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SECOND ANNUAL PROGRESS REPORT
FOR THE
OFFICE OF NAVAL RESEARCH
CONTRACT NONR 3085(01)

ADDITION AND SUBSTITUTION PRODUCTS OF OXYGEN FLUORIDES

A. G. STRENG AND A. V. GROSSE

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INTRODUCTION

This is the Second Annual Report for the Office of Naval Research, Contract Nonr 3085(01). It covers the period from January 1 to December 31, 1961.

The research program was specified by the Research and Development Task Order and consists of the two following subjects:

I. The synthesis and characterization of the oxygen fluorides.

II. The synthesis and characterization of certain substitution and addition products of the oxygen fluorides.

SUMMARY

A new type of highly colored deep-violet addition compounds of dioxygen difluoride has been obtained. These compounds are formed by addition to ClF, BrF_3 and SF_4, under mild reaction conditions. They have a remarkable oxidizing power, even at very low temperatures.

The analogous fluorides of the other elements adjoining oxygen and fluorine in the Periodic System, namely, N_2F_4, PF_3, SiF_4, CF_4 and IF_5, did not form addition compounds of this type.

The O_2F_2 + ClF reaction was studied extensively. Various combinations of the factors influencing the synthesis were investigated, and the yield of the violet addition product was raised to 81% of the theoretical value.

The investigation of the properties of the violet compound, the elementary composition of which was found to be O_2ClF_3, showed that the solid violet compound, contaminated only by ClF_3, is stable at 195°K. At this temperature it was kept for over 9 months without any noticeable decomposition. The compound is soluble in liquid ClF_3, ClF, O_2F_2 and HF, at 125-190°K., but is insoluble in liquid O_2, O_3, ClO_3F, C_3F_8, NF_3, CCl_2F_2 and $CClF_3$ in the range of 90-160°K. The solutions are less stable than the solid compound. The measurements of the electrical conductivity of a solution of the violet compound in anhydrous HF at -78°C. showed that O_2ClF_3 is not an electrolyte.

The study of the reactivity of the violet compound at low temperatures showed its extremely high oxidizing power. The compound reacts vigorously with ammonia, ethane and ethylene, even at 120-160°K. There was no reaction, however, with liquid methane at 90°K.; with gaseous methane at 150°K.; and with gaseous hydrogen at 120°K. under a pressure of 100 mm. Hg.

The violet addition product was synthesized also from ClF_3 and O_2 at 195°K. under pressure, by irradiation with ultraviolet light. The preliminary data on the visible absorption spectrum of this compound were obtained.

The decomposition of a solution of O_2ClF_3 in anhydrous HF led, under some conditions, to the formation of a blue compound or compounds. The nature of these compounds was not established.

The flow diagram and the description of the methods of preparation of O_2F_2 and O_3F_2 are given.

I. A NEW TYPE OF HIGHLY COLORED ADDITION PRODUCTS OF DIOXYGEN DIFLUORIDE

The reactions of oxygen fluorides with various lower fluorides of the elements close to oxygen and fluorine in the Periodic System were studied. It was found that at low temperatures, i.e. 110-140°K., dioxygen difluoride, O_2F_2, adds chlorine monofluoride, ClF, forming a highly colored, purple to violet, addition compound. The elementary formula of this compound is O_2ClF_3. This is a new type of compound with remarkable oxidizing properties.

Bromine trifluoride, BrF_3, and sulfur tetrafluoride, SF_4, also form, under very mild conditions, highly colored brown-to-violet addition products.

The fluorides of the other elements close to oxygen and fluorine in the Periodic System, namely, nitrogen, phosphorus, carbon and silicon do not form the violet addition compounds. Phosphorus trifluoride, PF_3, combines with O_2F_2, forming $(POF_3)_n$ and PF_5. The POF_3 is produced in the form of an interesting polymer which depolymerizes at higher temperatures to gaseous POF_3. Tetrafluorohydrazine, N_2F_4, reacts, giving O_2 and NF_3. Carbon tetrafluoride, CF_4, and silicon tetrafluoride, SiF_4, do not react, as was expected, in view of their saturated nature. Iodine pentafluoride, IF_5, does not react at low temperatures but under more drastic conditions will probably form iodine heptafluoride, IF_7.

II. THE O_2F_2 + ClF REACTION. FORMATION OF O_2ClF_3

A. Reaction Conditions

At 90°K., solid dioxygen difluoride (m.p. 109.7°K.) and solid chlorine monofluoride (m.p. 119°K.) do not react when ClF is condensed on a thin solidified layer of O_2F_2.

Gaseous O_2F_2, on the other hand, at about 195°K., reacts with ClF directly to give oxygen gas and ClF_3, without the formation of intermediate compounds. The reaction proceeds in accordance with the equation:

$$O_2F_2 + ClF \rightarrow O_2 + ClF_3 \quad -30.1 \text{ Kcal.}$$

At temperatures of about 110-140°K., however, O_2F_2 reacts with ClF, forming a deep violet intermediate addition compound, O_2ClF_3. The formation of the violet compound is usually accompanied by the evolution of gaseous oxygen and fluorine in varying ratios. At temperatures above 140°K. the reaction proceeds violently. The ClF abstracts the fluorine from O_2F_2 according to equation (1). If the addition of ClF is too rapid, some of the O_2F_2 is decomposed to O_2 and F_2.

At more moderate temperatures (110-140°K.) and with a slow addition of ClF, <u>three</u> reactions take place simultaneously in varying proportions.

The formation of the violet addition product:

$$O_2F_2 + ClF \rightarrow O_2ClF_3 \qquad (1)$$

The decomposition of the violet compound either at the time of formation or when the temperature is raised:

$$O_2ClF_3 \rightarrow O_2 + ClF_3 \qquad (2)$$

and the thermal decomposition of O_2F_2:

$$O_2F_2 \rightarrow O_2 + F_2 \qquad (3)$$

The extent of each reaction can be readily determined analytically, since reactions (2) and (3) produce gaseous oxygen and reaction (3), produces, in addition, free fluorine. The oxygen can be determined by standard Orsat analysis or other known methods; the fluorine by Hg-burette absorption; and the chlorine trifluoride by freezing it out (m.p. 190°K.) and checking its purity by vapor-pressure measurement, infrared spectrum or melting point.

Reaction (1) is difficult to control. Much effort was exerted to find the conditions necessary to minimize reactions (2) and (3); i.e., to increase the yield of the violet product.

Since the violet reaction product is energy rich, it decomposes rapidly if the reaction proceeds too violently or even under mild conditions, if impurities are present. In the presence of traces of water, nitrogen oxides or nitrogen oxyfluorides, the violet compound decomposes quickly or does not form.

In view of the intense color it was at first thought that ozone was formed, possibly following the equation:

$$3\ O_2F_2 + 3\ ClF \rightarrow 2\ O_3 + 3\ ClF_3$$

Although ozone is deep blue and the reaction product violet-blue, ozone and liquid O_2F_2 form a violet-blue solution.

It was found, however, that O_3 does not dissolve in ClF_3 and does not form an addition product with it. In the absence of O_2F_2 and in the presence of ClF_3, ozone, as expected, retains its characteristic deep blue color. Ozone can be isolated easily from such a mixture by two methods: (1) by extraction with liquid O_2, which immediately gives a deep blue solution, while ClF_3 remains practically insoluble, or (2) by high-vacuum distillation. At a total pressure of 12μ and at a temperature of 158°K., the violet compound does not distil. Ozone, on the other hand, has a vapor pressure of 600 mm. at 158°K. and would readily distil.

The violet reaction product may be prepared simply by adding pure ClF to pure O_2F_2. The dioxygen difluoride is condensed in a reaction tube cooled in a liquid-oxygen bath, the ClF is added and the tube is warmed slowly. In the temperature range of about 110 to 140°K., these compounds react, forming, together with other compounds, the intense violet addition product, which has strong oxidizing properties. The most favorable temperature is 119°K., the melting point of ClF.

The yield of the violet compound depends upon the rate of addition of ClF, temperature, area and uniformity of distribution of O_2F_2.

The three reactions mentioned previously take place simultaneously. The optimum yield attained was about 50%, based on reaction (1), although in most cases the yield was very much smaller.

The simplest way to increase the yield is to dilute the reagents. Freon 13 ($CClF_3$) was found to be a solvent for O_2F_2 at about 130°. When gaseous ClF diluted with helium is bubbled through a solution of O_2F_2 in Freon 13, cooled to 130-140°K., the reaction between O_2F_2 and ClF proceeds in most cases without gas evolution; i.e., without decomposition of the violet compound into O_2 and ClF_3, according to reaction (2), or without decomposition of O_2F_2 into O_2 and F_2, as in reaction (3). It was found, however, that in the presence of Freon 13, the thermal stability of the violet compound is substantially decreased. The violet compound is not soluble in Freon 13; it precipitates to the bottom of the reaction vessel and decomposes with considerable velocity at about 195°K. It may be that impurities in Freon 13 cause this decomposition.

There was no formation of a violet compound at all when Freon 12 (CCl_2F_2) was used as the solvent for O_2F_2. The synthesis was attempted with a 6.3 wt.% O_2F_2 solution in Freon 12. The solution was cooled to 90°K., ClF was added and the tube was slowly warmed up. The reaction between O_2F_2 and ClF started at about 130°K., but without the formation of a violet product.

The use of perchloryl fluoride as the solvent in the reaction between O_2F_2 and ClF did not increase the yield of the violet compound but did serve to lower its stability. A 14.0 wt.% O_2F_2 solution in ClO_3F was used. The solution was cooled to 90°K. and small portions of ClF gas were added. After each addition, the reaction vessel was warmed to 125°K. A slow reaction occurred, with the formation of a comparatively large amount of ClF_3 and a comparatively small amount of the violet product. Both these products are insoluble in ClO_3F at 125°K. and collect on the bottom of the vessel. The vessel was then cooled again to 90°K. and a new portion of ClF was added. When all the O_2F_2 was consumed, the reaction vessel was slowly warmed to 190°K. At this temperature, ClF_3 dissolves completely in ClO_3F and the violet compound remains on the bottom in the form of dark violet flakes. The yield of the violet compound was much smaller than that obtained in the reaction between pure O_2F_2 and ClF. At about 195°K. the violet compound decomposed completely.

Anhydrous hydrogen fluoride, HF, is also a good solvent for both O_2F_2 and the violet compound. At its melting point, 190°K., hydrogen fluoride dissolves about 23 mole % O_2ClF_3, forming a deep violet solution. A difficulty arises, however, from the fact that the solution of the violet compound in HF is stable at 190-195°K., only under an oxygen pressure of about two atmospheres. For this reason the removal of HF and the isolation of the violet compound are complicated.

The attempts to lower the melting point of HF by the addition of KF[1] and thereby to increase the stability of the solutions of the violet compound, gave no improvement. On the contrary, in the presence of KF the solutions of the violet compound in HF lost their color much faster than normally, most probably owing to the formation of $K(ClF_4)$.

Perfluoropropane, C_3F_8 (m.p. 90°K., b.p. 235°K.), was also investigated as a diluent for the $O_2F_2 + ClF$ reaction. It dissolves over 33 wt.% ClF at 150°K. and mixes homogeneously with it at 160°K. The solubility of O_2F_2 in C_3F_8, however, is very low.

Perfluoropropane used as a diluent increased the yield of the violet compound up to 81% of theory. The violet compound and ClF_3 are, however, not soluble in C_3F_8. The stability of the violet product in the presence of C_3F_8 was found to be low.

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(1) Cady, G. H., J. Am. Chem. Soc., 56, 1431 (1934).

B. Solvents for the Reagents and the Reaction Products

The effort is continuing to find a suitable solvent for the reagents, O_2F_2 and ClF, and for the reaction products, in order to facilitate the isolation of the pure violet compound. Hildebrand's generally useful concept of solubility parameters[2] does not always predict correctly the solubility behavior of liquefied gases at low temperatures.[3] It was, therefore, necessary to obtain miscibility and solubility information experimentally. The substances tested and the results obtained to date are as follows:

	Mixes homogeneously with:		Forms two practically insoluble layers with:	
O_2F_2:	O_3F_2	at 116°K.	N_2	at 77°K.
	CCl_2F_2	116	F_2	77
	$CClF_3$	116	CF_4	90
	CO_3F	127	O_2	90
	ClF_3	180	NF_3	130
	NO_2F	195	C_3F_8	140
			N_2F_4	130
ClF:	CO_3F	at 160°K.	O_3F_2	at 90°K.
	C_3F_8	160	NF_3	150
			ClF_3	174
			HF	173
ClF_3:	O_2F_2	at 180°K.	O_3F_2	at 90°K.
	ClO_3F	195	NF_3	140
	HF	195	ClF	174
			CCl_2F_2	125
			$CClF_3$	190
			C_3F_8	235

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(2) Hildebrand, J. H., and Scott, R. L., "The Solubility of Nonelectrolytes," 3rd Ed. Reinhold, New York, 1950.

(3) Streng, A. G., and Grosse, A. V., "The Different Solubility Behavior of the Isosteric Liquids CO and N_2 in Liquid Ozone," J. Inorg. & Nucl. Chem., 9, 315 (1959).

In the course of these investigations it was found also that:

1) O_2F_2 dissolves about 20 wt.% of SiF_4 at 150°K. and about 11 wt.% of HF at 186°K.
2) HF dissolves at least 6.6 mole % ClF at 190°K. and about 5.8 wt.% O_2F_2 at 176°K. and 11.6 wt.% O_2F_2 at 186°K.
3) FC-15 ($C_8F_{16}O$) dissolves about 3 wt.% ClF_3 at 195°K.
4) C_3F_8 dissolves some O_2F_2 at 130°K.
5) N_2F_4 dissolves some O_2F_2 at 140°K.

C. Formation of an Unknown Blue Compound or Compounds

If the violet compound is warmed up to about 140°K. in the presence of ClF and ClF_3, it changes into a greenish-blue compound, which exists only over a very narrow temperature range. The greenish-blue compound dissolves in ClF at about 125-130°K., to form a greenish-blue solution, but the color disappears in about three to five minutes. Probably another blue compound was formed while pumping off the oxygen from a violet solution of O_2ClF_3 in anhydrous HF at 190-195°K. The solution changed color and became deep blue like the color of ozone. The question might well be raised whether in the decomposition of O_2ClF_3 the oxygen is liberated as O_3 or whether a new type of compound is formed which has a color similar to that of ozone. This possibility will be checked later by determining the visible absorbtion spectrum of the solution.

It is of interest to mention here that over 3.5 wt.% of ozone dissolves in HF at 195°K. and at pressures less than one atmosphere to form a solution similar in appearance to the one described above.

D. Synthesis of the Violet Compound Directly From O_2 and ClF_3 Under the Influence of Ultraviolet Light

The discovery that oxygen pressure has an important effect on the stability of the violet compound dissolved in HF, led us to the experiment described below.

Pure ClF_3 was placed in a quartz tube surrounded by dry ice, i.e., at 195°K., and irradiated with ultraviolet light, principally at 2537 Ångstrom units with an intensity of 7 milliwatts/cm^2. Under a pressure of two atmospheres of oxygen a violet compound was produced after only a few seconds irradiation; the color increased appreciably with time. On the other hand, if the pressure of the oxygen was only 15 mm. the violet compound was not formed. A check experiment on pure ClF_3 in the absence of oxygen showed no change in color. Thus, at the present time we have a reversible reaction for the formation of the violet compound from the simple, commercially available materials, O_2 and ClF_3, merely by changing the pressure of the oxygen.

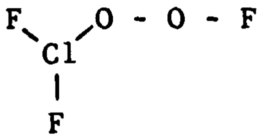
III. THE PROPERTIES OF THE VIOLET O_2F_2 + ClF ADDITION PRODUCT

A. General

From classical theories of structure of inorganic chemistry, and a knowledge of the structure of O_2F_2 certain simple structures of the new compound may be postulated. The structure of O_2F_2 has been determined to be:

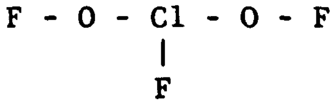
F - O - O - F.

Since the chlorine in ClF is monovalent and can be converted to trivalent chlorine, the simplest assumption is that the addition of ClF to F - O - O - F takes place either (a) across the O - F bond, leading to the compound:



,

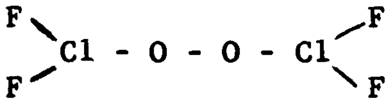
or (b) across the O - O bond, leading to the compound:



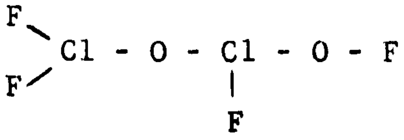
$$F - O - \underset{\displaystyle F}{\underset{|}{Cl}} - O - F$$

.

In case (a), the addition of a second molecule of ClF would lead to the compound:

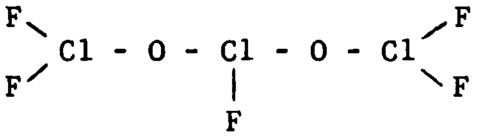


In the less likely case of addition of the second molecule across the O - O bond the isomeric compound



would be obtained.

The latter compound could also add a third molecule of ClF leading to the compound:



.

Either of the alternatives (a) and (b) is possible, because the bond strengths F - O - and - O - O - are not very different. They are estimated to be 61 Kcal. for - O - O - and 50 Kcal for F - O -, assuming a chain structure in O_2F_2.

The following properties of the compound have been determined so far:

The color is close to that of a 0.1% aqueous solution of the intense violet dye methyl violet.

It is solid at 195°K. and in the absence of impurities can be kept at this temperature for months without noticeable decomposition. The thermal stability of the compound depends on the presence of catalysts or inhibitors of decomposition. It was found that if the original O_2F_2 contains nitrogen compounds such as NOF, NO_2F, or NO_2 or other oxides of nitrogen, the decomposition of the violet compound is catalyzed so that the yields are very poor and the thermal stability is low.

The vapor pressure of the violet reaction product at 158°K. is below 12 microns.

The following observations were also made: If the O_2F_2 + ClF reaction is carried out with an excess of ClF or in the presence of ClO_3F or Freons 12 and 13 as diluents, the yield of the violet compound is low.

The violet compound is stable at temperatures up to 195°K. and has been kept at this temperature for 9 months. In general it was found that the stability of dry solid violet product is much higher than its stability in the dissolved state.

It was noted that the violet compound does not distil at 160°K. even at a pressure of 12 microns. It was found, however, that under these conditions it dissociates into O_2F_2 and ClF, which were recovered in a liquid-nitrogen trap. If these dissociation products are warmed to about 130°K. the deep violet compound forms again.

B. Solubility

The search for a suitable solvent for the O_2F_2 + ClF violet reaction product continues. The following substances have been tested, and the results obtained to date are listed below:

The violet compound is soluble in:

liquid ClF	at 125°K.
" O_2F_2	at 140
" ClF_3	at 190
" HF	at 190

The stability of all these solvents is lower than the stability of the violet compound in the solid state.

The violet compound is not soluble in:

liquid O_2	at 90°K.
" O_3	at 90
" ClO_3F	at 135
" C_3F_8	at 140
" NF_3	at 150
" CCl_2F_2	at 160
" $CClF_3$	at 160

C. Conductivity

The electrolytic conductivity of a solution of the violet compound in HF was measured by using a Wheatstone bridge* and a specially made Teflon cell with platinum electrodes.

(*) Impedance bridge, Type 650A of the General Radio Co., Cambridge, Mass.

A 0.5-molar solution of O_2ClF_3 in HF was investigated at 195°K. The anhydrous HF had a specific conductivity of 3.57 x 10^{-3} ohm^{-1} cm^{-1}. The conductivity of the violet solution was 3.33 x 10^{-3} and changed upon standing for an hour to 3.57 x 10^{-3} ohm^{-1} cm^{-1}. After this change, the violet compound was permitted to decompose by pumping off the oxygen, and the residual clean colorless solution of ClF_3 in HF had a conductivity of 3.57 x 10^{-3} ohm^{-1} cm^{-1}. The best data on the specific conductivity of pure HF indicate that our HF contained traces of water in the amount of 2 mg. per liter.[4]

It is obvious that our violet compound does not increase the specific conductivity of anhydrous HF and is consequently not an electrolyte. In contrast, a 0.5-molar solution of a typical electrolyte, namely, KF in HF, has a specific conductivity of 86.0 ohm^{-1} cm^{-1}. Thus, a similar concentration of potassium fluoride conducts the current approximately 25,000 times better than does our violet compound. The possibility that our violet compound, O_2ClF_3, might be ionic or salt like, dissociating for example into the ions,

$(O_2ClF_2)^+ + F^-$, is excluded.

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(4) Simons, J. H., "Fluorine Chemistry," Vol. 1, Academic Press, Inc., N. Y., 1950, p. 240.

D. Visible Spectrum

It was previously reported that the violet compound is also formed when liquid ClF_3 (in the presence of oxygen at 195°K.) is irradiated with ultraviolet light. The visible spectrum of this compound was taken.

The violet compound was prepared for this investigation directly in a specially made silica-glass spectroscopic cell. The cell was filled with ClF_3 to about two-thirds of its capacity and gaseous O_2 (two atmospheres pressure) was added. The cell was then exposed for 15-20 min. at 195°K. to ultraviolet light of 2537Å units and an intensity of 7 milliwatts/cm^2.

The spectrum was taken on a Beckman spectrophotometer, Model DU, fitted with a special cell compartment for measurements at low temperatures.[3]

The preliminary data obtained are given in Table I and Fig. 1.

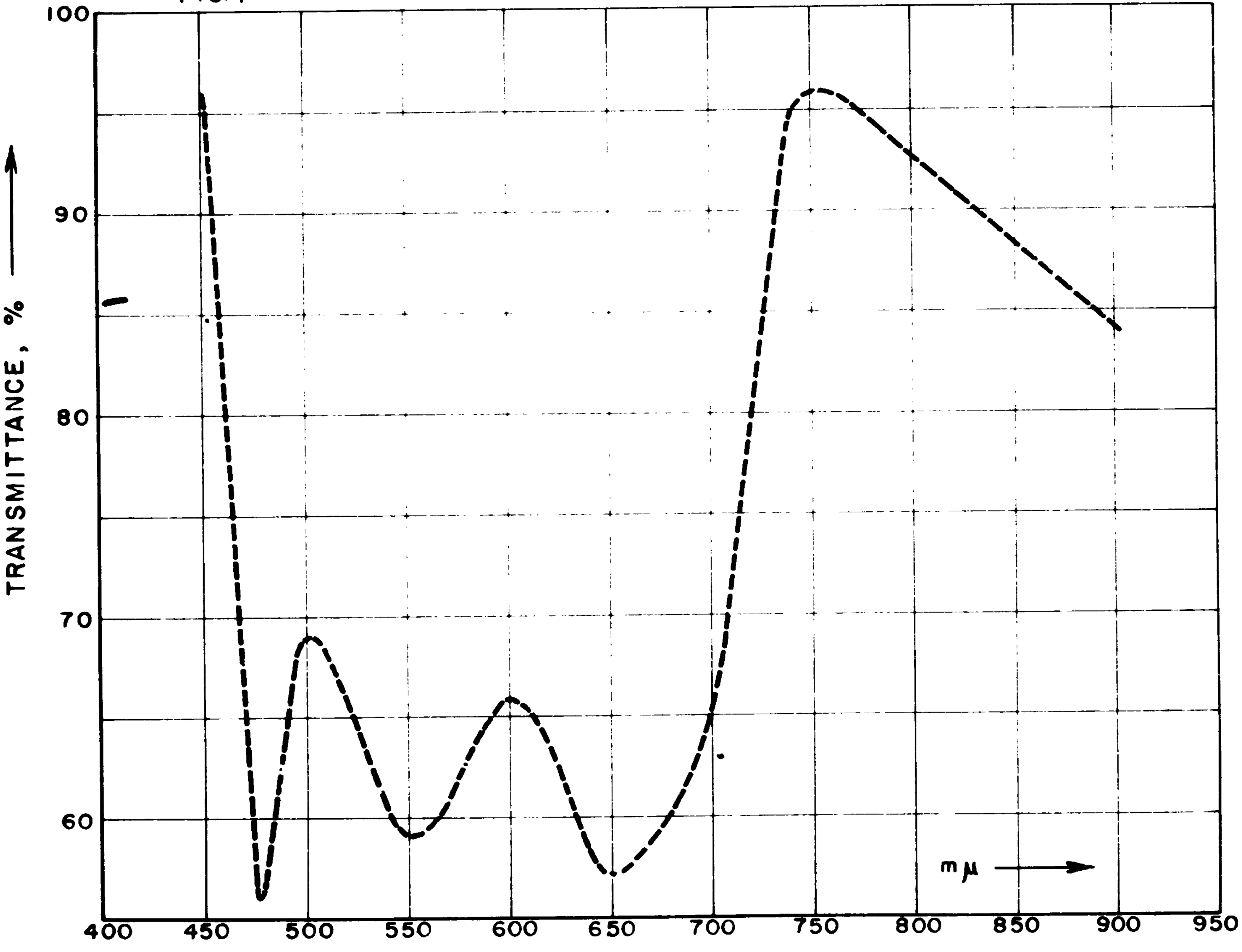
TABLE I

Preliminary Data on Visible Spectrum of Violet Compound Formed by $ClF_3 + O_2$ Under Ultra-Violet Light at 195°K.

Wave length, m	Transmittance, %	Estimated molar extinction coefficient, cm^{-1} $mole^{-1}$ lit.
450	96	--
475	56	50
500	69	--
550	59	46
600	66	--
650	57	49
700	67	--
750	96	--
850	88	--
900	84	--

The concentration of the solution used was estimated to be about 0.005 mole/lit.

FIG. 1 VIOLET SPECTRUM OF VIOLET PRODUCT



IV. CHEMICAL REACTIONS OF O_2ClF_3 AT LOW TEMPERATURES

It was found that dioxygen monochlorotrifluoride, O_2ClF_3, is highly reactive at low temperatures towards ammonia and various hydrocarbons. In this respect it is similar to the highly reactive ozone, which was found to react even at 150-160°K. with ammonia.[5] Usually no chemical reactions take place at a temperature range of 100-150°K. outside of exceptionally reactive systems; for example, free atoms or radicals, as has been strikingly demonstrated by Dr. H. Broida and his associates at the National Bureau of Standards.

Since O_2ClF_3 is of interest as a potential oxidizer, it was of importance to study its reactions with various hydrides.

A. Reaction with Ammonia

It was established in preliminary experiments, that gaseous ammonia entering a reaction vessel which contains the deep-violet O_2ClF_3, at a temperature of 90°K., reacts violently with a flash, forming some white solids and some nitrogen-containing gases, while the violet color disappears.

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(5) Grosse, A. V., and Streng, A. G., Technical Note No. 4, Contract No. AF 18(600)-1475, Project No. 7-7968, the Research Institute of Temple University, August 1, 1957.

If the ammonia is condensed first in the upper part of the reaction tube cooled to 90°K., then the reaction proceeds slowly as the vessel is warmed up to 150-160°K. Ammonia has a vapor pressure of about 1 mm. at 160°K. and therefore evaporates slowly and reacts as a gas with the solid violet compound. Under these conditions the reaction proceeds smoothly without any gas evolution. The violet color disappears and a white solid is formed.

Ammonium fluoride and other ammonium salts, HF, HCL, and the oxy-acids of chlorine (either free or as ammonium salts) were identified among the reaction products.

Hydrogen fluoride was identified by vacuum distillation, formation of NaF. HF and titration. Hydrogen chloride was identified through formation of silver chloride. Ammonia was determined quantitatively by Kjeldahl's method. The oxynitrogen acids or oxychlorine acids were identified qualitatively by Lunge's reagent. Anions of the oxychlorine acids, i.e., chlorite, chlorate or perchlorate, were identified by reduction with zinc to chloride ion.

In one experiment 0.25 g. O_2ClF_3 was reacted with about 0.10 g. of ammonia. 52 mg. of NH_3 was found in the reaction product together with about 3 mg. of N_2 (gas). Thus, about one-half of the ammonia added formed ammonium salts. This mixture of ammonium salts and oxidizers is potentially dangerous and can detonate!

B. Reaction with Methane

Dioxygen monochlorotrifluoride does not react with an excess of liquid methane at 90°K. It also does not react with gaseous methane at a pressure of 100 mm. Hg at 150°K. During one hour there was neither a decrease in pressure nor a disappearance of the violet color.

C. Reaction with Ethane

In contrast with the observations in the case of methane, ethane, when admitted to the violet compound at a temperature of 140°K., reacted immediately. The violet color disappeared and white solids were formed but no gas was evolved. That is, there was no formation of O_2, F_2 or CO.

Hydrogen fluoride was identified in the reaction products as was ClF_3, which was present as a contaminant in the original O_2ClF_3.

D. Reaction with Ethylene

The reaction vessel containing 1.39 g. of O_2ClF_3 was cooled to 120°K. and ethylene gas was introduced (ethylene has a vapor pressure of about 1.0 mm. Hg at 120°K.) in portions of about 5 mg. at a rate of about 1 mg. per sec. After an interruption of one to two minutes, new portions were added.

Under those conditions ethylene reacted immediately, causing decolorization of the violet compound and formation of the white solid products, while no measurable gas evolution, i.e. no formation of O_2, F_2 or CO, took place.

On one occassion when ethylene was added at a higher rate, the reaction proceeded with a flame which extinguished itself as soon as the ethylene flow was stopped. A total of 0.179 g. of ethylene was added to 1.3 g. of O_2ClF_3; the temperature of the bath after this addition was slowly raised at the rate of 1-1½°/min. No gas evolution was noticed up to 140°K. At 140°K. a violent explosion took place, shattering the reaction vessel and a large part of the reaction system. Evidently, intermediate or partly oxidized products were formed.

In all reactions of O_2ClF_3 with hydrogen-containing substances, HF is the most likely reaction product. Carbonyl fluoride, COF_2 and other intermediate oxyfluorides, for example, oxalyl fluoride, $C_2O_2F_2$, may be formed. In view of the violent explosion which took place, it is also likely that some C-H containing compounds were present.

E. Reaction with Hydrogen

During one hour at 90-120°K. there was no reaction between O_2ClF_3 and hydrogen gas at a pressure of 100 mm. Hg. Any reaction would be easily noticeable by disappearance or change of the violet color or a decrease in the pressure of hydrogen.

The nonreactivity of O_2ClF_3 with hydrogen and methane parallels the chemical properties of ozone. We have shown earlier that pure (100%) ozone can be mixed at -78°C. and even at room temperature with hydrogen and methane without reaction.[6,7] (The mixture 1.5 CH_4 + $2O_3$, at 804 mm. Hg., showed at +21°C. a pressure increase of 26 mm. Hg. on standing for 1.0 hour).

From the present preliminary evidence it is likely that O_2ClF_3 will be more reactive than ozone at low temperatures.

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(6) Streng, A. G., and Grosse, A. V., J. Am. Chem. Soc., 79, 3996 (1957).

(7) Streng, A. G., and Grosse, A. V., "Advances in Chemistry Series," Vol. 21, page 40, Am. Chem. Soc., Washington, 1959

V. REACTION OF O_2F_2 WITH BrF_3 AND SF_4

The lower fluorides of bromine and sulfur, BrF_3 and SF_4, under very mild conditions may also form highly colored addition products with O_2F_2, although the compounds so far made seem to have only a transitory existence. The reactions are not always reproducible. Silicon tetrafluoride, SiF_4, interferes with the formation of the addition products.

A. The O_2F_2 + BrF_3 Reaction

The bromine analog of ClF, bromine trifluoride, BrF_3, also reacts with O_2F_2.

If liquid BrF_3 cooled to its melting point, 282°K., is dropped onto solid O_2F_2 cooled to 90°K., a spontaneous reaction occurs with evolution of heat and gas. Analysis of the reaction products showed that the reaction proceeds in accordance with the equation:

$$O_2F_2 + BrF_3 \rightarrow BrF_5 + O_2 \quad -56.7 \text{ Kcal.}$$

Under milder conditions, a brown-violet compound may be formed. The reaction proceeds, analogously to the ClF reaction, according to the equation:

$$O_2F_2 + BrF_3 \rightarrow O_2F_2 \cdot BrF_3.$$

Bromine trifluoride was condensed on the walls of the reaction vessel at 90°K. A thin layer of O_2F_2 was then condensed on the BrF_3 surface. The bath temperature was slowly raised and at about 130°K. the reaction between BrF_3 and O_2F_2 began, forming a violet-brown compound, with some gas evolution. Analysis showed that the gas evolved consisted mainly of oxygen (with a small amount of fluorine), which forms according to the reaction:

$$BrF_3 \cdot O_2F_2 \rightarrow BrF_5 + O_2$$

The colorless liquid reaction product was identified as BrF_5. The small amount of F_2 gas formed is due to partial decomposition of O_2F_2.

The yield of the violet-brown compound was about 80%. The compound began to decompose at 150°K. and decomposed completely at 170°K. to oxygen and BrF_5.

B. The O_2F_2 +SF_4 Reaction

The sulfur analog of ClF, sulfur tetrafluoride, SF_4, can also form an intensely violet-colored compound. The difficultly reproducible reaction proceeds most likely in accordance with the equation:

$$O_2F_2 + SF_4 \rightarrow O_2SF_6.$$

Pure O_2F_2 and SF_4 react violently in accordance with the equation:

$$O_2F_2 + SF_4 \rightarrow SF_6 + O_2 \quad -121.5 \text{ Kcal.}$$

without the formation of an intermediate violet product. In an attempt to prevent a violent reaction both reactants were diluted with perchloryl fluoride. This solvent was used earlier in the O_2F_2 + ClF reaction.

The solubility of sulfur hexafluoride, SF_6, in ClO_3F at low temperatures was found to be much higher than the solubility of ClF_3, see Fig. 2. Therefore, the separation of an intermediate product would be comparatively easy.

It was found, however, that if both O_2F_2 and SF_4 are diluted with perchloryl fluoride, the intermediate violet product either forms only in very small amounts or does not form at all.

A 12.8 wt.% O_2F_2 solution was used, for example. It was frozen at 90°K. and a gaseous SF_4-ClO_3F (1:1) mixture was added in small portions containing 20-100 mg. of SF_4. After the addition of each portion, the reaction vessel was warmed to 130°K.

Only traces of violet compound formed, which deposited on the walls of the reaction vessel above the O_2F_2-ClO_3F mixture. The formation of the violet compound took place only at temperature of 90°-116°K. At 130°K. a slow visible reaction between O_2F_2 and SF_4 began with evolution of O_2 gas and formation of SF_6.

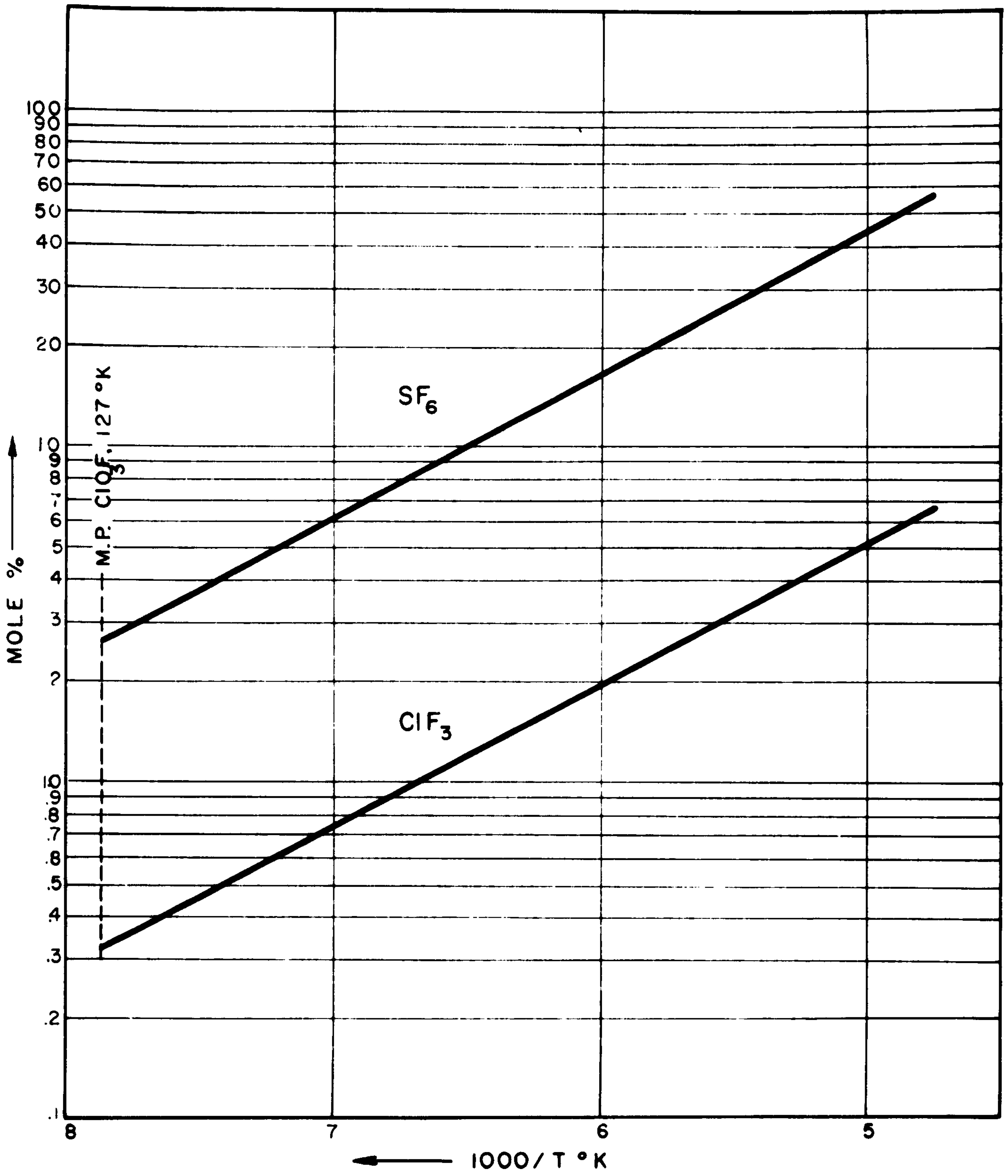


FIGURE [illegible].

SOLUBILITY OF SF_6 AND ClF_3 IN ClO_3F

Further warming to 150°-170°K. increased the reaction rate and caused decomposition of the violet compound. Also decomposition of O_2F_2 to O_2 and F_2 was noted.

Use of a smaller amount of diluent gave a largerquantity of the violet product, but the reaction was difficult to control.

Sulfur tetrafluoride diluted with ClO_3F was distilled into the reaction tube containing frozen O_2F_2 at 90°K. Traces of a violet-purple compound formed immediately on the walls of the reaction vessel, even at 90°K. Most of the SF_4 and ClO_3F condensed on the walls above the O_2F_2. The tube was then warmed above 125°K. At about 130°K. the SF_4-ClO_3F mixture began to melt and flow down to the O_2F_2. More purple-violet compound formed and the reaction went out of control with an explosively violent evolution of gas and heat. The excess O_2F_2 remained on the bottom of the shattered reaction tube.

C. Irradiation of $SF_4 + O_2$ with Ultraviolet Light

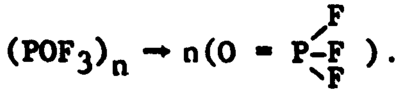
In contrast to ClF, sulfur tetrafluoride does not produce colored compounds with gaseous oxygen at two atmospheres pressure, when exposed to ultraviolet light. Sulfur tetrafluoride + O_2 was irradiated under the conditions used for $ClF_3 + O_2$, in the temperature range of 90°-195°K. No violet compound was formed.

VI. CHEMICAL BEHAVIOR OF O_2F_2 WITH FLUORIDES OF ELEMENTS CLOSE TO OXYGEN AND FLUORINE IN THE PERIODIC SYSTEM

A. The Reaction of O_2F_2 with PF_3

The phosphorus analog of ClF, namely the phosphorus trifluoride, PF_3 (an analog in the same sence as BF_3, SF_4 and IF_5, i.e., in that all these compounds add two atoms of fluorine to form the highest fluoride of the element), does not form a colored addition compound with O_2F_2.

Dioxygen difluoride, however, does react with PF_3, forming oxygen and PF_5. At the same time some of the oxygen liberated reacts with PF_3, forming a solid, white compound at 0°C. The white compound is fairly stable at 0°C. This compound is the only solid reaction product; it is not the well known POF_3, which melts at 233.4°K. and boils at 233.8°K. but is an interesting polymer of POF_3. On standing at 0°C. or at room temperature, the polymer depolymerizes completely to POF_3 (which was identified by its infrared spectrum) according to the equation:



$$(POF_3)_n \rightarrow n(O = P\begin{smallmatrix} F \\ -F \\ F \end{smallmatrix}).$$

Gaseous PF_3 was introduced in small portions (15-50mg.) into a Pyrex glass reaction tube containing O_2F_2 frozen at 90°K. The PF_3 solidified on the walls above the O_2F_2. The tube was then warmed slowly to 125°K. Both O_2F_2 and PF_3 melted and reacted at this temperature with gas evolution to form a white solid. If the amount of PF_3 added in one portion was larger than 50 mg. or if the compounds were warmed quickly, the reaction proceeded with flame. The gas evolved was found to be oxygen. Phosphorus pentafluoride and polymeric POF_3 were identified as the reaction products:

$$O_2F_2 + PF_3 \rightarrow PF_5 + O_2$$

$$O_2F_2 + 3\ PF_3 \rightarrow PF_5 + 2\ (POF_3)_n\ .$$

B. The Reaction of O_2F_2 with IF_5

In contrast to BrF_3, the analogous iodine compound, IF_5, does not form a colored compound. It was found that O_2F_2 decomposes in the presence of IF_5 to O_2 and F_2, without the formation of IF_7. Under the same conditions both ClF and BrF_3 formed violet addition compounds.

Liquid IF_5 was distributed on the walls of a reaction vessel and frozen at 90°K. The equivalent amount of O_2F_2 was then condensed upon the IF_5 surface. The reaction vessel was then warmed slowly to 195°K. There was no reaction between O_2F_2 and IF_5 over the temperature range 90°-195°K. Only a slow decomposition of O_2F_2 to O_2 and F_2 occurred.

C. The Reactions of O_2F_2 with SiF_4 and CF_4

Solid SiF_4 (m.p. 183°K.) does not react with liquid O_2F_2.

Approximately 20% SiF_4 is soluble in liquid O_2F_2 at 150°K. without noticeable formation of addition compounds. At about 195°K. O_2F_2 decomposes into O_2 and F_2, while SiF_4 remains unchanged.

A measured amount of SiF_4 was added to a known amount of O_2F_2 cooled in a reaction vessel to 90°K. The O_2F_2:SiF molar ratio was 1:0.4. The reaction vessel was warmed to 120°K. The O_2F_2 melted and dissolved some SiF_4, but did not react. The temperature of the bath was then increased to 150°K. More SiF_4 dissolved but no reaction occurred. After 2 hrs. at 150°K. the reagents were separated by distillation. Silicon tetrafluoride was collected in a U-tube and its purity was checked by infra-red spectroscopy and by melting point and vapor pressure measurements. $O_2F_2$was decomposed to O_2 and F_2 which were identified by standard procedures.

Similarly, carbon tetrafluoride, CF_4, does not react with O_2F_2.

D. The Reaction of O_2F_2 with N_2F_4

Dioxygen difluoride does not react with NF_3 but does react with the lower fluoride of nitrogen, tetrafluorohydrazine, N_2F_4.

According to Johnson and Colburn[8] condensation of cold

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(8) Johnson, F. A., and Colburn, C. B., J. Am. Chem.,Soc., 83, 3043 (1961).

gaseous N_2F_4 (-30°C.) at relatively high pressures, gives a water-white liquid. However, if the gas is condensed at elevated temperatures and low pressures, the liquid obtained has color varying from light blue to blue-black. The intensity of color is said to be a function of the concentration of NF_2 radicals in the gas phase prior to condensation and is supposedly due to an "association compound."

Our experience with N_2F_4 showed that upon distillation, either in Pyrex glass or in a Kel-F system, a violet compound is formed; it looks like the violet compound formed by the reaction between O_2F_2 and ClF but it has different properties.

A series of experiments was performed to determine the nature of this compound before using N_2F_4 for the reaction with O_2F_2. It was made clear that this violet compound is not of the same type as was obtained in the O_2F_2 + ClF reaction.

The violet compound formed by N_2F_4 can be distilled from one vessel into another together with N_2F_4 without decomposition, whereas our violet compound is nonvolatile.

About 0.6 g. O_2F_2 was reacted in a Kel-F system with 1.4 g. N_2F_4 at 130-170°K. A visible reaction started at 170°K. without the formation of any colored compounds.

The reaction products were O_2 and NF_3. The O_2 was identified by pyrogallol absorbtion and NF_3 as a colorless liquid in liquid N_2 (b.p. = 77°K.), while the original N_2F_4 is a white solid with a melting point of 110°K.

The most probable reaction is:

$$O_2F_2 + N_2F_4 \rightarrow O_2 + 2\ NF_3.$$

VII. EXPERIMENTS IN A U-SHAPE ELECTRICAL-DISCHARGE TUBE

The preparation of O_2F_2, O_3F_2 and O_4F_2 by an electrical-discharge method is best performed in specially designed vessels.* Entirely different reaction products may form in reaction vessels of different sizes and shapes.

An electrical discharge was passed, for example, through a $1.5O_2+F_2$ gas mixture (adequate for the preparation of O_3F_2) in the U-shape electrical discharge tube shown in Fig. 3. The conditions were: T = 77 K., P = 12-17mm. Hg., V = 2000-2500 v., A = 20-30 ma. Under these conditions O_3F_2 forms in the vessel recommended. But in the U-shape vessel, three quite different products were obtained: ozone, dioxygen difluoride and traces of a violet compound not yet investigated. The wall of the left side of the U-tube (the part where the O_2-F_2 mixture enters) was covered with a deposit of O_2F_2. On the wall of the lower part of the right side a blue layer of ozone was formed, while on the wall of the upper part of the right side (above the ozone ring) a very small amount of a violet compound was deposited. Several mild explosions occurred in the gaseous phase during the operation owing, mostprobably, to the formation of ozone. This was never the case in the recommended type of reaction vessel.

(*) See Fig. A-2 and A-3 in the Appendix of this Report.

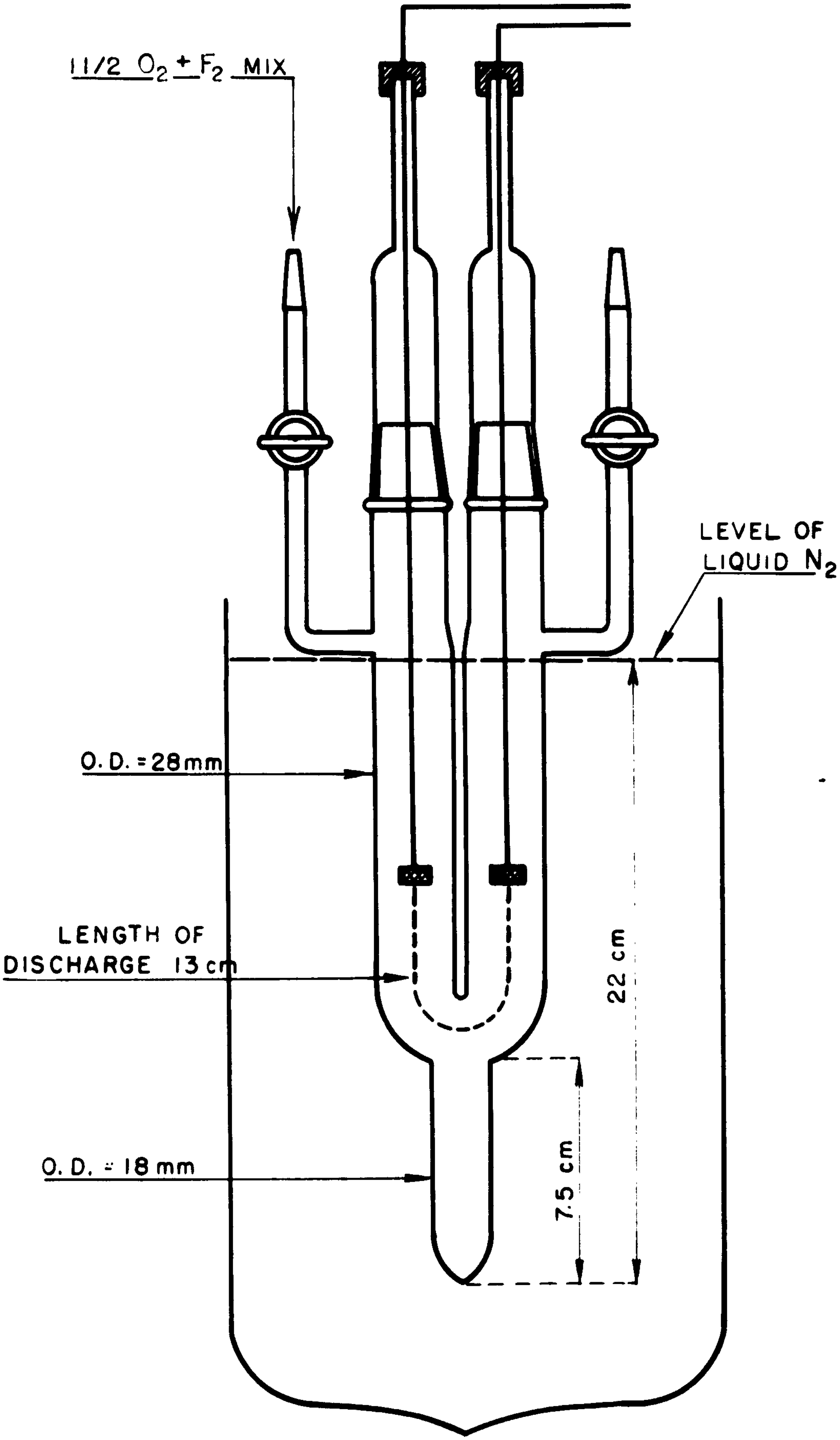

FIGURE 5.
THE U-SHAPED DISCHARGE TUBE

It is known that at temperatures above 125°K., liquid ozone causes explosions with liquid O_2F_2. We avoided, therefore, mixing these compounds.

The traces of the unknown violet compound resemble the violet compound obtained from the O_2F_2 + ClF reaction or from the reaction between O_2 and ClF_3 under ultraviolet light. If the formation of this violet product is due to the presence of traces of chlorine-containing compounds, its nature would be the same as that of our violet product obtained in the O_2F_2 + ClF reaction. To investigate this possibility, experiments were performed with $O_2 + F_2$ + ClF mixtures.

Attempts were made to synthesize the violet compound directly from a gaseous mixture of $O_2 + F_2$ + ClF, by passing an electrical discharge. A U-shape reaction tube, shown in Fig. 3 was used. To avoid a possible explosion if the reaction

$$ClF + F_2 \rightarrow ClF_3 \quad -26.5\ \text{Kcal.}^9$$

took place, only 3.3 vol.% ClF was added to the 1:1 oxygen-fluorine mixture. The gaseous $O_2 + F_2$ + ClF mixture was fed into the reaction vessel cooled in a liquid oxygen or liquid nitrogen bath. There was no difference in the results obtained at 90° and 77°K. An electrical discharge of 15-25 mA, 2000-3000V., was sent through the mixture at a pressure of 12 ± 5 mm Hg.

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(9) Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Supplement II, Part 1, Longmans, Green and Co., London, New York, Toronto, 1956.

Dioxygen difluoride and some trioxygen difluoride were formed as a precipitate on the walls of the cooled part of the U-tube between the electrodes. In addition, a grey-blue deposit (most probably ozone) appeared on the walls of the inlet side of the tube above the electrode. Some unreacted ClF also deposited just above the grey-blue compound. However, no violet compound was formed.

When the temperature was increased to 120°K., the grey-blue deposit disappeared. The melted ClF flowed down and combined with the O_2F_2 to form the violet compound (as in the usual O_2F_2 + ClF reaction), and ClF_3.

VIII. REMARKS ON HYDROGEN SUPEROXIDE, H_2O_4

In the First Annual Progress Report for the Office of Naval Research, 1960, (pp. 34-43), the synthesis and the characteristics of hydrogen superoxide, H_2O_4, were described. Hydrogen superoxide was produced by the bombardment of O_3 with hydrogen atoms at 77°K. The product obtained by us contained 52 wt.% of H_2O_4.

It is of interest that Zaslowsky, Martinez and Wojtowicz[10] of the Olin Mathieson Chemical Corporation have recently confirmed our findings and substantially increased the yield of H_2O_4. In nearly all their experiments, the molar ratio of oxygen to hydrogen peroxide is 1:1. This fact strongly supports the existence of a stoichiometric compound. The highest concentration obtained was 72 wt.% H_2O_4 and 28 wt.% H_2O. Regardless of the interpretation the important fact is that substantial quantities of oxygen above the composition H_2O_2 are introduced into the solid.

The above-named authors made the follosing statement: "No explanation can be offered at the present time to account for the failure by Giguere and Chin[11] to detect the superoxide by the spectroscopic method."

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(10) Martinez, F., and Wojtowicz, J. A., "Study of Superoxides," AFOSR-105, Contract No. AF 29(600)-1667, OMCC-9038-GFR-1, Olin Mathieson Chem. Corp., New Haven, Conn., April, 1961.

(11) Giguere, P. A., and Chin, D., <u>J. Chem. Phys</u>., <u>31</u>, 1685 (1959).

As we pointed out previously Giguere and Chin did not analyze their product for surplus oxygen content. Thus, it is not certain that they actually prepared H_2O_4.

Nekrasov, Skorohodov and Kobozev have emphasized[12] that Giguere and Chin[11] used solid, rather than liquid, O_3. In the opinion of the Soviet investigators, Giguere and Chin did not preclude the stabilization of the HO_2 radical by diffusion into the liquid O_3, but on the contrary increased its reduction by atomic hydrogen to H_2O_2.

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(12) Nekrasov, L. I., Skorohodov, I. I., and Kobozev, N. I., Zhurnal Fiz. Khim., 35, 691-693 (1961).

APPENDIX

THE REAGENTS USED

Dioxygen difluoride, O_2F_2, was prepared directly from the elements, essentially by the method described by Ruff and Menzel[1] and by Aoyama and Sakuraba.[2] The flow diagram for our modified apparatus is shown in Fig. A-1. The 1:1 gaseous mixture of fluorine and oxygen is prepared in the perfluorinated stainless-steel cylinder. The cylinder has a volume of about 8 l. and is used at pressures up to 80 p.s.i.a. The O_2-F_2 mixture is fed from this cylinder through the flowmeter containing Kel-F oil, through the trap cooled with liquid oxygen to eliminate impurities condensable at this temperature and into the reaction vessel. The reaction vessel 6.5 cm. in diameter and 18 cm. long, is made of Pyrex glass; it is cooled to 77 or 90°K. A detailed sketch of the reaction vessel is shown in Fig. A-2.

A high-voltage electrical discharge is established in the reaction vessel between two copper electrodes, which are fixed 10-cm. apart. The electrodes are 2 cm. in diameter and are connected to copper wires sealed into the reaction vessel by Teflon plugs. The other plugs in the system have ground-glass joints that are

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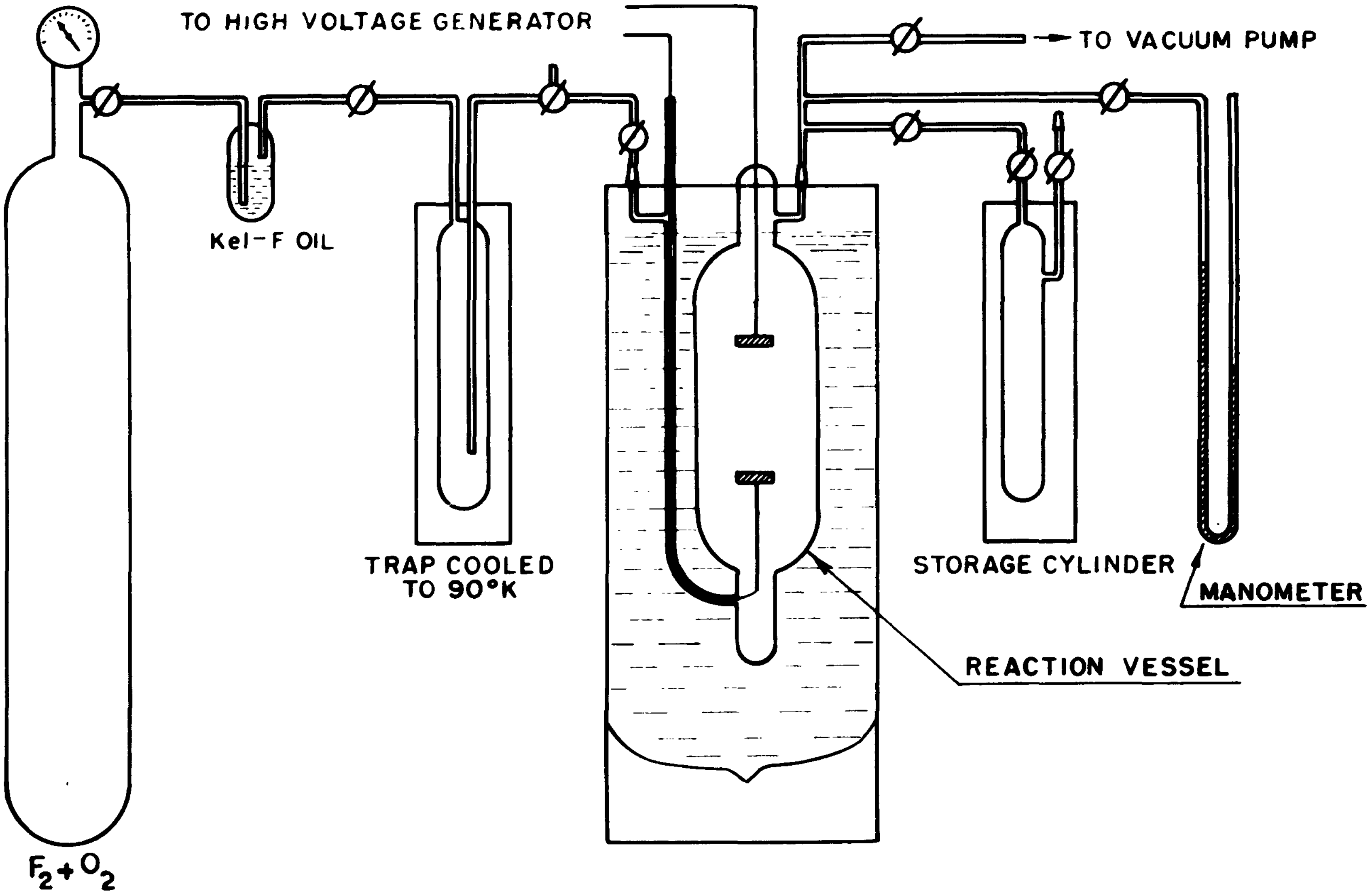
(1) Ruff, O., and Menzel, W., Z. anorg. allgem. Chem., 211, 204 (1933).

(2) Aoyama, S., and Sakuraba, S., J. Chem. Soc. Japan, 59, 1321 (1938).

[illegible] 2. THE APPARATUS FOR PREPARATION OF O[illegible]



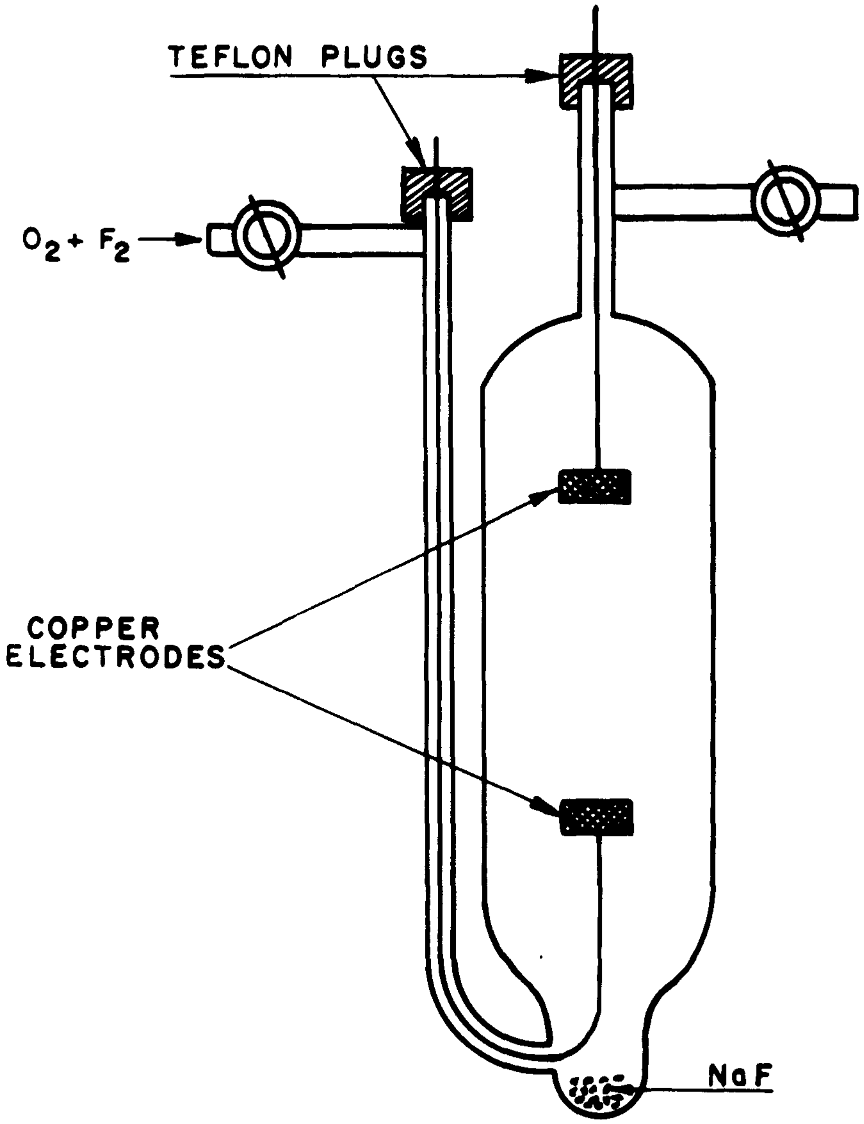


FIGURE A-[illegible].

REACTION VESSEL FOR PREPARATION OF O F

lubricated with Kel-F grease. The discharge varies from 25 to 30 ma. at 2100-2400V. The flow of the F_2-O_2 mixture is adjustable so that the pressure in the reaction vessel is maintained at 12 ± 5 mm. Hg.

The electrical part of the apparatus consists of a 110-5000V. 60-cycle, single-phase transformer, in series with a 1000-ohm Ohmite vitreous enameled limiting resistor, together with a 0-100 milliammeter and a 0-5000 voltmeter.

The formation of dioxygen difluoride consumes all the entering F_2-O_2 mixture. The product condenses in solid form on the walls of the reaction vessel. When the preparation is completed, the electrical discharge and the gas supply are stopped, the reaction vessel is warmed to dry-ice temperature and the O_2F_2 is distilled into the storage cylinder cooled in a liquid-nitrogen bath. Distillation is conducted at reduced pressure; all the connecting tubes must be cooled with dry ice. Some O_2F_2 may decompose upon distillation. Therefore, the O_2 and F_2 formed must be pumped off while the O_2F_2 is cooled with liquid nitrogen.

Sodium fluoride, NaF pellets (ignited) are placed into the reaction and storage vessels, in order to remove any HF and SiF_4 which may have formed. NaF combines with these compounds according to the equations:

$$NaF + HF \rightarrow NaF \cdot HF$$

$$2NaF + SiF_4 \rightarrow Na_2SiF_6 \ .$$

Pure dioxygen difluoride can be stored for extended periods of time in Pyrex glass cylinders cooled to 90°K.

Trioxygen difluoride, O_3F_2, was prepared by a method similar to that used for preparing O_2F_2. The gaseous F_2-O_2 mixture must contain three volumes of O_2 and two volumes of F_2. This mixture is found to combine quantitatively to form O_3F_2 in the same type of apparatus that is used for O_2F_2 preparation.[3,4,5] The construction of the reaction vessel is slightly different, as is shown in Fig. A-3. Slightly different also are the reaction conditions: the reaction vessel is cooled in a liquid-nitrogen bath, and the electrical discharge varies from 20 to 35 ma. at 2000-2200V. The gas pressure in the reaction vessel is the same, i.e., 12 ± 5 mm. Hg.

When the preparation is completed, the gas flow and the discharge are stopped and the reaction vessel is warmed to 90°K. by changing to a liquid-oxygen bath. Trioxygen difluoride liquefies

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(3) Kirshenbaum, A. D., Aston, J. G., and Grosse, A. V., Final Report, Contract No. DA-36-034-ORD-2250, Research Institute of Temple University, Nov. 18, 1958.

(4) Kirshenbaum, A. D., and Grosse, A. V., J. Am. Chem. Soc., **81**, 1277 (1959).

(5) Kirshenbaum, A. D., Grosse, A. V., and Aston, J. G., J. Am. Chem. Soc., **81**, 6398 (1959).

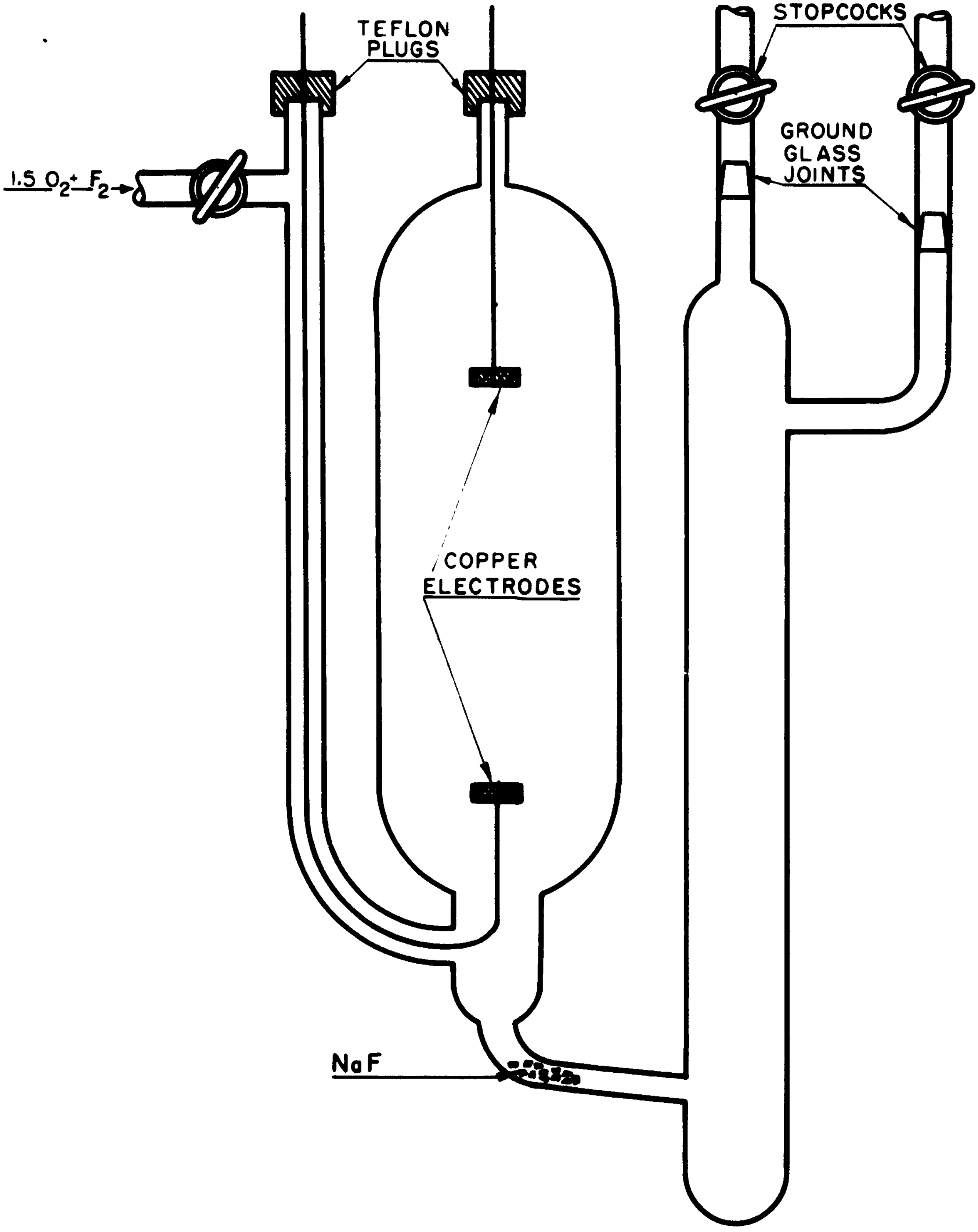

FIGURE A-3.

REACTION VESSEL FOR PREPARATION OF O_3F_2

and flows into the side tube. This tube is then disconnected and can be used as the storage vessel. Pure trioxygen difluoride can be stored for a long time at 77°K. in Pyrex-glass vessels. The rate of decomposition at this temperature is about 3.6 x 10^{-5}/hr.

Chlorine monofluoride, ClF, was prepared in our laboratories from gaseous Cl_2 and F_2[6,7] in accordance with the reaction:

$$Cl_2 + F_2 \rightarrow 2\ ClF\ .$$

About 250 cm^3/min. of each gaseous Cl_2 and F_2 were passed through a stainless-steel tube, vol. 56 cm^3, at 400-500°C. The residence time was about 7 sec. The product was passed through a trap cooled with dry ice to remove ClF_3, if formed in small amounts, or excess of free Cl_2, if present, and into a second trap cooled with liquid oxygen, where ClF was condensed. The apparatus was made of Kel-F traps, stainless-steel valves and copper tubing. The product was purified by distillation and contained over 99% ClF.

Silicon tetrafluoride, SiF_4, was prepared according to the reactions:

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(6) Ruff, O., Ascher, E., and Laas, F., Z. anorg. allgem. Chem., 176, 256 (1928).

(7) Brauer, Georg, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, 1954.

$$2\ CaF_2 + 2\ H_2SO_4 \rightarrow 2\ CaSO_4 + 4\ HF,$$

$$4\ HF + SiO_2 \rightarrow SiF_4 + 2\ H_2O\ .^{7,8,9}$$

The mixture of CaF_2, SiO_2 and H_2SO_4 was warmed slightly in a glass flask, and the gas formed was passed through two traps cooled with dry ice (to separate the possible excess of HF) into a glass trap cooled with liquid O_2, where SiF_4 was condensed. The product was purified by sublimation.

Phosphorus trifluoride, PF_3, was prepared according to the reaction:

$$PCl_3 + 3\ HF \rightarrow PF_3 + 3\ HCl.^7$$

Nitryl fluoride, NO_2F, was prepared in our laboratories according to the equation:

$$2\ NO_2 + F_2 \rightarrow 2\ NO_2F.^7$$

All other reagents were the commercial products of the highest available purity as supplied by Stauffer Chemical Co., General Chemical Division of Allied Chemical Co., Pennsalt Chemicals Corp., E. I. du Pont de Nemours and Co., Matheson Co., Air Reduction Co. and others.

Most of these reagents were further purified by fractional distillation.

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(8) Lebouche, L., Fischer, W., and Biltz, W., Z. anorg. allgem. Chem., 207, 64 (1932).

(9) Ruff, O., and Ascher, E., Z. anorg. allgem. Chem., 196, 413 (1931).