluorine the equation

$$\log_{10} p = -\frac{462.66}{T} + 8.7202 - 0.01656\,T$$

in which p is the vapor pressure in centimeters of mercury and T is the temperature on the Kelvin scale. No experimental point deviated by more than 0.15° from the curve.

The fluorine vapor pressure values given in Table XVIII were obtained by Kelley (Cf. pp. 46 and 111 of Ref. 59) from smoothed curves derived from a free energy of vaporization expression stated.

TABLE XVIII

VAPOR PRESSURE OF LIQUID FLUORINE

Temperature (°K)	Vapor Pressure (atm)
57.65	0.01
68.70	0.1
74.38	0.25
79.21	0.5
84.93	1.0

Tables XIX and XX contain the data of Aoyama and Kanda (Cf. Ref. 60). The equation used in determining the calculated vapor pressures in Table XIX was

$$\log_{10} p = -\frac{442.72}{T} + 9.1975 - 0.013150\,T$$

in which p is the vapor pressure in millimeters of mercury and T is the temperature on the Kelvin scale. The following equation represents the data given in Table XX:

$$\log_{10} p = -\frac{430.06}{T} + 8.233$$

In this equation, p is the vapor pressure in millimeters of mercury, and T is the temperature on the Kelvin scale.

TABLE XIX

VAPOR PRESSURE OF LIQUID FLUORINE

Temperature (°K)	Vapor Pressure (mm)		Calculated Vapor Pressure Minus Observed Vapor Pressure (mm)
	Observed	Calculated	
59.90	10.10	10.445	+0.35
63.61	26.30	25.20	-0.90
65.00	35.50	34.02	-1.50
66.70	65.20	70.78	+5.6
69.99	92.05	89.56	-2.4
72.85	143.35	145.34	+2.0
75.01	209.10	203.70	-5.4
77.51	289.50	292.81	+3.3
79.35	381.50	375.66	-5.8
79.98	402.35	407.85	-4.5
83.43	608.10	622.30	+14.2
84.52	712.75	704.85	+7.9
85.00	740.10	743.70	+3.6
86.21	845.20	848.20	+3.0

TABLE XX

VAPOR PRESSURE OF SOLID FLUORINE

Temperature (°K)	Vapor Pressure (mm)
51.85	0.10
52.55	1.55
53.90	1.75
54.50	2.10
55.15	2.70

B. Melting Point and Boiling Point

The melting point of fluorine is 55.20°K (Cf. Ref. 61).

Cady and Hildebrand (Cf. Ref. 57), by calculating from their vapor pressure equation, found the normal boiling point of fluorine to be 84.93°K. They stated that this value was probably within 0.1° of the true value. This procedure gave Claussen (Cf. Ref. 58) the value 85.21°K, in which the error was believed not to exceed 0.1°. Kelley (Cf. pp. 46 and 111 of Ref. 59) took 84.9°K as the normal boiling point. The equation of Aoyama and Kanda (Cf. Ref. 60) gave 85.19°K. Rossini and his associates (Cf. Tables 9 and 10 of Ref. 62) took 85.24°K as the value.

S. Heat of Vaporization, of Sublimation, and of Fusion

By making use of Berthelot's equation of state and the Clapeyron equation, Cady and Hildebrand (Cf. Ref. 57) calculated the heat of vaporization of fluorine at the normal boiling point from their vapor-pressure data. The value obtained was 1540 cal/mol. Without the use of Berthelot's equation, the result was 1600 cal/mol.

Claussen (Cf. Ref. 58) derived 1560 cal/mol from his vapor-pressure data. Kelley (Cf. pp. 46 and 111 of Ref. 59) took 1640 cal/mol as the value.

Aoyama and Kanda (Cf. Ref. 60), using their equation for the vapor pressure of solid fluorine, calculated the heat of sublimation. The value was 1970 cal/mol. Using their vapor-pressure data for liquid fluorine, they obtained 1581 cal/mol for the heat of vaporization. The subtraction of the latter value from the former gave approximately 390 cal/mol as the heat of fusion.

Kanda (Cf. Ref. 61) determined the heat of fusion calorimetrically. The result was 372 cal/mol (at 55.20°K). This value has been accepted by Rossini et al (Cf. Tables 9 and 10 of Ref. 62), who give 1.86 cal/deg mol as the increase in the heat capacity at constant pressure accompanying fusion. Rossini et al take 1510 cal/mol for the heat of vaporization of fluorine at 85.24°K (their value for the normal boiling point) and give 4.27 cal/deg mol as the decrease in the heat capacity at constant pressure accompanying vaporization.

T. Critical Temperature and Critical Pressure

Cady and Hildebrand (Cf. Ref. 57) found the critical temperature of fluorine to be approximately 144°K. They estimate the critical pressure to be 55 atmospheres.

U. Heat Capacity of the Solid, the Liquid, and the Gas

Kanda (Cf. Ref. 61) determined the heat capacity at constant pressure of solid fluorine and of liquid fluorine at a number of temperatures. His values are given in Table XXI.

Rossini and his collaborators (Cf. Table 9-1 of Ref. 63) give 7.52 cal/deg mol for the heat capacity at constant pressure of F_2 in the state of a perfect gas at 298.16°K. The heat-capacity values of Murphy and Vance (Cf. Ref. 64) are contained in Table XXII. The results were obtained by the application of the methods of statistical mechanics.

Calculations similar to those made by Murphy and Vance but with the introduction of certain refinements were carried out by Cole and Farber.* Their results are given in Table XXIII.

V. Various Thermodynamic Properties

Cole and Farber have calculated the enthalpy difference corresponding to selected temperature intervals starting at 298.1°K for F_2 behaving as a perfect gas.* Their

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*Unpublished data obtained by Leland G. Cole and Milton Farber of this Laboratory.

results are given in Table XXIV.

TABLE XXI

HEAT CAPACITY AT CONSTANT PRESSURE OF SOLID FLUORINE AND OF LIQUID FLUORINE

Temperature (°K)	Heat Capacity at Constant Pressure (cal/deg mol)
14.91	1.167
17.75	1.807
20.01	2.240
23.10	2.841
25.42	3.440
29.50	4.310
32.00	4.795
35.40	5.561
39.11	6.280
43.10	7.120
47.95	7.741
52.98	8.210
53.98	8.761
55.20	melting point
57.50	10.84
62.51	10.92
67.49	10.98
77.10	11.12
83.41	11.20
85.19	boiling point

TABLE XXII

HEAT CAPACITY AT CONSTANT PRESSURE OF GASEOUS FLUORINE

Temperature (°K)	Heat Capacity at Constant Pressure of F_2 in the State of a Perfect Gas (cal/deg mol)
298.1	7.522
300	7.530
400	7.912
500	8.186
600	8.373
800	8.594
1000	8.710
1200	8.777
1400	8.819
1600	8.847
1800	8.866
2000	8.880

TABLE XXIII

HEAT CAPACITY AT CONSTANT PRESSURE OF GASEOUS FLUORINE

Temperature (°K)	Heat Capacity at Constant Pressure of F_2 in the State of a Perfect Gas (cal/deg mol)	Temperature (°K)	Heat Capacity at Constant Pressure of F_2 in the State of a Perfect Gas (cal/deg mol)
298.1	7.45	2300	9.192
300	7.457	2400	9.208
400	7.835	2500	9.214
500	8.120	2600	9.229
600	8.341	2700	9.245
700	8.514	2800	9.262
800	8.648	2900	9.279
900	8.737	3000	9.297
1000	8.815	3100	9.314
1100	8.871	3200	9.328
1200	8.914	3300	9.344
1300	8.954	3400	9.359
1400	8.986	3500	9.374
1500	9.016	3600	9.388
1600	9.042	3700	9.403
1700	9.065	3800	9.418
1800	9.090	3900	9.433
1900	9.115	4000	9.447
2000	9.141	4100	9.461
2100	9.160	5000	9.591
2200	9.177	6000	9.733

TABLE XXIV

ENTHALPY VALUES FOR GASEOUS FLUORINE

Temperature (°K)	Enthalpy at Designated Temperature Minus Enthalpy at 298.1°K (kcal/mol)	Temperature (°K)	Enthalpy at Designated Temperature Minus Enthalpy at 298.1°K (kcal/mol)
298.1	0	3100	25.000
300	0.014	3200	25.932
400	0.779	3300	26.865
500	1.576	3400	27.800
600	2.399	3500	28.737
700	3.242	3600	29.675
800	4.100	3700	30.614
900	4.970	3800	31.556
1000	5.847	3900	32.498
1100	6.732	4000	33.442

TABLE XXIV (Cont'd)

Temperature (°K)	Enthalpy at Designated Temperature Minus Enthalpy at 298.1°K (kcal/mol)	Temperature (°K)	Enthalpy at Designated Temperature Minus Enthalpy at 298.1°K (kcal/mol)
1200	7.621	4100	34.388
1300	8.514	4200	35.344
1400	9.411	4300	36.304
1500	10.311	4400	37.264
1600	11.214	4500	38.224
1700	12.120	4600	39.184
1800	13.028	4700	40.144
1900	13.938	4800	41.104
2000	14.851	4900	42.064
2100	15.766	5000	43.024
2200	16.683	5100	43.984
2300	17.592	5200	44.944
2400	18.521	5300	45.904
2500	19.442	5400	46.864
2600	20.364	5500	47.824
2700	21.288	5600	48.784
2800	22.213	5700	49.744
2900	23.140	5800	50.704
3000	24.069		

Table XXV is a summary of F_2 entropy values from a number of sources. Table XXVI is derived from the work of Murphy and Vance (Cf. Ref. 64), and Table XXVII, from unpublished work by Cole and Farber of this Laboratory.

TABLE XXV

ENTROPY VALUES FOR GASEOUS FLUORINE

State	Entropy (cal/deg mol)	Scientist and Year
Real gas at 85.19°K and 1 atm	37.14	Kanda (Cf. Ref. 61), 1937
Perfect gas at 85.19°K and 1 atm	37.29	Kanda (Cf. Ref. 61), 1937
Perfect gas at 298.1°K and 1 atm	47.99±0.1	Kelley (Cf. p. 13 of Ref. 65), 1936
Perfect gas at 298°K and 1 atm	48.6	Garner and Yost (Cf. Ref. 66), 1937
Perfect gas at 298.16°K and 1 atm	48.6	Rossini et al (Cf. Table 9-1 of Ref. 63), 1947

TABLE XXVI

STANDARD ENTROPY OF FLUORINE

Temperature (°K)	Standard Entropy (cal/deg mol)
298.1	48.576
300	48.623
400	50.844
500	52.642
600	54.151
800	56.594
1000	58.580
1200	60.119
1400	61.476
1600	62.659
1800	63.694
2000	64.637

In 1941, Kelley (Cf. p. 41 of Ref. 67) confirmed the value given by Murphy and Vance for the standard molal entropy of F_2 at 298.1°K, 48.58±0.1 cal/deg.

TABLE XXVII

STANDARD ENTROPY OF FLUORINE

Temperature (°K)	Standard Entropy (cal/deg mol)	Temperature (°K)	Standard Entropy (cal/deg mol)
298.1	48.60	2400	66.33
300	48.65	2500	66.71
400	50.79	2600	67.07
500	52.56	2700	67.42
600	54.06	2800	67.76
700	55.36	2900	68.09
800	56.50	3000	68.41
900	57.52	3100	68.72
1000	58.44	3200	69.02
1100	59.28	3300	69.31
1200	60.05	3400	69.59
1300	60.76	3500	69.86
1400	61.42	3600	70.12
1500	62.04	3700	70.38
1600	62.62	3800	70.63
1700	63.17	3900	70.88
1800	63.69	4000	71.12
1900	64.18	4100	71.35
2000	64.65	4500	72.25
2100	65.10	5000	73.26
2200	65.53	5500	74.18
2300	65.94	6000	75.01

The constant of the equilibrium represented by

$$\tfrac{1}{2}\,F_2 \rightleftarrows F$$

is given in Table XXVIII* for temperatures ranging from 300 to 6000°K.

TABLE XXVIII

DISSOCIATION EQUILIBRIUM OF F_2

Temperature (°K)	$K = p_F/p_{F_2}^{1/2}$ ($\mathrm{atm}^{1/2}$)
300	6.84×10^{-21}
500	1.36×10^{-11}
1000	1.52×10^{-4}
1500	3.62×10^{-2}
1600	7.18×10^{-2}
1700	1.32×10^{-1}
1800	2.26×10^{-1}
1900	3.68×10^{-1}
2000	5.70×10^{-1}
2100	8.47×10^{-1}
2200	1.215
2300	1.691
2400	2.286
2500	3.021
2600	3.906
2700	4.961
2800	6.184
2900	7.594
3000	9.209
3100	1.10×10
3200	1.31×10
3300	1.53×10
3400	1.78×10
3500	2.05×10
3600	2.34×10
3700	2.66×10
3800	3.01×10
3900	3.39×10
4000	3.78×10
4100	4.20×10
4500	6.10×10
5000	8.94×10
5500	1.22×10^{2}
6000	1.60×10^{2}

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*Unpublished data obtained by Cole and Farber of this Laboratory.

For the standard free energy of vaporization of F_2 at temperatures near the normal boiling point, Kelley (Cf. pp. 46 and 111 of Ref. 59) gives $\Delta F^\circ = 1640 - 19.31\,T$ where T is the temperature on the Kelvin scale and the units of F are cal/mol.

Kelley (Cf. p. 41 of Ref. 67) gives 37.93±0.01 cal/deg for the standard molal entropy of monatomic fluorine at 298.1°K.

The thermodynamic data on monatomic fluorine presented in Table XXIX is given by Rossini and his collaborators (Cf. Table 9-1 of Ref. 63).

TABLE XXIX

THERMODYNAMIC DATA ON MONATOMIC FLUORINE

State		Standard Heat Capacity at Constant Pressure (cal/deg mol)	Standard Enthalpy of Formation (kcal/mol)	Standard Entropy (cal/deg mol)	Standard Free Energy of Formation (kcal/mol)	Log_{10} (Equilibrium Constant of Formation) (pressures in atm)
Description	Condition					
$2s^2\ 2p^5\ \left({}^2P^0_{3/2}\right)$	gas at 0°K		31.8			
	gas at 298.16°K	5.436	32.25	37.917	28.19	-20.663
$\left({}^2P^0_{1/2}\right)$	gas at 0°K		32.96			
	gas at 298.16°K		33.41			

Table XXX gives additional thermodynamic data on monatomic fluorine from the unpublished work of Cole and Farber of this Laboratory. The gas was taken as perfect, of course.

TABLE XXX

THERMODYNAMIC DATA ON MONATOMIC FLUORINE

Temperature (°K)	Heat Capacity at Constant Pressure (cal/deg mol)	Enthalpy at Designated Temperature Minus Enthalpy at 298.1°K (kcal/mol)	Standard Entropy (cal/deg mol)
298.1	5.440	0	37.93
300	5.433	0.010	37.96
400	5.359	0.550	39.36
500	5.280	1.082	40.47
600	5.216	1.607	41.37
700	5.167	2.126	42.14
800	5.130	2.641	42.84
900	5.104	3.152	43.38

TABLE XXX (Cont'd)

Temperature (°K)	Heat Capacity at Constant Pressure (cal/deg mol)	Enthalpy at Designated Temperature Minus Enthalpy at 298.1°K (kcal/mol)	Standard Entropy (cal/deg mol)
1000	5.080	3.661	43.91
1100	5.063	4.168	44.38
1200	5.049	4.674	44.81
1300	5.038	5.178	45.21
1400	5.029	5.682	45.58
1500	5.022	6.184	45.92
1600	5.015	6.686	46.24
1700	5.010	7.188	46.54
1800	5.006	7.689	46.82
1900	5.002	8.189	47.10
2000	4.998	8.689	47.35
2100	4.996	9.189	47.59
2200	4.993	9.688	47.82
2300	4.991	10.187	48.04
2400	4.989	10.686	48.25
2500	4.987	11.185	48.46
2600	4.985	11.684	48.65
2700	4.984	12.182	48.84
2800	4.983	12.681	49.02
2900	4.982	13.179	49.19
3000	4.981	13.677	49.36
3100	4.980	14.175	49.52
3200	4.979	14.673	49.68
3300	4.978	15.171	49.84
3400	4.977	15.669	49.98
3500	4.977	16.167	50.13
3600	4.976	16.664	50.27
3700	4.975	17.162	50.39
3800	4.974	17.659	50.53
3900	4.974	18.157	50.67
4000	4.974	18.654	50.79
4100	4.973	19.152	50.92
4200		19.649	
4300		20.147	
4400		20.644	
4500	4.972	21.141	51.38
4600		21.638	
4700		22.135	
4800		22.632	
4900		23.129	
5000	4.971	23.626	51.90
5100		24.123	
5200		24.620	

TABLE XXX (Cont'd)

Temperature (°K)	Heat Capacity at Constant Pressure (cal/deg mol)	Enthalpy at Designated Temperature Minus Enthalpy at 298.1°K (kcal/mol)	Standard Entropy (cal/deg mol)
5300		25.117	
5400		25.614	
5500	4.970	26.111	52.38
5600		26.608	
5700		27.105	
5800		27.602	
6000	4.969		52.81

W. Dissociation Energy

Gaydon (Cf. pp. 188 and 189 of Ref. 68) discusses the dissociation energy of fluorine. In commenting upon the values listed in Table XXXI, he states that the value given by Desai, 76 kcal/mol, can be disregarded, since it is based upon discredited thermochemical data. Also, Gaydon points out evidence which favors a value considerably lower than 63 kcal/mol. He favors a value of about 51 kcal/mol.

TABLE XXXI

DISSOCIATION ENERGY OF FLUORINE

Value for Dissociation Energy of F_2 (kcal/mol)	Scientist and Year
63.3	Wartenberg, Sprenger, and Taylor, 1931
76	Desai, 1932
70	Bodenstein, Jockusch, and Shing Hou Chong, 1937
63.3	Herzberg, 1939

Schmitz and Schumacher (Cf. Ref. 69) found the dissociation energy of ClF to be either 60.3±0.5 or 58.9±0.5 kcal/mol, the value depending upon the interpretation of the spectrum. The former value agrees with that obtained by Wahrhaftig (Cf. Ref. 70). By combining these values with their value for the heat of formation of ClF (Cf. Section IV-H) and the value for the dissociation energy of Cl_2, Schmitz and Schumacher obtained the alternative values 33.4 and 30.6 kcal/mol for the dissociation energy of F_2.

X. Safety Precautions

Fluorine in the atmosphere can be detected by means of its odor in concentrations of a few parts per million (Cf. Ref. 37), as low as 5 to 6 ppm (Cf. Ref. 49). No tolerance level had been established for fluorine by March 1947, although extensive experimental work had been done (Cf. Ref. 37).

The following safety measures given by Landau and Rosen (Cf. Ref. 37) are recommended:

1. Valves handling pure fluorine at pressures above 5 psig should be operated by means of extension handles passing through barriers of metal, brick, or concrete.
2. Containers holding fluorine under pressure should be stored behind a suitable barricade and should not be approached by operators unless the containers are completely closed and known to be not leaking. Leaking containers should be allowed to vent in an open field.
3. Systems containing fluorine under pressure should be inspected for leaks, and leaky equipment should be repaired immediately. Leaks can be detected by directing aqueous ammonia from a wash bottle at suspected points or by using filter paper moistened with potassium iodide solution. In the case of ammonia, the formation of a fog indicates a leak. The potassium iodide paper will detect fluorine in concentrations as low as 25 ppm.
4. When fluorine is introduced into untested equipment, the gas should be diluted, and the process should be carried out slowly, in order that any impurities present may be burned out without igniting of the containers.
5. All equipment which has held fluorine must be thoroughly flushed with inert gas prior to opening and, if possible, should also be evacuated.
6. The use of fine adjustment valves to throttle the gas from a high-pressure cylinder in stages is preferable to depending upon the cylinder valve for throttling.
7. Foreign matter, particularly grease, should be completely removed from all containers before use.
8. Containers for fluorine under pressure should be as small as possible. In the laboratory, where cylinders are handled directly, the total weight of pure fluorine at 50 psig should not be greater than 1 pound.
9. The amount of flux which is permitted to remain in a vessel when welding or soldering is carried out should be reduced to the minimum.
10. All equipment handling fluorine should be designated by means of colors.
11. Goggles of Lucite, Plexiglas, or Lumarith should be used whenever operators must approach apparatus containing pure fluorine under pressure.
12. Structures in which fluorine is to be handled should be fireproof.
13. A vessel containing fluorine should not be heated.
14. It is desirable that two persons be present in all operations involving fluorine, but they should be at some distance from each other, in order that one can assist the other in an emergency.
15. Only trained and competent personnel should be allowed to handle fluorine, and frequent examinations of each operation should be made. All personnel connected with an operation should be familiar with the dangers involved and with the safety precautions.

16. Ventilation is important. The capacity of the ventilating system should be at least great enough to produce ten changes of air per hour in enclosed spaces.
17. It is desirable that critical valves be locked in either the open or closed position. They should be tagged.
18. A suitable alarm system should be installed, and should be tested at regular intervals.

The following safety rule was prescribed for general application to both fillers and users of cylinders: No equipment containing fluorine under pressure may be approached unless it is shielded by an adequate protective barricade, with the exception of a closed cylinder or storage tank of a tested and approved type (Cf. Ref. 27).

Diluted fluorine has properties considerably different from those of pure fluorine, and the precautions required in the case of a gas mixture containing 20 per cent fluorine and 80 per cent nitrogen are not as rigid as the precautions required in the case of pure fluorine (Cf. Ref. 37).

Y. Treatment of Burns Due to Fluorine

Landau and Rosen (Cf. Ref. 37) discuss the treatment of burns due to contact with fluorine. According to their discussion, the skin should be flooded with tepid tap water. In cases of extensive exposure, an emergency shower fitted with a quick-acting valve is advantageous. The washing should go on for 15 minutes or more and should not be discontinued even while contaminated garments are being removed. If the burn is considered slight by a physician, it can then be covered with a water-base paste containing magnesium hydroxide.

If there is a possibility, even though small, that the burn will develop beyond the erythema stage, the tissue beneath and around the affected region should be treated by injections of 10 per cent calcium gluconate solution. This solution causes precipitation of the fluoride as calcium fluoride, which is inert. The injection of calcium gluconate is not particularly painful, but it may be advisable to inject procaine first. The calcium gluconate treatment produces immediate cessation of pain and favorable pathological changes.

Fluorine burns of the eye require copious and prolonged washing with tepid tap water, as by the use of an upturned faucet or a basin of water. Such washing should be followed by irrigation with 3 per cent boric acid solution. Further treatment should take place at the direction of an ophthalmologist. It consists of the use of pontocaine to relieve pain, mydriatics, and the removal of any necrotic tissues in the cornea. Ointments should not be applied to either the skin or the eye under any circumstances.

The inhalation of fluorine at a high concentration would probably produce asphyxia through laryngeal and bronchiolar spasm and later through bronchiolar obstruction and pulmonary edema. The bronchiolar obstruction would result from swelling of mucous membrane and the secretion of tenacious mucus. Gastrointestinal symptoms and irritation of the eyes, throat, and skin would be present also, but would be of minor importance in comparison with the lung damage; the survival of the patient would be subject to the extent of oxygenation of the blood. The treatment of a patient suffering from lung damage would probably affect the final outcome but little.

III. OXYGEN BIFLUORIDE

A. Notes on Handling Oxygen Bifluoride

In the pure form, oxygen bifluoride as a gas is colorless (Cf. pp. 109-111 of Ref. 71). Koblitz and Schumacher (Cf. Ref. 72) prepared the compound by condensing with liquid air the crude oxygen bifluoride formed by the action of fluorine upon dilute sodium hydroxide solution (principally a mixture of oxygen bifluoride and oxygen) and raising the concentration of the oxygen bifluoride in the liquid by pumping off the vapor, which is richer in oxygen than the liquid, through a water aspirator.

To pump gaseous OF_2 from their reaction vessel, Koblitz and Schumacher admitted air and pumped out with a water aspirator, carrying out the process three times, and finally connected a mercury diffusion pump. Such a laborious method is necessary, because OF_2 attacks mercury.

To pump off gaseous OF_2, Ruff and Menzel (Cf. Ref. 3) used a system in which water jet pumps were combined with active carbon in liquid air, since mercury vapor jet pumps become fouled in a short time. They had to take care that the gas residue remaining after the preliminary pumping with the water jet pump (about 20 mm pressure) was adsorbed slowly by the carbon. When the adsorption was too rapid, violent explosions occurred.

B. Analysis

Oxygen bifluoride gas can be analyzed by allowing a known volume of the gas at a known pressure and temperature to react with a solution of potassium iodide in hydrochloric acid and titrating the iodine liberated with sodium thiosulfate solution. The equation (Cf. Ref. 72) is

$$OF_2 + 4HI \rightarrow 2I_2 + 2HF + H_2O$$

C. Solubility in Water

The solubility of oxygen bifluoride in water is 6.8 cc (gas) per 100 cc of water at 0°C and 1 atmosphere (Cf. Ref. 3 and pp. 109-111 of Ref. 71).

Ishikawa, Murooka, and Hagisawa (Cf. Refs. 73 and 74) gave the equation

$$C_L = 0.04297\ C_g$$

for the solubility of oxygen bifluoride in water at 20°C. C_L represents the volume of oxygen bifluoride, measured at 0°C and 760 mm, in 100 cc of solution. C_g represents the volume percentage of oxygen bifluoride in the gaseous phase. Presumably, the equation refers to a pressure of 1 atmosphere.

D. Behavior with Various Substances

The characteristics of the reactions of oxygen bifluoride with various substances are summarized in Table XXXII (Cf. Ref. 3).

Koblitz and Schumacher (Cf. Ref. 72) attempted to use reaction vessels of copper and silver in studying the thermal decomposition of OF_2 at temperatures around 250°C. They state that although both metals are well suited for experiments with fluorine at room temperatures, these metals were unsatisfactory for the study of the thermal decomposition of OF_2 at 250°C. At room temperatures, the fluoride coat which forms protects the metal underneath it from attack, but at 250°C, fluorine is still absorbed after a matter of days. Magnesium, however, was found satisfactory.

TABLE XXXII

REACTIONS OF OXYGEN BIFLUORIDE WITH VARIOUS SUBSTANCES

Substance	Conditions	Results
Potassium Sodium Lithium	400°C	brilliant light; complete absorption of the OF_2
Magnesium Calcium Strontium Barium	strong heating	brilliant light
Aluminum	dust form; 400°C	brilliant light
Manganese	powder form; 500°C	formation of fluoride with glowing
Zinc Cadmium	powder form; heating	glowing and flashing
Chromium	powder form; heating	flashing of individual particles; yellow sublimate
Flowers of sulfur	150°C	detonation; formation of SF_4 and SO_2
Boron Silicon	fine powder form; weak heating	flashing in parts
	heating to dull red	frequent explosions
Charcoal		small heat development (heat of adsorption)
	weak heating	explosion
Iron Cobalt Nickel	heating	formation of fluorides with glowing
Tin Lead	below melting point	formation of fluorides
Molybdenum	powder form; heating	glowing of entire mass; formation of MoO_3 and molybdenum oxyfluorides

TABLE XXXII (Cont'd)

Substance	Conditions	Results
Tungsten	powder form; 400°C	explosive reaction; colorless condensate (WF_6); blue coating
Antimony Arsenic	powder form; heating	small bluish flames; formation of SbF_5 and AsF_3, respectively
Bismuth		coating of BiF_3
Copper	heating	red-brown coating; later, black-brown coating
Iodine	vapor; slight heating	explosion
Silver		black coating
Mercury		coating with brown film
	boiling	at first, yellow Hg_2F_2
Palladium Platinum Iridium Osmium Ruthenium Rhodium	fine powder form; relatively low temperature	glowing; formation of traces of PdF_3, PtF_4, IrF_6, or OsF_6
Bromine	vapor; slight heating	explosion
Chlorine	heating	weak explosion
	mixture flowing into wide copper tube heated to 300°C	explosions, sometimes violent; incomplete reaction; production of ClF
Gold		brown coating
Calcium oxide	ordinary temperatures	no reaction
	heating to incandescence	formation of CaF_2 and O_2
Quartz	pointed object; heating	burning with brilliant light
Glass	dull red heat	formation of SiF_4
Sodium chloride	heating	formation of NaF and Cl_2
Sodium carbonate	heating	formation of NaF, CO_2, and O_2
Sodium nitrite	heating	formation of NaF and gaseous nitrogen compounds

TABLE XXXII (Cont'd)

Substance	Conditions	Results
Potassium nitrate	heating	formation of KF and gaseous nitrogen compounds
Phosphorus pentoxide Arsenic trioxide Aluminum chloride Chromic anhydride	heating	explosion
Tungsten trioxide	heating	formation of blue oxyfluoride
Litharge	heating	formation of PbF_2 and PbO_2
Mercuric chloride	heating	formation of brown oxyfluoride
Sulfur dioxide	equal volumes of SO_2 and OF_2; total pressure between ½ and 1 atm	pressure decrease of 15 mm in a period of several hours; small white coating of $(SO_3)_2$
Hydrogen sulfide	contact of gases	violent explosion
Ammonia	mixing of gases	slow decrease of total pressure; formation of a fog, also a white coating of NH_4F
Nitric oxide	equal volumes of NO and OF_2; total pressure between ½ and 1 atm	slow appearance of brown color; etching of walls of glass bulb (NO_2F, NOF)
	spark in mixture	explosion
Methane	equal volumes; total pressure between ½ and 1 atm.; ordinary temperatures	no reaction
	spark in mixture	violent explosion
Carbon monoxide	equal volumes; total pressure between ½ and 1 atm; ordinary temperatures	no reaction
	spark in mixture	violent explosion
Aqueous solution of silver nitrate		dark gray precipitate of Ag_2O_2
Aqueous solution of manganous sulfate		precipitate of $MnO_2 \cdot aq$
Cobaltous hydroxide	suspension in water	slow oxidation to peroxide

TABLE XXXII (Cont'd)

Substance	Conditions	Results
Nickelous hydroxide	suspension in water	slow oxidation to peroxide
Chromic ion	alkaline solution; heating	slow conversion to chromate
Aqueous solution of potassium thiocyanate	concentrated solution	opalescence followed by turbidity and separation of brick-red substance; giving off of SO_2 and C_2N_2; large heat evolution
Aqueous solution of hydrogen sulfide		formation of colloidal sulfur

Oxygen bifluoride does not attack dry glass or quartz at ordinary temperatures, but it does attack mercury. A mercury manometer used with oxygen bifluoride soon becomes so fouled that the meniscus cannot be seen. The gas attacks stopcock grease slowly (Cf. pp. 109-111 of Ref. 71).

At room temperatures, there is practically no attack of oxygen bifluoride upon glass. At temperatures above 250°C, oxygen bifluoride decomposes into its elements, and fluorine attacks "hard" glass with the formation of silicon tetrafluoride, oxygen, and fluosilicates at these temperatures. Also fluorine attacks vitreous silica with the formation of silicon tetrafluoride and oxygen at these temperatures (Cf. Ref. 72).

Oxygen bifluoride can be stored over water for days without the occurrence of appreciable reaction (Cf. Ref. 75), since it reacts only very slowly with cold water (Cf. Ref. 3). However, Ruff and Menzel found that a quantity of oxygen bifluoride which had been placed in a gasometer with water as the sealing liquid had reacted completely within 4 weeks.

Ishikawa and Sato (Cf. Refs. 76 and 77) investigated the stability of oxygen bifluoride and mixtures of oxygen bifluoride and water vapor. They found that at 20°C the decrease in the amount of oxygen bifluoride did not exceed a few per cent of the total amount present in 150 days.

A spark causes a mixture of oxygen bifluoride and water vapor to explode (Cf. Ref. 3).

Oxygen bifluoride reacts rapidly with sodium hydroxide solutions, even when the latter are very dilute (Cf. Refs. 73 and 74). Also, oxygen bifluoride reacts very rapidly with stannous chloride solutions (Cf. Refs. 78 and 79).

Dry hydrogen does not react with dry oxygen bifluoride at ordinary temperatures. However, a spark causes a mixture of the two gases to explode violently (Cf. Ref. 3).

E. Density of the Gas and of the Liquid

Experimental values of the density of gaseous OF_2 are given in Table XXXIII (Cf. Ref. 80).

The density of liquid OF_2 can be represented by the equation

$$d = 2.1315 - 0.004695T$$

in which d is the density in grams per cubic centimeter and T is the temperature on the Kelvin scale (Cf. Ref. 3). The density of liquid OF_2 is 1.53 gm/cc at -144.8°C, its normal boiling point (Cf. Ref. 81).

TABLE XXXIII

DENSITY OF GASEOUS OF_2

Temperature (°C)	Pressure (mm)	Density (gm/cc)
0	714.5	0.002254
21.5	717.0	0.002116
0	750.5	0.002398
0	750.5	0.002394
0	730.5	0.002328

F. Vapor Pressure

Ruff and Menzel (Cf. Ref. 3) report the values of the vapor pressure of OF_2 given in Table XXXIV. The values in the third column were obtained from the equation

$$\log_{10} p = 7.3892 - \frac{578.64}{T}$$

in which p is the vapor pressure in millimeters of mercury and T is the temperature on the Kelvin scale.

TABLE XXXIV

VAPOR PRESSURE OF LIQUID OXYGEN BIFLUORIDE

Temperature (°K)	Vapor Pressure (mm)	
	Observed	Calculated
80.9	1.6	1.7
82.9	2.6	2.6
84.3	3.3	3.4
85.4	4.2	4.1
87.9	6.3	6.4
91.2	10.9	11.1
94.0	17.2	17.1
95.9	22.9	22.7
98.1	30.8	31.0
100.1	41.3	40.6
101.8	50.4	50.7
103.4	62.2	62.1
104.9	76.0	74.7
106.3	89.6	88.2

TABLE XXXIV (Cont'd)

Temperature (°K)	Vapor Pressure (mm)	
	Observed	Calculated
109.8	134.0	131.6
110.6	145.0	143.7
112.7	180.4	179.8
116.7	270.2	269.7
118.4	316.7	317.7
120.6	393.5	390.1
121.9	439.5	438.8
123.4	501.0	501.3
123.8	521.8	519.0
124.3	546.4	542.0
125.2	586.2	585.3
125.4	598.2	595.5
126.3	646.9	642.2
127.0	680.9	680.6
127.9	733.1	732.8
128.1	737.9	744.9

The values of the vapor pressure of OF_2 presented in Table XXXV were obtained by Kelley (Cf. pp. 46 and 111 of Ref. 59) from smoothed curves derived from a free energy of vaporization expression given.

TABLE XXXV

VAPOR PRESSURE OF LIQUID OXYGEN BIFLUORIDE

Temperature (°K)	Vapor Pressure (atm)
68.0	0.0001
77.1	0.001
88.9	0.01
104.9	0.1
113.3	0.25
120.5	0.5
128.3	1.0

G. Melting Point and Boiling Point

The melting point of OF_2 is -223.8°C (Cf. pp. 109-111 of Ref. 71; also Refs. 81 and 82).

By calculating from their vapor pressure data, Ruff and Menzel (Cf. Ref. 3) found -144.8±0.2°C, or 128.3±0.2°K, for the normal boiling point of OF_2. Ruff (Cf. Ref. 81) gave -144.8°C. Kelley (Cf. pp. 46 and 111 of Ref. 59), Yost (Cf. pp. 109-111 of Ref. 71), and Rossini et al (Cf. Tables 9 and 10 of Ref. 62) took 128.3°K as the value.

H. Heat of Vaporization

The value of the heat of vaporization of OF_2 at temperatures a little below the normal boiling point, obtained by Ruff and Menzel (Cf. Ref. 3) from vapor pressure data through the use of the Clapeyron equation, was 2650 cal/mol. Kelley (Cf. pp. 46 and 111 of Ref. 59) takes 2650 cal/mol as the value at temperatures near the normal boiling point. Yost (Cf. pp. 109 and 111 of Ref. 71) gives 2508 cal/mol for the heat of vaporization. Rossini et al (Cf. Tables 9 and 10 of Ref. 62) take 2650 cal/mol for the heat of vaporization at the normal boiling point.

I. Critical Temperature

Ruff and Menzel (Cf. Ref. 3) estimate the critical temperature of OF_2 to be -81°C.

J. Heat of Formation

The standard heat of formation of OF_2 at room temperature was given provisionally in 1930 by Ruff and Menzel (Cf. Ref. 80) as -4.6±2 kcal/mol; that is, the value of the enthalpy increase accompanying the reaction represented by

$$F_2 + \tfrac{1}{2}O_2 \rightarrow OF_2$$

where each substance is in its standard state at room temperature was given as 4.6±2 kcal/mol. Von Wartenberg (Cf. Ref. 75) found 9 kcal/mol for the enthalpy increase at about 25°C. Later, Ruff and Menzel (Cf. Ref. 83) found 7±2 kcal/mol at 32°C. Yost (Cf. pp. 109-111 of Ref. 71) took approximately 7 kcal/mol as the value. Rossini and his associates (Cf. Table 9-1 of Ref. 63) took 5.5 kcal/mol at 25°C.

K. Various Thermodynamic Properties

Table XXXVI is a summary from several sources.

TABLE XXXVI

ENTROPY OF GASEOUS OF_2

State	Entropy (cal/deg mol)	Scientist and Year
Perfect gas at 298°K and 1 atm	approx 58	Yost (Cf. pp. 109-111 of Ref. 71), 1939
Perfect gas at 298.1°K and 1 atm	58.95±0.5	Kelley (Cf. p. 41 of Ref. 67), 1941
Perfect gas at 298.16°K and 1 atm	58.95	Rossini et al (Cf. Table 9-1 of Ref 63), 1947

The standard free energy of formation of OF_2 at 298°K is given by Yost (Cf. pp. 109-111 of Ref. 71) as approximately 11 kcal/mol. Rossini et al (Cf. Table 9-1 of

Ref. 63) give 9.7 kcal/mol for 298.16°K; they give also

$$\log_{10} \frac{p_{OF_2}}{p_{O_2}^{1/2}\, p_{F_2}} = -7.126$$

for 298.16°K (pressures in atm).

For the standard free energy of vaporization of OF_2 at temperatures near the normal boiling point, Kelley (Cf. pp. 46 and 111 of Ref. 59) gives $\Delta F^\circ = 2650 - 20.66\,T$ where T is the temperature on the Kelvin scale and the units of F are cal/mol.

L. Stability

According to Emelius (Cf. Ref. 6), OF_2 "does not under any conditions explode though it is a strong oxidizing agent." Ruff and Menzel (Cf. Ref. 3), writing in 1931, stated that an explosive spontaneous decomposition of OF_2 had never been observed. They conducted OF_2 through a 1-cm platinum tube containing a platinum gauze and heated to 300°C (at its middle). The OF_2 decomposed quietly. Koblitz and Schumacher (Cf. Ref. 72) state that OF_2 is a fairly stable gas at ordinary temperatures and that in contrast with its analogue Cl_2O, it is not explosive.

Sparks do not cause OF_2 to explode (Cf. Ref. 3). Experiments in which sparks were passed through dry oxygen bifluoride at atmospheric pressure in a glass flask showed that it could not be caused to explode under these conditions, even with the use of a high-capacity Leyden jar (Cf. Ref. 80). Von Wartenberg (Cf. Ref. 75) was unsuccessful in an attempt to cause OF_2 gas at about 10 atmospheres to explode by passing sparks through it.

M. Rate of Thermal Decomposition

OF_2 does not decompose except at elevated temperatures (Cf. pp. 109-111 of Ref. 71). Koblitz and Schumacher (Cf. Ref. 72) investigated the thermal decomposition of OF_2 experimentally at total pressures between about 100 and about 800 mm of mercury and at temperatures between about 250 and about 270°C. They found that under these conditions the reaction is a homogeneous gas reaction in quartz, "hard" glass, and magnesium. The decomposition can be represented by the following equation:

$$-\frac{d[OF_2]}{dt} = k_{OF_2}[OF_2]^2 + k_{O_2}[OF_2][O_2] + k_{SiF_4}[OF_2][SiF_4] + \cdots + k_X[OF_2][X]$$

where $[OF_2]$, $[O_2]$, $\cdots$ $[X]$ are the concentrations of OF_2, O_2, $\cdots$ X, respectively, t is the time, and k_{OF_2}, k_{O_2}, $\cdots$ k_X are constants. Values of the constants are given in Table XXXVII. The temperature coefficients for the different cases have the same value, 2.0±0.1 per 10°.

N. Toxicity

Oxygen bifluoride is a very toxic compound* (Cf., also, Ref. 53), having approxi-

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*Personal communication from S.G. Osborne of Hooker Electrochemical Co. (1947).

mately the same toxicity* as phosgene, and is more dangerous to handle than fluorine with respect to its physiological action* (Cf., also, Ref. 3). It penetrates deeper into the lungs and causes an irresistible coughing and emetic irritation, as well as difficulty in breathing. The full effect develops some time after inhalation. Menthol brings relief; complete rest is advisable (Cf. Ref. 3).

TABLE XXXVII

CONSTANTS IN EXPRESSION FOR RATE OF DECOMPOSITION OF OXYGEN BIFLUORIDE

	k (liter /mol sec)		
	at 250°C	at 260°C	at 270°C
k_{OF_2} (quartz vessel)	1.40×10^{-2} 1.39×10^{-2}	2.85×10^{-2} 2.86×10^{-2}	5.70×10^{-2} 5.71×10^{-2}
k_{OF_2} (magnesium vessel)	---	2.87×10^{-2}	---
k_{O_2}	1.34×10^{-2}	2.80×10^{-2}	5.6×10^{-2}
k_{SiF_4}	1.21×10^{-2}	2.48×10^{-2}	5.0×10^{-2}
k_{F_2}	---	2.83×10^{-2}	---
k_{N_2}	1.34×10^{-2}	---	---
k_{He}	0.95×10^{-2}	---	---
k_{Ar}	0.60×10^{-2}	1.22×10^{-2}	---

IV. CHLORINE TRIFLUORIDE

A. Behavior with Various Substances

Ruff and Krug (Cf. Ref. 2) found chlorine trifluoride to be extremely reactive. Many elements react almost explosively with the compound. Also, many oxides react similarly. The reaction between chlorine trifluoride and water is said to occur with a report like the crack of a whip. The reaction with water is so vigorous that incandescent gases are given off (Cf. Ref. 84). In general, organic substances react with chlorine trifluoride as soon as contact is made, the reaction being accompanied by flames. A drop of the liquid falling upon wood, cloth, or paper causes ignition immediately (Cf. Ref. 2). Domange and Neudorffer (Cf. Ref. 85) have confirmed the statements by Ruff and Krug concerning the great reactivity of chlorine trifluoride. Cotton, paper, wood, mineral oil, and glass wool ignite spontaneously in the compound. The reactions may be explosive. Glass wool is said to burn in chlorine trifluoride with a flame (Cf. Ref. 84).

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*Personal communication from S.G. Osborne of Hooker Electrochemical Co. (1947).

In the preparation of chlorine trifluoride, Ruff and Krug (Cf. Ref. 2) used a copper vessel to carry out the reaction between chlorine and fluorine. The receiving vessel for the chlorine trifluoride was of fused quartz and was held at -70°C. The investigators kept the receiving vessel in a copper block, because of the dangerous nature of the material.

Chlorine trifluoride was produced in pilot-plant quantities in Germany during the recent war. The product was collected in iron cylinders (Cf. Ref. 86). Kwasnik (Cf. Ref. 87) refers to the use of a Monel reaction chamber in the large-scale production of chlorine trifluoride in Germany. Fluorine and chlorine were brought together in this chamber at 260°C, and chlorine trifluoride together with a little chlorine monofluoride was formed. The chamber was vigorously attacked. Schmitz and Schumacher (Cf. Ref. 88) used nickel and magnesium vessels in their study of the equilibrium represented by

$$ClF + F_2 \rightleftarrows ClF_3$$

at 250, 300, and 350°C.

The characteristics of the reactions of liquid chlorine trifluoride with various substances as reported by Ruff and Krug (Cf. Ref. 2) are summarized in Table XXXVIII. The tests were made by allowing the liquid to drip from vitreous silica bulbs into small tubes containing the substances. Details of the conditions are not reported, but probably many of the metals were finely divided.

TABLE XXXVIII

REACTIONS OF LIQUID CHLORINE TRIFLUORIDE WITH VARIOUS SUBSTANCES

Substance	Results
Potassium Iron Molybdenum Tungsten Iridium Osmium Rhodium	flames
Sodium Calcium	at first, no reaction, because of crust formation; violent reaction upon heating
Magnesium Aluminum Zinc Tin Lead Copper Silver	at first, no reaction; explosive reaction after ignition with carbon
Mercury	slow reaction

TABLE XXXVIII (Cont'd)

Substance	Results
Palladium Platinum	no reaction
Sulfur	flames; formation of a white fog; odor like that of S_2Cl_2
Silicon Antimony Arsenic Tellurium Selenium Phosphorus (red)	flames
Iodine	flames; formation of a colorless liquid which freezes below 0°C, fumes in air, etches glass, and reacts violently with water, benzene, and ether (probably IF_5)
Bromine	formation of a red liquid which evaporates completely between 0°C and room temperatures (perhaps BrF_3)
Water	formation of SiF_4 and a red liquid which freezes at about -70°C ($ClOF$?)
Calcium oxide Magnesium oxide Aluminum oxide Manganese dioxide Vanadium pentoxide Chromium sesquioxide Lead dioxide Molybdic anhydride Tungsten trioxide Tantalum pentoxide	flames
Chromic anhydride	violent reaction with the formation of brown vapors (CrO_2F_2 ?)
Stannic oxide Lanthanum oxide Titanium dioxide Arsenic trioxide Boron oxide Phosphorus pentoxide	chemical activity but no flames
Quartz glass, completely dry Quartz wool, completely dry	slow reaction

TABLE XXXVIII (Cont'd)

Substance	Results
Quartz glass, traces of moisture Quartz wool, traces of moisture	formation of a green gas and a red easily volatilized liquid; occasional formation of long colorless needles on the surface
Glass wool	flames
Zinc oxide Ferric oxide Thorium oxide Zirconium oxide Mercuric oxide	no reaction
Mercuric iodide Tungsten carbide (WC)	flames
Potassium iodide Potassium carbonate Silver nitrate	chemical activity but no flames
Potassium sulfate Potassium nitrate Sodium chloride Mercuric sulfate Mercuric chloride	no reaction
Concentrated sulfuric acid Fuming nitric acid Aqueous solution of sodium hydroxide (10%)	chemical activity but no flames
Hydrogen sulfide Ammonia Sulfur dioxide	flames; formation of a white fog
Hydrogen Illuminating gas	flames
Charcoal	flames
Graphite Powdered graphite	flames from smallest particles
Rubber (tubing)	brisk reaction; production of gas; change to white brittle material
Picein Paraffin High-vacuum grease Wood Paper Cloth Cotton	immediate ignition

TABLE XXXVIII (Cont'd)

Substance	Results
Benzene Ether Glacial acetic acid	violent reaction
Carbon tetrachloride	reaction only after heating

Teflon reacts with chlorine trifluoride under special conditions (Cf. Ref. 89). ClF_3 reacts completely with Cl_2 to form ClF (Cf. Ref. 88).

B. Analysis

Ruff and Krug (Cf. Ref. 2) analyzed chlorine trifluoride by allowing a weighed sample to react with a relatively large quantity of 10 per cent sodium hydroxide solution, reducing most of the chloric acid formed by means of hydrazine hydrate or chlorine-free zinc dust, determining the fluoride as CaF_2, and determining the chloride as AgCl after completing the reduction of the chloric acid with sulfurous acid.

C. Density of the Liquid

The density of liquid ClF_3 is 1.77 gm/cc at 12.1°C, its normal boiling point (Cf. Ref. 81).

D. Vapor Pressure

Ruff and Krug (Cf. Ref. 2) give the following equation for the vapor pressure of ClF_3:

$$\log_{10} p = 7.42 - \frac{1292}{T}$$

in which p is the vapor pressure in millimeters of mercury and T is the temperature on the Kelvin scale.

E. Melting Point and Boiling Point

The melting point of ClF_3 was given by Ruff and Krug (Cf. Ref. 2) in 1930 as approximately -83°C. Later, Ruff (Cf. Ref. 81) gave -82.6°C.

Using their vapor pressure equation, Ruff and Krug (Cf. Ref. 2) found 11.3°C for the normal boiling point of ClF_3. Ruff (Cf. Ref. 81) gave 12.1°C. Rossini et al (Cf. Tables 9 and 10 of Ref. 62) took 284.6°K as the value.

F. Heat of Vaporization and Entropy of Vaporization

The entropy of vaporization of ClF_3 at the normal boiling point was calculated by Ruff and Krug (Cf. Ref. 2) from their vapor pressure data. The value obtained was 20.8 cal/°K mol.

Rossini and his associates (Cf. Tables 9 and 10 of Ref. 62) give 5740 cal/mol for the heat of vaporization of ClF_3 at the normal boiling point.

G. Critical Temperature

Ruff and Krug (Cf. Ref. 2) estimate the critical temperature of ClF_3 to be 426.7°K, or 153.5°C.

H. Various Thermodynamic Properties

Schmitz and Schumacher (Cf. Ref. 88) have studied the equilibrium represented by

$$ClF + F_2 \rightleftarrows ClF_3$$

From manometric measurements, the following values were obtained for the equilibrium constant:

$$K = \frac{p_{ClF}\, p_{F_2}}{p_{ClF_3}}$$

Temperature (°C)	$K = \frac{p_{ClF}\, p_{F_2}}{p_{ClF_3}}$ (atm)
250	2.98×10^{-4}
300	24×10^{-4}
350	143×10^{-4}

The value for the heat of reaction at 300°C derived from these data is 25±2 kcal.

Schmitz and Schumacher (Cf. Ref. 88) have calorimetrically determined the following heats of reaction:

$$NaCl + \tfrac{1}{2}F_2 \rightarrow NaF + \tfrac{1}{2}Cl_2 \text{ at } 18^\circ C \quad Q = 39.5 \pm 0.5 \text{ kcal}$$

$$NaCl + ClF \rightarrow NaF + Cl_2 \text{ at } 18^\circ C \quad Q = 24.5 \pm 0.1 \text{ kcal}$$

$$3NaCl + ClF_3 \rightarrow 3NaF + 2Cl_2 \text{ at } 18^\circ C \quad Q = 76.5 \text{ kcal}$$

From these values the following heats of reaction can be derived:

$$\tfrac{1}{2}F_2 + \tfrac{1}{2}Cl_2 \rightarrow ClF \text{ at } 18^\circ C \quad Q = 15.0 \pm 0.5 \text{ kcal}$$

$$ClF + F_2 \rightarrow ClF_3 \text{ at } 18^\circ C \quad Q = 27.0 \pm 1.5 \text{ kcal}$$

$$\tfrac{1}{2}Cl_2 + \frac{3}{2}F_2 \rightarrow ClF_3 \text{ at } 18^\circ C \quad Q = 42.0 \text{ kcal}$$

The second of these derived values is in good agreement with the value which these investigators obtained from their study of the equilibrium among the three substances.

The equilibrium represented by

$$2ClF_3 \rightleftarrows (ClF_3)_2$$

has been investigated by the same men. The following values have been obtained for the equilibrium constant:

$$K = \frac{p^2_{ClF_3}}{p_{(ClF_3)_2}}$$

Temperature (°C)	$K = \frac{p^2_{ClF_3}}{p_{(ClF_3)_2}}$ (atm)
9.5	26.9
20.0	32.1
24.2	35.4

The value for the heat of reaction at about 20°C derived from these data is 3.3±0.5 kcal. The measurements were made at pressures between 300 and 800 mm (Cf. Ref. 90).

I. Miscellaneous Properties

In the pure form, chlorine trifluoride as a solid is white and as a gas is nearly colorless (Cf. Refs. 2 and 85). As a liquid, it is a light green, and it has a characteristic penetrating odor, similar to ClF (Cf. Ref. 2).

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