# THE OXYGEN FLUORIDES

A. G. STRENG

*The Research Institute of Temple University, Philadelphia 44, Pennsylvania*

*Received June 6, 1963*

## CONTENTS

## I. INTRODUCTION

There are four oxygen fluorides known to date: oxygen difluoride, $OF_2$; dioxygen difluoride, $O_2F_2$; trioxygen difluoride, $O_3F_2$; and tetraoxygen difluoride, $O_4F_2$. All members of the group are endothermic compounds and have a remarkably strong oxidizing power. In recent years, oxygen fluorides attracted much attention. Some are considered to be possible ingredients for the high energy propellant and explosive systems; the others are potential reagents for chemical reactions at extremely low temperatures.

An attempt is made in this review to systematize the published material on the synthesis and properties of oxygen fluorides. The review covers the literature through 1962, plus a few publications of 1963.

## II. OXYGEN DIFLUORIDE, $OF_2$

The first success in combining fluorine with oxygen was reported in 1927, by Lebeau and Damiens (52). They observed the formation of $OF_2$ while preparing fluorine in an electrolytic cell at about 100° with molten (slightly moist) KF–HF as electrolyte. Later, in an attempt to purify the fluorine gas with a caustic soda solution, Lebeau and Damiens found that $OF_2$ is formed also by the reaction of $F_2$ with aqueous NaOH (53). This reaction is generally employed now for the preparation of oxygen difluoride.

### A. PREPARATION

The most common method of preparation of oxygen difluoride (10, 13, 54, 67, 71) is based on the reaction

$$2F_2 + 2NaOH \rightarrow OF_2 + 2NaF + H_2O$$

Both NaOH and KOH may be used. The yield depends on the strength of the solution. Cady (16) found that the yield rises to a maximum of about 60% in 0.5 *N* KOH. Other investigators (49, 80, 86, 102, 108) reported much lower yields. A supply of the base must be maintained and the concentration must be kept at about 2% in order to avoid the secondary reaction

$$OF_2 + 2OH^- \rightarrow O_2 + 2F^- + H_2O$$

TABLE I

PHYSICAL AND PHYSICOCHEMICAL PROPERTIES OF OXYGEN DIFLUORIDE

| Properties | | References |
|---|---|---|
| Appearance | | |
| Colorless gas at room temperature. Yellow liquid below 128°K. | | |
| Molecular weight | | |
| 54.000 | | |
| Molecular structure | | |
| Triatomic, nonlinear with two equivalent O–F bonds | | (107) |
| Molecular constants | | |
| Interatomic distance *r*(O–F), Å. | 1.3896 | (33) |
| | 1.409 | (63) |
| FOF angle | 104° 163′ | (33) |
| | 103° 18′ | (63) |
| Dipole moment, D. | 0.297 ± 0.005 | (63) |
| | 0.1759 ± 0.0010 | (9) |
| | 0.4 ± 0.1 | (18) |
| Ground-state rotational constants, Mc./sec. | | |
| *A* | 61,567.71 | (33) |
| | 58,780.09 | (63) |
| *B* | 11,066.54 | (33) |
| | 10,895.87 | (63) |
| *C* | 9,343.85 | (33) |
| | 9,166.53 | (63) |
| Asymmetry constant *k* | −0.93400 | (33) |
| Moments of inertia, a.m.u., Å.$^2$ | | |
| $I_A$ | 8.21096 | (33) |
| | 8.60037 | (63) |
| $I_B$ | 45.6809 | (33) |
| | 46.3966 | (63) |
| $I_C$ | 54.1088 | (33) |
| | 55.1496 | (63) |
| Rotational inertial defect, a.m.u., Å.$^2$ | 0.115–0.175 | (63) |
| | 0.217 | (33) |
| Force constants | | |
| $K_{O-F}$, dyne/cm. | $3.21\text{–}5.23 \times 10^{-5}$ | (5) |
| $K_\alpha$, dyne/cm. | $0.05\text{–}1.67 \times 10^{-5}$ | (5) |
| Melting point | | |
| 49.4° K., −223.8°C. (of the 98.5% pure compound) | | (71) |
| Boiling point | | |
| 128.4° K., −144.8°C. | | (73) |
| 127.9°K., −145.3°C. | | (80) |
| Vapor pressure | | |
| $\log P_{mm.} = 7.3892 - 578.64/T$ | | (73) |
| $\log P_{mm.} = 7.2242 - 555.42/T$ | | (80) |
| $P =$ 0.010 mm. at 60.213°K. | | |
| 0.10 67.535 | | |
| 1.0 76.883 | | |
| 10.0 89.236 | | |
| 100.0 106.317 | | |
| 760.0 127.856 | | |
| $P =$ 0.03 mm. at 63°K. (m.p. $N_2$) | | |
| 1.0 77°K. (b.p. $N_2$) | | |
| 11.3 90°K. (b.p. $O_2$) | | |
| 273.0 116°K. (m.p. $CCl_2F_2$) | | |
| Density | | |
| Gas, 2.41 mg./cc. at N.T.P. | | |
| Liquid, $d = 2.190 - 0.00523T$ g./cc. | | (2) |
| 1.521 g./cc. at b.p. | | |
| 1.583 at 116°K. | | |
| 1.719 at 90°K. | | |
| 1.787 at 77°K. | | |
| 1.932 at m.p. | | |
| Molar volume | | |
| 31.6 cc./mole at 90.3°K. | | |
| 28.4 at m.p. | | (73) |
| Critical temperature | | |
| 215.2 ± 0.1°K., −58.0 ± 0.1°C. | | (2) |
| Critical pressure | | |
| 48.9 atm. | | (2) |
| Critical density | | |
| 0.553 g./cc. | | (2) |
| Critical volume | | |
| 97.6 cc./mole | | (2) |
| Viscosity | | |
| Liquid, between 120 and 127°K., $\log \eta = 131.5T - 1.5768$ cp. | | (2) |
| 0.2826 cp. at 127.9°K. | | |
| 168 μp. at 300°K. (estimated) | | |

TABLE I (*Continued*)

| Properties | References |
|---|---|
| Heat of vaporization | |
| 2.650 kcal./mole at b. p. | (73) |
| Entropy of vaporization (Trouton's constant) | |
| 20.65 cal./°K. mole | (73) |
| Hildebrand's solubility parameter at b.p. | |
| $\delta = 8.22$ (cal./cc.)$^{1/2}$ | (32) |
| Heat of formation (from the elements) | |
| $\Delta H_{298.15} = 7.6 \pm 2.0$ kcal./mole | (20) |
| Total energy of atomization | |
| 89.4 ± 2.0 kcal/mole or 3.9 ± 0.1 e.v. | (17) |
| Bond energy | |
| $E_{\text{O-F}} \simeq 58$ kcal./bond, 2.52 e.v. | (27) |
| 57 | (61) |
| 57.5 | (103) |
| 58.5 | (88) |
| Rate of irreversible thermal decomp. $OF_2 - 0.5O_2 + F_2$ (at 250–270°C.) | |
| $-0.5\,d[OF_2]\,dt = dp/dt = kp[OF_2]\,[P_{\text{total}}]$ | |
| In a glass vessel the evolving $F_2$ forms $SiF_4$, therefore, $dp/dt = K_1[OF_2]^2 + K_2[OF_2][O_2] + K_3[OF_2][SiF_4] + K_\chi[OF_2][\chi]$, where $\chi$ is an added gas: He, Ar, Ne, $O_2$, $N_2$, etc.; $K_1 \sim K_2 \sim K_3$. | (27, 49, 54, 62, 82, 83, 84) |
| Decomposition constant (mole$^{-1}$ sec.$^{-1}$) | |
| $K_c \times 10^2 = 1.40$ at 250° | |
| 2.85 at 260° | |
| 5.70 at 270° | |
| Temperature coefficient = 2.0 + 0.1 per 10° | |
| The relative efficiencies of added gases, $OF_2{:}O_2{:}N_2{:}F_2{:}S{:}F_4{:}He{:}Ar$ = 1:1.13:1.01:1.13:0.88:0.40:0.52 | |
| Activation energy of thermal decomposition | |
| 40.6 ± 3 kcal./mole | (27) |
| Lifetime of activated molecules | |
| $<10^{-12}$ sec. | (27) |
| Thermodynamic functions | |

| Temp., °K. | $C_p^0$ | $S^0$ | $-(F^0 - H_{298}^0)/T$ | References |
|---|---|---|---|---|
| | cal. mole$^{-1}$ deg.$^{-1}$ | | | |
| 0 | 0.000 | 0.000 | Infinite | (42, 65) |
| 100 | 8.067 | 49.409 | 67.487 | |
| 200 | 9.098 | 55.275 | 60.053 | |
| 298 | 10.353 | 59.146 | 59.146 | |
| 300 | 10.375 | 59.210 | 59.146 | |
| 400 | 11.377 | 62.340 | 59.566 | |
| 500 | 12.064 | 64.957 | 60.390 | |
| 600 | 12.526 | 67.201 | 61.342 | |
| 700 | 12.843 | 69.157 | 62.322 | |
| 800 | 13.067 | 70.887 | 63.287 | |
| 900 | 13.229 | 72.436 | 64.219 | |
| 1000 | 13.349 | 73.836 | 65.112 | |

| Temp., °K. | $H^0 - H_{298}^0$ | $H_f^0$ | $F_f^0$ | Log $K_p$ |
|---|---|---|---|---|
| | kcal. mole$^{-1}$ | | | |
| 0 | −2.604 | 8.143 | 8.143 | Infinite |
| 100 | −1.808 | 7.888 | 9.093 | −19.872 |
| 200 | −0.956 | 7.700 | 10.377 | −11.339 |
| 298 | −0.000 | 7.600 | 11.715 | −8.587 |
| 300 | 0.019 | 7.599 | 11.741 | −8.553 |
| 400 | 1.110 | 7.564 | 13.129 | −7.173 |
| 500 | 2.284 | 7.565 | 14.520 | −6.346 |
| 600 | 3.515 | 7.587 | 15.909 | −5.795 |
| 700 | 4.784 | 7.616 | 17.294 | −5.399 |
| 800 | 6.080 | 7.647 | 18.673 | −5.101 |
| 900 | 7.396 | 7.680 | 20.050 | −4.869 |
| 1000 | 8.725 | 7.710 | 21.423 | −4.682 |

| Properties | References |
|---|---|
| Absorption spectrum between 8000 and 2100 A. | |
| Absorption of light starts at about 5400 Å., is purely continuous, and shows maxima at:<br>4210 Å., 23,800 cm.$^{-1}$<br>3580 Å., 28,000 cm.$^{-1}$<br>2940 Å., 34,000 cm.$^{-1}$<br>a very abrupt ascent is observed at about 2640 Å., 38,000 cm.$^{-1}$, the maximum of which is not yet reached at 2130 Å., 47,000 cm.$^{-1}$ | (13, 26, 27) |
| Extinction coefficients (1 mm. pressure at 0°, film thickness 1 cm.) | |

| λ | $10^5\epsilon$ | λ | $10^5\epsilon$ | References |
|---|---|---|---|---|
| 5460 | 0.08 | 2893 | 1.90 | (26) |
| 5435 | | 2806 | 1.80 | |
| 4916 | 0.14 | 2759 | 1.79 | |
| 4715 | 0.18 | 2700 | 2.07 | |
| 4580 | 0.23 | 2655 | 2.28 | |
| 4450 | 0.26 | 2576 | 3.20 | |
| 4358 | 0.27 | 2537 | 4.10 | |
| 4280 | 0.32 | 2482 | 5.70 | |
| 4210 | 0.35 | 2447 | 7.70 | |
| 4040 | 0.30 | 2399 | 10.00 | |
| 3990 | 0.31 | 2378 | 12.00 | |
| 3960 | 0.36 | 2345 | 17.50 | |
| 3870 | 0.51 | 2295 | 20.00 | |
| 3800 | 0.67 | 2253 | 27.00 | |
| 3780 | 0.84 | 2236 | 30.00 | |
| 3650 | 0.98 | 2210 | 34.00 | |
| 3500 | 1.10 | 2181 | 40.00 | |
| 3340 | 1.33 | 2165 | 42.00 | |
| 3131 | 1.74 | 2137 | 47.00 | |
| 3027 | 1.85 | 2114 | 52.00 | |
| 2967 | 1.87 | 2102 | 75.00 | |
| 2925 | 1.88 | | | |

| Properties | References |
|---|---|
| Infrared spectrum bands, cm.$^{-1}$<br>1740<br>929<br>909<br>840<br>826<br>461 | (5, 29, 30, 31, 43, 60, 64, 67) |
| Relative abundances and appearance potentials of positive and negative ions in the mass spectrum of $OF_2$ | |

| Ion | Relative abundance, % | Appearance potential, e.v. | Remarks | References |
|---|---|---|---|---|
| $OF_2^+$ | 100 | 13.7 ± 0.2 | $I(OF_2) = 13.7 \pm 0.2$ e.v. | (17) |
| $OF^+$ | 91 | 15.8 ± 0.2 | Negligible excess KE<br>$I(OF) = 13.0 \pm 0.2$ e.v. | |
| $O^+$ | 4.3 | . . . | Indeterminate threshold | |
| $F^+$ | 0.5 | . . . | Immeasurably small | |
| $F^-$ | 63 | 1.2 ± 0.2 | $KE(F^-) = 1.3$ e.v.<br>$KE(F^- + OF)$ 2.0 e.v.<br>$D(FO\text{-}F) = = 2.8$ e.v.,<br>$D(O\text{-}F) = 1.1$ e.v. | |

A Pyrex glass reactor, 6-in. long and 1-in. in diameter, is provided with a bottom inlet for the caustic solution and an overflow located at about $^2/_3$ of the height of the reactor. Another inlet for fluorine gas, made of *ca.* 2 mm. i.d. copper or platinum tubing, enters through the top and dips about 0.5-in. into the caustic solution. An outlet tube for gaseous reaction products is provided near the top of the reactor. Caustic solution is fed through the reactor at the rate of about 1 l./hr. and fluorine gas at the rate of 1 to 3 l./hr.

The gaseous $OF_2$ produced is washed with water and dried by passing it through the traps cooled with Dry Ice. It is collected in the form of a pale yellow liquid in a trap cooled with liquid nitrogen. The crude product is purified by fractional distillation in a low-temperature column.

Oxygen difluoride may be obtained also by electrolysis of aqueous HF containing 10% NaF (19). The anode gas contains about 60% $OF_2$ when 80–99% HF is used. Some ozone also is formed. The other methods reported in the literature (15, 69, 76) were shown to be inefficient.

### B. PHYSICAL PROPERTIES

Oxygen difluoride is a colorless gas that is relatively stable at room temperature but begins thermal decomposition at about 200–250°. At temperatures below 128°K., it is a pale yellow liquid. Oxygen fluoride has an unpleasant, irritating odor and is very poisonous.

Considerable effort was made to study the molecular structure of $OF_2$ (6, 7, 11, 37, 38, 50, 81, 97–100). The most recent values of the structural parameters and selected data on the main physical and physicochemical properties of oxygen difluoride are given in Table I.

### C. SOLUBILITY

Geaseous $OF_2$ is slightly soluble in water, and the solution obeys Henry's law with an absorption coefficient (liter of gas in 1 l. of water) of 0.04297 at 20° (38) and 0.068 at 0° (71). The solutions are not stable; a slow hydrolysis reaction takes place at room temperature.

$$OF_2 + H_2O \rightarrow O_2 + 2HF + 80.08 \text{ kcal.}$$

Liquid oxygen difluoride mixes homogeneously in all proportions with liquid $F_2$ at 77°K., with liquid $O_2$ and $O_3$ at 90°K., with liquid $O_3F_2$ at 116°K., and with liquid ClF at 125°K. (91). It also mixes homogeneously with liquid $CH_4$ at 90°K. but this mixture is very dangerous. It may detonate upon the slightest provocation or temperature rise. Oxygen difluoride dissolves small amounts of $O_2F_2$ at 135°K. and about 0.05% by weight of $ClF_3$ at 140°K.

### D. STABILITY

Pure and dry oxygen difluoride is relatively stable at room temperature. It can be kept in glass vessels at room temperature for a long period of time without any noticeable decomposition (27). At elevated temperatures, however, it reacts with glass forming $SiF_4$ and oxygen (22, 23).

The thermal decomposition of $OF_2$, studied at 250–270° in glass, silica, silver, copper, and magnesium vessels, was unimolecular but followed a second-order rate (49, 82). $SiF_4$ was formed in glass and silica vessels; silver and copper showed steady absorption of fluorine over many days, but in the magnesium vessel the fluorine, formed by decomposition of $OF_2$, remained uncombined (54). The equation of thermal decomposition of $OF_2$ is given in Table I.

About 72% of $OF_2$ did decompose to $O_2$ and $F_2$ when pure $OF_2$ was blown (12.5 cm.$^3$/min.) through a platinum tube, 1 cm. in diameter, containing a Pt net heated to 300° (51).

Oxygen difluoride is slightly decomposed by light. In a mixture containing 25% $OF_2$ and 75% $O_2$ exposed to diffuse light for 24 hr., 1–2% $OF_2$ did decompose. Mainly the short wave length light ($\lambda > 3000$ Å., predominantly $\lambda > 2500$ Å.) was absorbed, and $OF_2$ was decomposed to $O_2$ and $F_2$ (26). The fluorine formed in the quartz vessel was extensively converted to $SiF_4$. The light with $\lambda < 2150$ Å. did not decompose $OF_2$ in a mixture containing 60% $OF_2$ and 40% $O_2$ (102).

### E. EXPLOSIVENESS

Pure and dry $OF_2$ gas did not explode from a spark even at the pressure of 10 atm. (101). In the presence of water, however, $OF_2$ is dangerous. Concentrated $OF_2$ (25–70%), diluted with oxygen, exploded violently from a spark when kept over water, due to the reaction

$$OF_2 + H_2O \rightarrow 2HF + O_2$$

An $OF_2 + O_2$ mixture containing 12% $OF_2$ exploded weakly. A dry mixture of 25% $OF_2$ with $O_2$ (confined over sulfuric acid) could not be exploded by a spark (99). A mixture of $OF_2$ and steam exploded easily.

There are no reports in the literature on spontaneous explosions of liquid $OF_2$ at temperatures below its boiling point.

### F. CHEMICAL REACTIONS

Chemically, oxygen difluoride is a powerful oxidizer. Its reactivity is considered to be lower than that of fluorine. In reactions with solids and upon warming, $OF_2$ acts as a fluorinating agent, while in aqueous solutions the addition of oxygen is the main reaction (40, 51, 72, 74, 75). Following are the known chemical reactions of $OF_2$.

### *1. In Aqueous Solutions* (6, 13, 27, 39, 54, 71, 109)

With aqueous solutions of HCl, HBr, and HI, oxygen difluoride reacts quantitatively, liberating free halogens.

$$OF_2 + 4HCl \rightarrow 2Cl_2 + 2HF + H_2O$$

Halogens are displaced also from their salts. In the reaction with aqueous $NH_3$, nitrogen is liberated, and the formation of $HNO_3$ takes place. The aqueous solutions of KOH, NaOH, and $Ca(OH)_2$ absorb $OF_2$. Reactions with KOH and NaOH are of the first order, all the oxygen is liberated as gas and no oxidizing compounds remain in solution.

The rate constants, over the temperature range of 0–35°, are described by the equation

$$\log K = 4.1257 - 1625/T$$

The rate constant increases about 1.5 times for each 10° of temperature rise (38). In the reaction with 1% NaOH solution, $K = 0.045$ min.$^{-1}$ at 21° and 0.10 min.$^{-1}$ at 59°; in the reaction with 10% NaOH at 29°, $K = 0.34$ min.$^{-1}$. Agitation causes a considerable increase in reaction rate.

From aqueous solution of $H_2S$, oxygen fluoride precipitates colloidal sulfur. With KCNS solutions, $OF_2$ reacts with heat evolution forming colloidal S, a black-red substance of unknown composition, and $(CN)_2$ and $SO_2$. With $K_4[Fe(CN)_6]$ oxygen difluoride gives an alkali-stable wine-red solution, which by addition of $H_2SO_4$ first turns green and then decomposes, losing color, forming $H_2O_2$, and evolving oxygen. $Pb(NO_3)_2$ forms yellow-brown crystals which react with $HNO_3$ producing $PbO_2$. $Cr^{+3}$ ions in alkali solutions are oxidized to chromate. From $MnSO_4$ solutions, $OF_2$ precipitates $MnO_2$; from $AgNO_2$ solutions, $Ag_2O_2$. The suspensions of $Ni(OH)_2$ and $Co(OH)_2$ are oxidized to peroxides.

The reducing compounds such as $Na_2SO_3$, $Na_2S_2O_3$, $SnCl_2$, $FeSO_4$, and $NaAsO_2$ react with $OF_2$ in accordance with the equations

$$4FeSO_4 + 2H_2SO_4 + OF_2 \rightarrow 2Fe_2(SO_4)_3 + 2HF + H_2O$$

$$2SnCl_2 + HCl + OF_2 \rightarrow 2SnCl_4 + 2HF + H_2O$$

$$2NaAsO_2 + H_2O + OF_2 \rightarrow 2NaAsO_3 + 2HF$$

### *2. With Metals* (27, 54, 73, 79, 87, 96)

Metals in finely divided form usually react with $OF_2$ upon gentle warming.

Au, Cu, Ni, Co, Mn, Ag, and Fe are fluorinated by heating with $OF_2$. Ba, Ca, Sr, Zr, Mg, Cd, Zn, and Al react by warming intensively with evolution of light. Sn and Pb form fluorides below their melting points. Cr, by heating, gives an orange-yellow sublimate. Powdered Mo reacts forming $MoO_3$ and oxyfluorides. W powder reacts at 400° with an explosion forming colorless $WF_6$ and a blue compound. Bi is coated with a layer of $BiF_3$.

K, Na, and Li react at about 400° with brilliant light and complete absorption of $OF_2$.

Hg reacts with $OF_2$ at room temperature forming a mercury "mirror" on the walls of a glass vessel (similar to that forming by $F_2$). Contrary to the $Hg + F_2$ reaction, which is used for quantitative determination of $F_2$ gas, the reaction of $OF_2$ with Hg proceeds very slowly and cannot be used for analysis of $OF_2$. Only about $^1/_3$ of the $OF_2$ volume, taken at 545 mm. pressure and 23°, was caused to react with Hg during 16 hr. Yellow $Hg_2F_2$ is formed on warming.

Pulverized Pt, Ir, Os, Ru, Rh, and Pd glow when gently warmed in a stream of $OF_2$ and form $OsF_6$, $PtF_4$, $IrF_4$, $PdF_3$, etc.

### *3. With Nonmetallic Solid Substances* (27, 54, 73, 87)

At moderate temperatures $OF_2$ does not attack glass, neither wet nor dry, but at about 250° it reacts with glass forming $SiF_4$ and liberating $O_2$. A quartz fiber can be ignited in an $OF_2$ atmosphere. Charcoal adsorbs $OF_2$ and can be exploded by heating. S, Se, and Te react vigorously at 150°; $SO_2$, $SF_4$, $SeF_4$, and $TeF_4$ have been found among the reaction products. With red P, reaction proceeds slowly at room temperature, but upon slightly warming an energetic reaction with flame occurs; $PF_5$ and $POF_3$ are forming. $P_2O_5$ reacts spontaneously.

As and Sb react energetically by warming to about 150°, forming $AsF_5$ and $SbF_5$. Powdered B and Si spark when heated with $OF_2$.

$CrO_3$, $As_2O_3$, and $WO_3$ react spontaneously or upon gentle warming yielding fluorides. CaO reacts only on strong heating forming $CaF_2$ and $O_2$. PbO forms lead oxides and fluorides.

$SbCl_5$ reacts with $OF_2$ at 150° with light explosion liberating $Cl_2$. NaCl forms NaF and evolves $Cl_2$. $NH_4Cl$ forms $NH_4F$. $HgCl_2$ forms a brown oxyfluoride. $TiCl_4$ forms a lemon yellow solid, slowly at 50°, rapidly at 50–90°. $AlCl_3$ reacts with an explosion yielding $AlF_3$.

$Na_2CO_3$ reacts with $OF_2$ forming NaF, $CO_2$, and $O_2$. $NaNO_2$ or $KNO_3$ form fluorides and nitrogen oxides.

### *4. With Halogens* (27, 54, 73, 87, 93)

$OF_2$ does not react with $F_2$ either in gaseous phase at temperatures up to 300° or in liquid phase at cryogenic temperatures. The mixtures of $OF_2$ with $Cl_2$, $Br_2$, or $I_2$ explode upon warming. When a mixture of $OF_2$ with $Cl_2$ was passed through a copper tube warmed to 300°, reaction proceeded with paffs or more violent explosions. ClF and also probably $Cl_2O$ and ClOF were formed. The formation of iodine oxide has been reported in a reaction with solid $I_2$.

### 5. *With Gases* (3, 4, 13, 73, 78, 93, 96)

Gaseous $OF_2$ does not react with gaseous $O_2$ at normal temperatures, but the liquid $OF_2$ under the action of ultraviolet light reacts with liquid $O_2$ forming small amounts of $O_2F_2$ and $O_3F_2$.

Gaseous $OF_2$ may be safely mixed with $H_2$, $CH_4$, and CO but the mixtures explode violently when a spark is created.

Without an ignition by spark or flame, the molecular hydrogen gas, $H_2$, does not react with gaseous $OF_2$ at room temperature and at a pressure up to 1 atm. The atomic hydrogen, however, reacts with gaseous and liquid $OF_2$ even at 77°K. and 0.4–1.0 mm. pressure, forming HF, $H_2O$, $H_2O_2$, and $N_2O_4$.

There was no noticeable reaction between anhydrous HCl and $OF_2$ in a 1:1 molar mixture at 25° and 1 atm. pressure. HCl does not react in solidified state with gaseous or liquefied $OF_2$ at 90–140°K.

A strong explosion occurs when gaseous $H_2S$ and $OF_2$ are mixed at normal temperatures. At 90–150°K., gaseous and liquid $OF_2$ do not react with solidified $H_2S$. At 195°K. and 400 mm. pressure, a 1:1 gaseous mixture of $OF_2$ and $H_2S$ reacts slowly forming a white solid. During 1 hr. the pressure decreased to about 100 mm. When the reaction vessel was taken out of Dry Ice, a violent explosion occurred shattering the reaction vessel.

With $SO_2$, oxygen difluoride reacts forming $(SO_3)_2$. $OF_2$ does not react with $ClF_3$ either in gaseous phase at room temperature or with liquid at low temperatures. There was no reaction also with ClF at 125°K.

With anhydrous $NH_3$ oxygen fluoride reacts slowly yielding $NH_4F$. A mixture with NO is slowly colored brown; NOF and $NOF_2$ are forming. A gaseous NO–$OF_2$ mixture may explode from a spark. The 1:1 mixture of liquefied $OF_2$ and NOF explodes on warming. A flame may be obtained when a stream of NOF is let into a flask filled with $OF_2$. The reaction proceeds most probably in accordance with the equation

$$NOF + OF_2 \rightarrow NF_3 + O_2$$

With water vapor $OF_2$ explodes violently when initiated by a spark or flame.

$OF_2$ reacts with Xe forming $XeF_4$ and xenon oxyfluorides. Reactions were carried out in an electric discharge apparatus at 195°K. and 3–62 mm. pressure and in a nickel tube heated to about 400° at the starting pressure of about 3.5 atm. $XeF_4$ and xenon oxyfluorides were obtained in the form of colorless transparent crystals stable at room temperature.

### 6. *With Organic Compounds* (49, 73, 102)

Benzene and paraffinic compounds absorb $OF_2$ gas readily. Benzene forms quinone and hydroquinone, no phenol or pyrocatechol being observed. Indigo solution becomes colorless. Methanol and ethanol react slowly at room temperature. One-half of $OF_2$ dissolved in $CCl_4$ at room temperature reacted in 48 hr.

## G. $OF_2$ IN PROPELLANT SYSTEMS

Oxygen difluoride is a high energy oxidizer suitable for rocket and missile propellants. It has received great attention as a space-storable oxidizer (44, 57).

Bipropellant systems using liquid $OF_2$ have high specific impulses. At a favorable oxidizer–fuel ratio, $OF_2$ with ethanol, for example, has an $I_{sp}$ of 336 sec.; with $N_2H_4$, 345 sec.; with JP-4, 350 sec.; and with liquid $CH_4$, 357 sec. (all at $P_c$ = 1000 p.s.i.a., $P_e$ = 14.696 p.s.i.a.). With liquid $H_2$ the value of the specific impulse reaches 457 sec. at $OF_2/H_2$ ratio of 7.5, $P_c$ = 300, $P_e$ = 0.62 p.s.i.a. In addition, the bipropellant systems with $OF_2$ have many advantages over the other high-performance propellants (44). $OF_2$ provides good performance with both carbonaceous and noncarbonaceous fuels (35, 36), with which $F_2$, for example, does not. Oxygen difluoride has a comparatively high density which results in more compact vehicles of lower weight. The $OF_2$–fuel combinations are hypergolic and belong to low $\gamma$-systems.

$OF_2$ was suggested also for a monopropellant mixture consisting of 2.6 parts by weight of $OF_2$ and 1 part of 1-fluoropropane (45). This mixture is liquid over the temperature range of 156–276°K. and has a theoretical specific impulse of 291 sec.

## H. METHODS OF ANALYSIS OF $OF_2$

Oxygen difluoride is often identified by its infrared spectrum and by determination of its physical constants: melting point, boiling point, and vapor pressure.

By chemical means the analysis may be performed by shaking the gas with a 0.5 *N* solution of NaOH (71). The reaction proceeds according to the equation

$$OF_2 + 2NaOH \rightarrow 2NaF + H_2O + O_2$$

The excess of NaOH is then determined by titration with HCl. In addition, the fluorine ion may be determined by titration with thorium nitrate (87, 104–106)

$$4NaF + Th(NO_3)_4 + nH_2O \rightarrow ThF_4 \cdot nH_2O + 4NaNO_3$$

or precipitated in the usual manner as $CaF_2$.

Another method is based on the reaction with KI (4).

$$OF_2 + 4KI + H_2O \rightarrow 2KF + 2KOH + 2I_2$$

The sample is shaken with or bubbled through to a 15% KI solution acidified with $H_2SO_4$ and the amount of the liberated $I_2$ determined by titration with a 0.1 *N* solution of $Na_2S_2O_3$.

Finally, $OF_2$ may be analyzed by passing the gas over melted metallic Na (59, 87). The fluorine ion is then determined either by titration with $Th(NO_3)_4$ or by precipitation as $CaF_2$.

## III. DIOXYGEN DIFLUORIDE, $O_2F_2$

The formation of dioxygen difluoride, $O_2F_2$, was first achieved by Russ and Menzel (1933), who passed an electric discharge through a gaseous $O_2$–$F_2$ mixture at low pressure and liquid-air temperature (76, 77).

### A. PREPARATION

At the present time, dioxygen difluoride is prepared directly from the elements, essentially by the principle described by Ruff and Menzel (76) and by Aoyama and Sakuraba (3, 4). The 1:1 gaseous mixture of fluorine and oxygen is prepared in the perfluorinated stainless steel cylinder. The 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 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 lubricated with Kel-F grease. The discharge varies from 25 to 30 ma. at 2100–2400 v. The flow of the $F_2$–$O_2$ mixture is adjusted so that the pressure in the reaction vessel is maintained at $12 \pm 5$ mm.

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

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

and

$$2NaF + SiF_4 \rightarrow Na_2SiF_6$$

Pure dioxygen difluoride can be stored for a long time in darkness in Pyrex glass cylinders cooled to 93°K.

### B. PHYSICAL PROPERTIES

Dioxygen difluoride is an orange-yellow solid, melting at 109.7°K. to an orange-red liquid. It decomposes rapidly into $O_2$ and $F_2$ at temperatures close to its normal boiling point of 216°K.

The most recent values of the structural parameters and selected data on the main physical and physicochemical properties of $O_2F_2$ are given in Table II.

### C. SOLUBILITY

Experimental results on solubility and miscibility of liquid $O_2F_2$ obtained to date (91, 92, 94) are as follows:

| $O_2F_2$ mixes homogeneously with: | | Forms two practically insoluble layers with: | |
|---|---|---|---|
| $O_3F_2$ | at 116°K. | $N_2$ | at 77°K. |
| $CCl_2F_2$ | 116 | $F_2$ | 77 |
| $CClF_3$ | 116 | $O_2$ | 90 |
| $O_3$ | 116 (the mixture explodes at about 125°K.) | $CF_4$ | 90 |
| $N_2F_2$ | 120 | $NF_3$ | 130 |
| $CO_3F$ | 127 | $N_2F_4$ | 130 |
| $ClF_3$ | 180 | $C_3F_8$ | 140 |
| $NO_2F$ | 195 | | |

The solubility of $O_2F_2$ in anhydrous HF is about 5.8% by weight at 176°K. and about 11.6% at 186°K. Less than 1% of $O_2F_2$ is soluble in $CF_4$ at 116°K. $C_3F_8$ dissolves some $O_2F_2$ at 130°K. and $N_2F_2$ dissolves some $O_2F_2$ at 140°K.

Dioxygen difluoride dissolves about 40% by weight of $OF_2$, about 20% of $SiF_4$ at 150°K., and about 10% of HF at 186°K.

### D. STABILITY

Dioxygen difluoride is thermally unstable. It decomposes into $O_2$ and $F_2$ at temperatures below its theoretical boiling point (216°K.). The activation energy and the rate of thermal decomposition of $O_2F_2$ are given in Table II.

To our knowledge, the photochemical stability of $O_2F_2$ was not studied.

### E. EXPLOSIVENESS AND INFLAMMABILITY

Samples of the liquid dioxygen difluoride were subjected at Dry-Ice temperature to the flame of a safety fuse, to a 1.25-joule electric spark, and to an impact of a 22-caliber bullet. There was no explosion or inflammation of $O_2F_2$ in any of these tests. A 50-g. cartridge of liquid $O_2F_2$ at 195°K. in a prefluorinated 1.25-in. brass tube (loading density about 1.507 g./cm.$^3$) did not detonate when affected by a

## TABLE II

## PHYSICAL AND PHYSICOCHEMICAL PROPERTIES OF DIOXYGEN DIFLUORIDE

| Properties | References |
|---|---|
| Appearance<br>Pale brown gas (dec.)<br>Orange-red liquid at 110°K.<br>Orange-yellow solid below 110°K. | |
| Molecular weight<br>70.000 | |
| Molecular structure<br>Nonplanar atomic chain, F—O—O—F | (41, 47, 55, 56) |
| Molecular constants<br>Interatomic distance $r$(O—O) = 1.217 ± 0.003 Å.<br>Interatomic distance $r$(F—O) = 1.575 ± 0.003 Å.<br>OOF angle = 109°30′ ± 30′<br>Dihedral angle = 87°30′ ± 30′<br>Dipole moment = 1.44 ± 0.04 D. | (41) |
| Ground-state rotational constants and moments of inertia | |

| | $O_2^{16}F_2$ | $O^{18}O^{16}F_2$ | $O_2^{18}F_2$ |
|---|---|---|---|
| $A$(Mc./sec.) | 20,266.18 | 19,531.98 | 18,859.19 |
| $B$ | 5,011.09 | 4,975.78 | 4,938.34 |
| $C$ | 4,360.14 | 4,318.68 | 4.279.31 |
| Asymmetry constant $K$ | −0.91815 | −0.91362 | −0.90960 |
| $I_A$ (a.m.u. Å.$^2$) | 24.94456 | 25.88222 | 26.80555 |
| $I_B$ | 100.8824 | 101.5981 | 102.3686 |
| $I_C$ | 115.9438 | 117.0570 | 118.1338 |

| Properties | References |
|---|---|
| Force constants, dynes/cm.<br>$K_{O-F} = 5.2 \times 10^{-5}$<br>$K_{O-O} = 2.9 \times 10^{-5}$ | (47) |
| Melting point<br>109.7°K., −163.5°C. | (76) |
| Boiling point<br>216°K., −57°C. dec. | (76) |
| Vapor pressure<br>$\log P_{mm.} = 7.515 - 1000/T$ (at the temperatures below 173°K.) | (76) |

| | |
|---|---|
| $P$ = 0.010 mm. | at 105.097°K. |
| 0.100 | 117.440 |
| 1.00 | 133.067 |
| 10.00 | 153.492 |
| 100.00 | 181.324 |

| Properties | References |
|---|---|
| Density<br>Liquid, over the temperature range of 117–186°K.<br>$d = 2.074 - 0.00291T$ g./cc.<br>1.736 g./cc. at 116°K. | (77) |
| Molar volume<br>40.4 cc./mole at 116°K. | (77) |
| Activation energy of thermal decomposition<br>17.3 kcal./mole | (24, 25, 85) |
| Rate of thermal decomposition<br>$\frac{-d[O_2F_2]}{dt} = [O_2F_2] \times 10^{12.4} \exp(-1700/4.57T)$<br>4.3% per day at 195°K.<br>96.5% per day at 214.5°K.<br>Half-life at 223°K. = 220 min., increasing sevenfold for a 10° drop of temperature | (21, 22, 24, 46, 85) |
| Heat of vaporization<br>$\Delta H_{vap.} = 4.583 \pm 0.100$ kcal./mole, at 216.2°K. | (46) |
| Entropy of vaporization (Trouton's constant)<br>21.22 cal./°K. mole | |
| Hildebrand's solubility parameter at b.p.<br>9.26 (cal./cc.)$^{1/2}$ | |
| Heat of formation (from the elements)<br>$\Delta H_{298} = 4.73 \pm 0.30$ kcal./mole | (47) |
| Heat of atomization<br>151.5 kcal./mole | (47) |
| Heat of decomposition<br>For the reaction:<br>$O_2F_{2\,liq.} \rightarrow O_{2\,gas} + F_{2\,gas}$, at 190°K., $\Delta E = -1120 \pm 100$ cal./mole | |
| For the reaction:<br>$O_2F_{2\,gas} \rightarrow O_{2\,gas} + F_{2\,gas}$, at 298°K., $\Delta E = -5324 \pm 300$ cal./mole | (47) |
| Bond energy<br>$E_{O-O} = 62.1$ kcal./bond | (47) |
| Specific heat<br>Gas, $C_v = 10 \pm 1$ cal./mole °K. (estimated)<br>Liquid, over the temperature range of 121–186°K.<br>$C_v = 24.5 \pm 0.7$ kcal./mole | (47) |
| Infrared spectrum bands, cm.$^{-1}$<br>1024<br>628<br>463 | (46) |
| Molar extinction coefficients[a] | |

| | | | |
|---|---|---|---|
| Gas, at 195°K. | 28.1 | at 340 mμ | (12) |
| | 19.4 | 350 | |
| | 15.2 | 360 | |
| | 12.5 | 365 | |
| | 10.6 | 370 | |
| | 8.13 | 380 | |
| | 13.8 | 400 | |
| | 16.5 | 405 | |
| | 9.04 | 420 | |
| | 4.52 | 440 | |
| | 1.63 | 470 | |
| | 0.72 | 500 | |
| Liquid, dissolved in a mixture of 23% (by volume) Freon 12 + 77% Freon 13, at 77°K. | | | |
| | 13.13 | at 350 mμ | (48, 93) |
| | 14.10 | 360 | |
| | 11.79 | 380 | |
| | 8.02 | 400 | |
| | 5.15 | 420 | |
| | 2.52 | 450 | |
| | 1.24 | 470 | |
| | 0.63 | 500 | |
| | 0.24 | 580 | |
| | 0.10 | 600 | |
| | 0.07 | 625 | |
| | 0.09 | 650 | |
| | 0.10 | 700 | |

The maximum absorption
at 140°K.: 15.27 at 360 mμ
at 175°K.: 15.65 at 360 mμ

---

[a] In the visible range, cm.$^{-1}$ mole$^{-1}$ l.

pentaerythritol tetranitrate primacord. In contact with a sheet of Pt, covered with Pt fluoride, $O_2F_2$ exploded at 160°K. (46, 90, 96).

### F. CHEMICAL REACTIONS

Dioxygen difluoride has a remarkably high oxidizing power. With most of the substances tested, it reacted at cryogenic conditions. Following are the main results obtained to date in the study of the basic chemistry of $O_2F_2$ (90, 93–96).

#### *1. With Organic Compounds* (90, 96)

$O_2F_2$ reacts vigorously with organic compounds, even at temperatures close to its melting point. It reacted instantaneously with solid ethyl alcohol, producing a blue flame and an explosion. When a drop of liquid $O_2F_2$ was added to liquid methane, cooled at 90°K., a white flame was produced instantaneously, which turned green upon further burning. When 0.2 cm.$^3$ of liquid $O_2F_2$ was added to 0.5 cm.$^3$ of liquid $CH_4$ at 90°K., a violent explosion occurred.

When added to Dry Ice, dioxygen difluoride does not react and is only absorbed by the solid. Addition of acetone to this mixture resulted in sparking accompanied by an explosion.

A 2% solution of $O_2F_2$ in HF reacts violently with a flash with benzene at 195°K.

#### *2. With Ammonia, Water, and Hydrogen* (90, 93)

Liquid $O_2F_2$ reacts vigorously when added to solid anhydrous ammonia at temperatures close to 110°K. It causes explosions when added to ice at 130–140°K. and reacts also with traces of water if dissolved in HF containing $H_2O$, at 195°K.; the brown color of the solution disappears and the $O_2$ gas escapes.

There was no reaction between $O_2F_2$ and molecular hydrogen when gas was pumped through to the U-tube at 77°K., in amounts of 1.25 l./hr. (1 mm.). Atomic hydrogen, however, reacted with $O_2F_2$ at the same conditions. The reaction proceeds in accordance with the equation

$$3O_2F_2 + 15H\cdot \rightarrow 6HF + 1.5H_2O_2 + 3H_2O$$

Traces of $H_2O_4$ also form. No radical or other intermediate products have been found.

#### *3. With $Cl_2$, ClF, and HCl* (90, 93–95)

A rapid introduction of chlorine to $O_2F_2$, cooled to about 140°K., causes a violent explosion. However, when small portions of $Cl_2$ are added slowly to $O_2F_2$ cooled to 130°K., a violet intermediate product forms, together with $ClF_3$. Here, the first step is the fluorination of $Cl_2$ to ClF. After ClF is formed, it reacts further with $O_2F_2$ as described below.

The study of the reaction of $O_2F_2$ with ClF showed that if the reaction is carried out without special precautions at temperatures above 140°K., the two substances react violently with heat evolution following the stoichiometric equation

$$O_2F_2 + ClF \rightarrow O_2 + ClF_3 + 30.1 \text{ kcal.}$$

The ClF abstracts the fluorine from $O_2F_2$, forming $ClF_3$ and liberating $O_2$. Simultaneously, due to the heat of the $O_2F_2$ + ClF reaction, a part of $O_2F_2$ decomposes to $O_2$ and $F_2$.

$$O_2F_2 \rightarrow O_2 + F_2 + 4.73 \text{ kcal.}$$

However, if the reaction between $O_2F_2$ and ClF is carried out at moderate temperatures (119–130°K.) and with a slow addition of ClF, a third reaction takes place, forming an intermediate compound of the elementary composition $(O_2ClF_3)_n$ in accordance with the scheme

$$nO_2F_2 + nClF \rightarrow (O_2ClF_3)_n$$

The extent of each of these three reactions depends upon the reaction conditions.

The intermediate compound, dioxygen chlorine trifluoride, has an intense violet color and is a very strong oxidizer. Its properties are described elsewhere (95).

Much effort was exerted to increase the yield of $O_2ClF_3$. Freon 12, $CCl_2F_2$, Freon 13, $CClF_3$, perfluoropropane, $C_3F_8$, perchloryl fluoride, $ClO_3F$, hydrogen fluoride, HF, and oxygen difluoride, $OF_2$, were tried as diluents. There was no formation of the violet intermediate product when Freon 12 or $OF_2$ was used as the solvent for $O_2F_2$ and cooled ClF gas (diluted by He or $O_2$) was bubbled through the solutions. With Freon 13 or $ClO_3F$ as the solvent, the violet product formed in small amounts and collected on the bottom of the reaction vessel. Its stability, however, in the presence of these compounds is low and the compound decomposes completely at about 195°K. With HF, solutions of about 23% of $O_2ClF_3$ were obtained. A difficulty arises, however, from the fact that the solution of the violet compound in HF is stable at 193–195°K. only under an oxygen pressure of 2 atm. For this reason the removal of HF and the isolation of the violet compound are complicated. Attempts to lower the melting point of HF by the addition of KF (14), 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 $K(ClF_4)$.

With $C_3F_8$ as a diluent, the yield of the violet compound was increased to 81% of theory, but again the stability of $O_2ClF_3$ in the presence of $C_3F_8$ was found to be low.

It was found also that in the presence of traces of water, nitrogen oxides, or nitrogen oxyfluorides, the violet compound decomposes quickly or does not form.

If the violet compound, $O_2ClF_3$, is warmed 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 3–5 min. 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.

Dioxygen chlorine trifluoride, $O_2ClF_3$, also forms in the reaction of HCl with $O_2F_2$ at 130–140°K.

$$2O_2F_2 + HCl \rightarrow O_2ClF_3 + HF + O_2$$

The reaction steps probably are the formation of $Cl_2$ and then of ClF, which reacts in the usual manner to form $O_2ClF_3$. An excess of HCl and a rise of temperature above 143°K. cause decomposition of $O_2ClF_3$.

At 130 and 140°K., HCl is solid (m.p. 158.9°K.) but it has a vapor pressure of about 10 mm. at 140°K. Thus, the reaction actually takes place between the gaseous HCl and gaseous or liquid $O_2F_2$. The violet compound partly deposits on the walls, but also dissolves in the liquid $O_2F_2$. Solutions containing up to 8.5% by weight of $O_2ClF_3$ in $O_2F_2$ were obtained.

At temperatures above 140°K. the reaction proceeds rapidly with substantial amounts of $O_2ClF_3$ decomposing to $O_2$ and $ClF_3$.

No reaction was observed between $O_2F_2$ and $ClF_3$ in the solid state at 90°K. or in the liquid state at temperatures up to 190°K.

### *4. With $Br_2$, Bromine Fluorides, and HBr* (90, 93, 94)

Liquid $O_2F_2$, at temperatures close to its melting point (109.7°K.), reacts vigorously when added to solid bromine cooled at 90°K.

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. The reaction proceeds in accordance with the equation

$$O_2F_2 + BrF_3 \rightarrow BrF_5 + O_2 + 46.1 \text{ kcal.}$$

Under milder conditions, when very small amounts of $BrF_3$ are added to $O_2F_2$ cooled to 90°K. and the reaction vessel is slowly warmed to 130°K., an intermediate brown-violet compound may form. The reaction proceeds analogously to the $O_2F_2$ + ClF reaction, in accordance with the equation

$$O_2F_2 + BrF_3 \rightarrow O_2BrF_5$$

The reaction is accompanied by some gas evolution due to the decomposition of $O_2BrF_5$ to $BrF_5$ and $O_2$ and to partial decomposition of $O_2F_2$ to $O_2$ and $F_2$.

An 80% yield was achieved, but the compound began to decompose at 150°K. to $O_2$ and $BrF_5$. The reaction of $O_2F_2$ with $BrF_3$ is more difficult to control than the reaction with ClF.

In approximately the same condition, dioxygen difluoride reacted also with a mixture of $Br_2$, BrF, and $BrF_3$. A product obtained by mixing $BrF_3$ with 10% of $Br_2$ and consisting of $Br_2$, BrF, and $BrF_3$ was used in the experiments with $O_2F_2$. This product reacted with $O_2F_2$ between 90 and 130°K., forming a dark brown (violet shaded) intermediate, which decomposed to $BrF_3$ and $BrF_5$ at temperatures above 130°K. If the reaction was carried out at temperatures above 130°K., it proceeded rapidly and directly to $BrF_3$, $BrF_5$, and $O_2$, without forming any colored intermediate. The colored intermediate reaction products formed with $BrF_3$ and $Br_2$–BrF–$BrF_3$ mixture have only a transitory existence and attempts to stabilize them were not successful. Moreover, these reactions are not always reproducible.

The study of the reaction between $O_2F_2$ and HBr showed that when a small amount of $O_2F_2$ reacts with an excess of HBr at about 130°K., the reaction proceeds according to the equation

$$O_2F_2 + 2HBr \rightarrow 2HF + Br_2 + O_2$$

but when an excess of $O_2F_2$ reacts with a small amount of HBr, the reaction follows the equation

$$3O_2F_2 + HBr \rightarrow O_2BrF_5 + HF + O_2$$

The colored intermediate product, $O_2BrF_5$, decomposed at higher temperatures, forming $BrF_5$ and liberating gaseous $O_2$.

### *5. With $I_2$ and $IF_5$* (90, 93, 94)

A spontaneous reaction occurred when liquid $O_2F_2$, cooled to about 110°K., was added rapidly to iodine crystals cooled to 90°K., but there was no visible reaction between 8–50% solutions of $O_2F_2$ in Freon 13 ($CClF_3$) and iodine at temperatures up to 195°K.

Iodine pentafluoride, $IF_5$, in contrast to its chlorine and bromine analogs (ClF and $BrF_3$) did not react with $O_2F_2$ over the temperature range of 90–195°K. Only a slow decomposition of $O_2F_2$ to $O_2$ and $F_2$ took place.

### *6. With Phosphorus, $PF_3$* (90, 93, 94), *and $PF_5$* (88a)

With red phosphorus, $O_2F_2$ reacts vigorously when rapidly added at about 110°K.

Phosphorus trifluoride, $PF_3$, reacts with $O_2F_2$ at 125°K. forming $PF_5$ and $O_2$.

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

At the same time some of the oxygen liberated reacts with $PF_3$, forming a solid white compound at 0°. The white compound is fairly stable at 0°. 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 $POF_3$.

$$nO_2F_2 + 3nPF_3 \rightarrow nPF_5 + 2(POF_3)_n$$

On standing at 0° or at room temperature, the polymer depolymerizes completely to $POF_3$ according to the equation

$$(POF_3)_n \rightarrow n(POF_3)$$

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.

A new compound, tentatively assigned the formula $O_2PF_6$, has been obtained by the reaction of $O_2F_2$ with $PF_5$.

### 7. *With $NO_2F$, $NF_3$, and $N_2F_4$* (90, 93, 94)

Dioxygen difluoride is soluble in nitryl fluoride, $NO_2F$, at 195°K., forming a very fluid orange solution. A slow decomposition of $O_2F_2$ takes place at this temperature, but no reaction with $NO_2F$ was observed.

There was no visible reaction between nitrogen trifluoride, $NF_3$, and $O_2F_2$ at 130–140°K. Tetrafluorohydrazine, $N_2F_4$, reacts with $O_2F_2$ at 170°K., forming $NF_3$ and $O_2$, but without the formation of any colored intermediate product.

### 8. *With S, $SF_4$, and $H_2S$* (90, 93, 94)

When added rapidly to sulfur cooled to 90°K., liquid $O_2F_2$ reacts instantaneously with a flash. $SOF_4$, $SO_2F_2$, and $(SO_3)n$ were found among the reaction products (88a). Sulfur tetrafluoride, $SF_4$, reacts with $O_2F_2$ at 125°K. and may form an intensely violet-colored intermediate product.

$$O_2F_2 + SF_4 \rightarrow O_2SF_6$$

This reaction is not always reproducible. Once started, the reaction between $O_2F_2$ and $SF_4$ is difficult to control. In most cases it proceeds directly to the formation of $SF_6$ and $O_2$

$$O_2F_2 + SF_4 \rightarrow SF_6 + O_2 + 121.5 \text{ kcal.}$$

and leads to an explosion. With perchloryl fluoride, $ClO_3F$, as a solvent, explosions could be avoided in some cases (at temperatures below 116°K.), but the yield and the stability of the intermediate product were very low.

With $H_2S$, dioxygen difluoride reacts in accord with the equation

$$4O_2F_2 + H_2S \rightarrow 2HF + 4O_2 + SF_6 + 432.9 \text{ kcal.}$$

It was observed that a very slow reaction starts in the gas phase at 130°K. The vapor pressure of $O_2F_2$ at this temperature is about 1 mm. and of $H_2S$, about 0.5 mm. When the reaction vessel is further warmed slowly to 195°K., the rate of the reaction increases. In distinction to the $O_2F_2$ + HCl and $O_2F_2$ + HBr reactions, there was no formation of any colored intermediate compound with $H_2S$.

### 9. *With Tetrafluoroethylene* (34)

When $C_2F_4$ was allowed to condense into a vessel containing $O_2F_2$ at 77°K., flashes were observed upon gradual lowering of the refrigerant; $COF_2$, $CF_4$, and in smaller amounts also $C_2F_2$, $SiF_4$, and $CF_2OOCF_3$ were formed. Reaction proceeded with flashes also when several cm.$^3$ of liquid argon were condensed into the reaction vessel containing $O_2F_2$, and $C_2F_4$ was allowed to diffuse to the cold zone; $CF_3OF$, $OF_2$, and $C_4F_{10}$ did form in addition to the products formed at the previous reaction conditions. When $C_2F_4$ was highly diluted with helium and passed at a pressure of 2–4 mm. through the reaction vessel cooled to 77°K., no flashes were noticed, but on warming a few flashes occurred again. The reaction products contained all the compounds obtained previously (except $OF_2$) plus $CO_2$, $C_2F_5OCF_3$, and perfluorotetramethylene oxide, $C_4F_8O$.

### 10. *Behavior of $O_2F_2$ with Some Other Substances* (90)

Liquid dioxygen difluoride, at temperatures close to its melting point, reacts vigorously when added to charcoal cooled to 90°K. It did not appear to react, however, with beryllium powder, quartz fiber, and chromium trioxide, even upon warming to room temperature.

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 reaction. At about 195°K., $O_2F_2$ decomposes into $O_2$ and $F_2$, while $SiF_4$ remains unchanged. Similarly, $CF_4$ does not react with $O_2F_2$.

In contact with a Pt sheet covered with Pt fluoride, dioxygen difluoride exploded at 160°K.

The reactions of Na, Li, and K with $O_2F_2$ are surprisingly mild. The products of these reactions are not identified yet. Ca shows no sign of reaction with $O_2F_2$ (88a).

### G. METHOD OF ANALYSIS OF $O_2F_2$

The sample is warmed to room temperature. $O_2F_2$ decomposes quantitatively to $O_2$ and $F_2$. The gas is then analyzed for fluorine by shaking with metallic Hg or any other known methods, and for oxygen by absorbing it with an alkali solution of pyrogallol (46).

## IV. TRIOXYGEN DIFLUORIDE, $O_3F_2$

The next member of the family, trioxygen difluoride, or ozone fluoride, $O_3F_2$, was obtained by Aoyama and Sakuraba (1938) when the proper mixture of $O_2$ and $F_2$ was subjected to an electrical discharge at low

TABLE III

PHYSICAL AND PHYSICOCHEMICAL PROPERTIES OF TRIOXYGEN DIFLUORIDE

| Properties | Reference |
|---|---|
| Appearance | |
| Dark red liquid at 84°K. Reddish brown solid below 83°K. | |
| Molecular weight | |
| 86.000 | |
| Melting point | |
| 83-84°K., −189 to −190°C. | (46) |
| Boiling point | |
| 213°K., −60°C. dec. | (46) |
| Vapor pressure[a] | |
| $\log P_{\mathrm{mm.}} = 6.1343 - 675.57/T$ | |
| (over the temp. range of 79 to 114°K.) | |
| $P =$ 0.010 mm. at 83.052°K. | |
| 0.100 94.693°K. | |
| 1.00 110.130°K. | |
| 10.00 131.580°K. | |
| Density[b] | |
| Liquid, $d = 2.357 - 0.00676T$ g./cc. | (46) |
| 1.573 g./cc. at 116°K. | |
| 1.749 g./cc. at 90°K. | |
| 1.895 g./cc. at m.p. | |
| Molar volume | |
| 49.3 cc./mole at 90.3°K. | |
| Activation energy of thermal decomposition | |
| 3.7 kcal./mole | (46) |
| Rate of thermal decomposition | |
| $3.6 \times 10^{-5}$/hr. at 77.3°K. | (46) |
| $6.2 \times 10^{-5}$/hr. at 77.8°K. | |
| $8.3 \times 10^{-5}$/hr. at 79.4°K. | |
| $1.6 \times 10^{-3}$/hr. at 89.6°K. | |
| $7.2 \times 10^{-2}$/hr. at 113.8°K. | |
| Heat of vaporization | |
| $\Delta H_{\mathrm{vap.}} = 4.581 \pm 0.200$ kcal./mole, at 121°K. | (47) |
| Entropy of vaporization (Trouton's constant) | |
| 21.51 cal/°K. mole | |
| Hildebrand's solubility parameter at b.p. | |
| 6.66 (cal./cc.)$^{1/2}$ (10.7, at 90°K.) | |
| Heat of formation (from the elements) | |
| $\Delta H_{298} = 6.24 \pm 0.75$ kcal./mole | (47) |
| Heat of decomposition | |
| For the reaction: | |
| $O_3F_{2\ \mathrm{liq.}} \rightarrow O_2F_{2\ \mathrm{liq.}} + 0.5O_{2\ \mathrm{gas}}$, at 121°K., $\Delta E = -2040 \pm 150$ cal./mole | (47) |
| For the reaction: | |
| $O_3F_{2\ \mathrm{liq.}} \rightarrow 1.5O_{2\ \mathrm{gas}} + F_{2\ \mathrm{gas}}$, at 121°K., $\Delta E = -2160 \pm 250$ cal./mole | |
| For the reaction: | |
| $O_3F_{2\ \mathrm{gas}} \rightarrow 1.5O_{2\ \mathrm{gas}} + F_{2\ \mathrm{g.s}}$, at 121°K., $\Delta E = -6500 \pm 450$ cal./mole | |
| For the reaction: | |
| $O_3F_{2\ \mathrm{gas}} \rightarrow 1.5O_{2\ \mathrm{gas}} + F_{2\ \mathrm{gas}}$, at 298°K., $\Delta E = -7130 \pm 750$ cal./mole | |
| Bond energy | |
| $E_{\mathrm{O-O}} = 61.1$ kcal./bond | (68) |
| Specific heat | |
| Gas, at 121°K., | |
| $C_v = 16 \pm 1.5$ cal./mole °K. (estd.) | (47) |
| Molar extinction coefficient[c] | |
| 18.76 (350) | |
| 17.63 (365) | |
| 16.59 (380) | (48, 93) |
| 16.95 (400) | |
| 17.28 (420) | |
| 17.28 (430) | |
| 15.21 (450) | |
| 13.26 (470) | |
| 13.94 (480) | |
| 11.96 (500) | |
| 5.48 (540) | |
| 1.98 (580) | |
| 0.12 (600) | |
| 0.12 (625) | |
| 0.12 (650) | |
| 0.12 (675) | |
| 0.00 (700) | |
| 0.12 (750) | |

[a] This equation was derived from the experimental data. The equation given in the original work (36) and quoted in other publications (1, 66) is in error. [b] Preliminary data. [c] In the visible range for liquid $O_3F_2$ dissolved in a mixture of 23% (by volume) of Freon 12 + 77% Freon 13, in cm.$^{-1}$ mole$^{-1}$ (mμ).

temperatures (3). The same investigators showed also that $O_3F_2$ is formed by the action of ultraviolet light on a mixture of liquid oxygen and fluorine (4). For many years the claims of these Japanese scientists were not accepted for our standard reference books or were regarded with skepticism. This action was due to the fact that Aoyama and Sakuraba did not give a quantitative analysis of their product. Grosse and Kirshenbaum (1958) confirmed, however, that $O_3F_2$ is a definite compound and investigated its properties (46).

### A. PREPARATION

Trioxygen difluoride is prepared by the principle that is used for preparing $O_2F_2$. The gaseous fluorine–oxygen mixture must contain three volumes of oxygen and two volumes of fluorine. This mixture combines quantitatively to $O_3F_2$ in the same type of apparatus that is used for $O_2F_2$ preparation (47, 94). Slightly different are the reaction conditions: the reaction vessel is cooled in a liquid nitrogen bath, and the electrical discharge is varied from 20 to 25 ma. at 2000–2200 v. The gas pressure in the reaction vessel is the same, 12 ± 5 mm.

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 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 darkness in a Pyrex glass vessel. The rate of decomposition at this temperature is about $3.6 \times 10^{-5}$/hr.

### B. PHYSICAL PROPERTIES

Trioxygen difluoride is a dark red, viscous liquid at 90°K. Since the compound is liquid at 90°K., it can be easily distinguished from $O_2F_2$.

Trioxygen difluoride is a very strong oxidizer, very similar to $O_2F_2$. It is also an endothermic compound and decomposes quantitatively, with heat evolution, at about 115°K., according to the equation

$$2O_3F_2 \rightarrow O_2 + 2O_2F_2$$

At about 200°K., $O_2F_2$ dissociates quantitatively, again with heat evolution, to $O_2$ and $F_2$. Trioxygen difluoride may be distilled in the range of 96–114°K. at a pressure of 0.1 to 1.5 mm. with only slight decomposition.

The selected data on the main physical and physicochemical properties of trioxygen difluoride are presented in Table III.

In regard to the density of $O_3F_2$, it is pertinent to recall that in our study of the miscibility and solubility of the liquefied and solidified gases, liquid $O_3F_2$ proved to be heavier at 90.3°K. than liquid $NF_3$. According to the literature (70), the density of liquid $NF_3$ at this temperature is 1.772 g./cc. The density of $O_3F_2$ at the same temperature, according to the equation based on preliminary measurements (46), presented in Table III, is 1.747 g./cc. However, the layer of liquid $O_3F_2$, which is immiscible with $NF_3$ at 90°K., lay below the layer of $NF_3$. Thus, the preliminary data on density of $O_3F_2$ (the only available to date) must be considered inaccurate.

The molecular structure of trioxygen difluoride is still unknown. The electron paramagnetic absorption measurements showed that $O_3F_2$ is paramagnetic in both the solid and the liquid state. The two-line electron paramagnetic resonance absorption spectrum of liquid $O_3F_2$ (dissolved in Freon 13 at 93°K.) was interpreted to be due to two unpaired-electron spins, each of which is localized near a fluorine atom. From the complicated multiline e.p.r. spectrum of the solidified (at 77°K.) $O_3F_2$–$CClF_3$ solution, it appears that a triplet state is not involved, and the $O_3F_2$ has the structure of an asymmetric top (55).

### C. SOLUBILITY

An experimental investigation of the solubility of liquid $O_3F_2$ in some liquefied gases and the miscibility with them was made in our laboratories. The results obtained to date are as follows:

| $O_3F_2$ mixes homogeneously with: | | | Forms two practically insoluble layers with: | |
|---|---|---|---|---|
| $O_3$ | at 90°K. | the mixture explodes readily | $N_2$ | at 77°K. |
| $OF_2$ | 116 | | $F_2$ | 77 |
| $O_2F_2$ | 116 | | $NF_3$ | 90 |
| $NO_2F$ | 116 | | $ClF$ | 90 |
| $CCl_2F_2$ | 116 | | $ClF_3$ | 90 |
| $CClF_3$ | 116 | | $CF_4$ | 90 |
| $ClO_3F$ | 127 | | | |

At 90°K., $CCl_2F_2$ and $CClF_3$ dissolve about $^1/_3$ of a volume of $O_3F_2$. Trioxygen difluoride is slightly soluble in $CF_4$ at 116°K. It is also slightly soluble in liquid oxygen; 0.110% by weight of $O_3F_2$ is soluble in liquid $O_2$ at 90°K. and 0.046% at 77°K. The solutions of trioxygen difluoride in liquid oxygen are of great interest in connection with rocket propulsion systems (91).

### D. STABILITY

Although $O_3F_2$ is very reactive even at cryogenic temperatures, it is considered to be safer to handle than ozone. Liquid $O_3F_2$ can be evaporated rapidly, refluxed, or thermally decomposed without explosion. In contact with organic or other oxidizable materials, however, it will either cause burning or explosions.

Trioxygen difluoride decomposes thermally above its melting point to $O_2F_2$ and $O_2$. At higher temperatures $O_2F_2$ decomposes further to $O_2$ and $F_2$ (46). The activation energy and the rate of thermal decomposition of $O_3F_2$ are presented in Table III.

Direct light also causes a slow decomposition of $O_3F_2$ to $O_2F_2$ and $O_2$ (3, 4).

The saturated solutions of $O_3F_2$ in liquid oxygen are relatively stable when stored in darkness at 90°K. A sample maintained its pale yellow color for about 3.5 weeks. Under the influence of fluorescent light, however, the color disappeared in 2–3 days (1).

### E. EXPLOSIVENESS

Electric spark did not cause $O_3F_2$ to explode. In contact with oxidizable materials $O_3F_2$ causes burning or explosions (93).

An approximate "detonation velocity" of pure $O_3F_2$ was calculated to be about 550 m./sec. for the reaction

$$2O_3F_2(\text{liq.}) \rightarrow 3O_2(\text{gas}) + 2F_2(\text{gas});\quad \Delta H_{90°\text{K.}} = -6.94 \text{ kcal.}$$

assuming products to be perfect gases. From the preliminary experimental tests performed at 90°K., it could not be concluded, however, whether $O_3F_2$ detonates when initiated by tetryl (1).

### F. CHEMICAL PROPERTIES (46, 47, 93, 94, 96)

Trioxygen difluoride is considered to be one of the most potent oxidizers known. It is definitely more reactive than $F_2$, $OF_2$, or mixtures of $O_2$ and $F_2$. Its reactivity is demonstrated by its ability to initiate spontaneous combustion when added to organic matter, even when very diluted in liquid oxygen. When a saturated solution of $O_3F_2$ in liquid oxygen (~0.1% $O_3F_2$) is poured onto absorbent cotton, the cotton bursts into flame and explodes. When similar liquid mixtures of small amounts of $F_2$ in $O_2$ and of $O_3$ in $O_2$ are used, no visible reaction takes place. This phenomenon, which is unique for $O_3F_2$, is best explained as follows. After the liquid oxygen has evaporated, the temperature of the cotton soaked with the concentrated $O_3F_2$ increases. When the temperature rises to about 120°K., the $O_3F_2$ starts to decompose with heat evolution and initiates the reaction. When the liquid solutions of $F_2$ in $O_2$ and $O_3$ in $O_2$ are used, no spontaneous combustion occurs, since $F_2$ cannot decompose and $O_3$ evaporates completely (b.p. 161°K.), long before its decomposition temperature (~373°K.) is reached.

The addition of one drop of $O_3F_2$ to solid anhydrous ammonia (both at 90°K.) results in an instantaneous yellow-white flame, accompanied by mild explosions. When one drop of $O_3F_2$ is added to a few drops of either liquid methane or solid hydrazine at 90°K. an instantaneous, loud, sharp, powerful explosion occurs, shattering the reaction vessel. A mild explosion and bright white flame result upon contact of a drop of liquid $O_3F_2$ with red phosphorus powder at 90°K., and an instantaneous blue flame is produced upon adding liquid $O_3F_2$ to sulfur at 90°K. The addition of liquid $O_3F_2$ to powdered wood charcoal resulted immediately in a yellow flame at 90°K.

Trioxygen difluoride does not react with solid ethyl alcohol at 90°K. When removed from the liquid oxygen bath, however, the mixture bursts immediately into a blue-white flame, accompanied by mild explosions.

When liquid $O_3F_2$ comes into contact with solid bromine or iodine at 90°K. a white flash and mild explosions occur. With an 8% $O_3F_2$ solution in Freon 13, however, no reaction with iodine could be observed. A 50% solution of $O_3F_2$ cooled to 90°K. reacts visibly with $I_2$ crystals; a mild flash and gas evolution occur when iodine crystals, precooled to 195°K., are added. $IF_5$, $IF_7$, and $I_2O_5$ were found among the reaction products.

When a 5% solution of $O_3F_2$ in $CClF_3$ is mixed with pure nitryl fluoride, $NO_2F$, at 90°K., a homogeneous solution is formed. No visible reaction, gas evolution, or color change takes place. Pure $O_3F_2$ does not dissolve solid $NO_2F$ at 90°K. and does not react with it at this temperature. At 116°K., however, both substances are liquid and mix homogeneously, forming a red-brown, very fluid solution. No reaction could be noticed at 116°K., but on warming to 125°K. slow $O_2$ evolution was observed due to the decomposition of $O_3F_2$ to $O_2F_2$ and oxygen. At higher temperatures, up to 160°K., the decomposition of $O_3F_2$ proceeds faster. The formation of $N_2O_5$ that was observed may be due to a reaction of the stainless steel parts of the apparatus with $NO_2F$ (+ subsequent oxidation by oxygen fluorides).

Tetryl detonates spontaneously upon contact with $O_3F_2$ (1).

Gaseous fluorine does not react with liquid $O_3F_2$ at 77°K. When the fluorine was activated, however, by an electrical discharge of 30–60 ma. at 3000–4000 v., it reacted and was converted quantitatively to $O_2F_2$, in accord with the equation

$$2O_3F_2 + F_2 \rightarrow 3O_2F_2$$

There was no noticeable reaction between $O_3F_2$ and molecular hydrogen when the latter was pumped through the reaction tube at 77°K. in amounts of about 1.25 l./hr. (1 mm.), but when the H atoms were pumped through the reaction tube, they reacted with $O_3F_2$ forming a white solid. There was neither $O_3$ nor any other colored reaction product formation, nor was any $H_2O_4$ formed. Only HF, $H_2O$, and $H_2O_2$ were found in the reaction product.

A 1.5% solution of $O_3F_2$ in Freon 13 does not react with $KO_3$ at 90°K. At a higher temperature, $O_3F_2$ decomposes first to $O_2F_2$ then at 170°K., to $F_2$ and $O_2$. The potassium ozonide remains unchanged.

Trioxygen difluoride does not react with solid $ClF_3$ at 90°K. No reaction was observed between $O_3F_2$ and $NF_3$ at 77 and at 90°K.

A spontaneous reaction with sparks and evolution of gas was observed when liquid $O_3F_2$ was dropped into an open tube containing solid ClF cooled in a liquid oxygen bath.

At 77°K., the reaction between the solid $O_3F_2$ and solid ClF proceeds so slowly that the formation of colored reaction products was noticed *only after 5 days.* At the points of contact of reagents, violet and blue compounds formed. Their amount increased with the time. The compounds have not been identified yet, but the violet compound is very similar to $O_2ClF_3$.

The blue compound is new. It was kept at 77°K. for 25 days without noticeable decomposition. It was found that the new blue compound is not ozone. This was accomplished by extracting the reaction product with liquid $O_2$ at 77°K.; the blue compound was found to be insoluble in liquid $O_2$, while ozone is readily soluble under the same conditions.

The reaction between $O_3F_2$ and ClF dissolved in liquid oxygen at 77°K. proceeds even slower. Only 0.05 wt. % of $O_3F_2$ is soluble in liquid oxygen at 77°K., and the formation of a violet compound was noticed *only after 10 days.* At 90°K., when solid ClF, condensed on the walls of a reaction vessel, is soaked with liquid $O_3F_2$, the formation of a violet compound (or compounds) was observed after 2–3 hr.

### G. THE COMPATIBILITY OF $O_3F_2$–$O_2$ SOLUTIONS WITH VARIOUS ENGINEERING MATERIALS

The results of the compatibility tests of $O_3F_2$–$O_2$ solutions with various engineering materials, including those most frequently used in space-vehicle liquid oxygen systems, are presented in Table IV (66). They show that with the possible exception of some chlorotrifluoroethylene base materials (Halocarbon No. 11–15, Kel-F elastomer, and Kel-F alkane No. 464 oil) 0.05 or 0.10% of $O_3F_2$ does not cause liquid oxygen to react spontaneously with those materials that are employed most frequently in liquid oxygen systems.

### H. HYPERGOLIC EFFECT

In spite of the very low solubility of $O_3F_2$ in liquid oxygen, these solutions were shown to be hypergolic with most of the fuels used in rocket propellants.

A series of open-cup tests showed that an instantaneous ignition occurs at the contact of a 0.05% solution of $O_3F_2$ in liquid $O_2$ with U-DETA and with 50, 10, 5, and 1% (by volume) solutions of UDMH in JP-4. An instantaneous explosion occurred with pure UDMH. In these experiments 1–5 cm.$^3$ of $O_3F_2$ solution was poured into an aluminum cup containing 5 cm.$^3$ of fuel.

An ignition occurred with 5 cm.$^3$ of pure JP-4 after a delay of 3.4 sec., and an explosion with 10 cm.$^8$ of JP-4 after a delay of 12.4 sec (66, 89).

A series of experiments with gaseous $H_2$ and with pure liquid $O_3F_2$ or its solutions in liquid $O_2$, performed at 77 and 90°K. in a hypergolic ignition test apparatus (1), showed a hypergolic ignition in every test made at 0.25 and 0.5 atm. pressures of $H_2$. Confusing results, requiring further investigation, were obtained at 1 atm. pressure of $H_2$ (1).

Tests performed in a small-scale rocket motor (of about 20 lb. thrust) resulted in a hypergolic ignition with alcohol, JP-4, U-DETA, and hydrogen (66, 89).

These tests showed also an improved combustion stability which was evident from visual observation, high-speed photography, and chamber-pressure traces. No significant difference in specific-impulse values was obtained.

The mechanism of hypergolic ignition is assumed to be as follows. As oxygen boils from the solution, the liquid remaining becomes enriched in $O_3F_2$ and, therefore, more reactive, to the point where a spontaneous reaction occurs. The degree of reactivity is dependent on the nature of the fuel, some requiring longer times than others for ignition. This requirement can be met by proper injector design, which may depend upon motor size. With the fuel and oxidizer impinging at 45° from a two-part injector, it was found that hypergolic ignition occurred only in about half of the trials with JP-4. However, by widening the impingement angle to 90°, immediate ignition resulted in each of nine tests.

TABLE IV

COMPATIBILITY TESTS OF ENGINEERING MATERIALS WITH 0.05% $O_3F_2$ (BY WEIGHT) SOLUTION IN LIQUID OXYGEN

| Materials | Results |
|---|---|
| Metals | |
| Stainless steel No. | No appreciable reaction[a] |
| 303[b] | |
| 303 | |
| 316 | |
| 321 | |
| 347 | |
| Aluminum | |
| Copper | |
| Brass | No appreciable reaction; surface pitted on continued exposure |
| Stainless steel carpenter 20 cb[c] | No appreciable reaction |
| Titanium alloy β-120-VCA[c] | |
| Magnesium–lithium (14.1%) alloy[c] | |
| Magnesium–thorium alloy XK 31 | |
| Packing materials | |
| Kel-F elastomer (plasticized) | Delayed (50 sec.) slight reaction |
| Allpax 500 | No appreciable reaction |
| Allpax 500 (fluorolube T-80 treated) | |
| Teflon | |
| JM 76 | |
| Duroid 3400[c] | |
| JM "Lo-Flo" | |
| Polyethylene film | Delayed (60 sec.) ignition |
| Lubricants and sealants | |
| Fluorolube T-80, (T-45) | No appreciable reaction |
| Halocarbon, series 11–14 | Delayed (50 sec.) slight reaction |
| Kel-F oil, Alkane No. 464 | Delayed (50 sec.) slight reaction |
| Molykote "Z"[b] | No appreciable reaction |
| Oxylube 702[b,c] | |
| AR-1F, LOX lube | Delayed (50 sec.) slight reaction |

[a] No appreciable reaction indicates no fire, flame, or other visible evidence of reaction. [b] These samples were tested additionally by being immersed in 0.10% of $O_3F_2$–$O_2$ solution, which was cooled with liquid nitrogen for a specified time, then allowed to warm up and the solution evaporated. These samples again showed no tendency to react. [c] The residue indicated a possible reaction, although no obvious reaction took place during evaporation of solutions.

It is of interest to indicate here that in a small rocket engine at least a 35% solution of fluorine in liquid oxygen is required to get a hypergolic ignition with hydrogen (8). The 0.05% $O_3F_2$ solution offers this characteristic without the change in physical properties that results from a higher concentration of additive. The density difference between liquid oxygen and a 0.05% $O_3F_2$–$O_2$ solution is less than 0.03%. The viscosity of the solution has not been measured, but it cannot be expected that such a small concentration of $O_3F_2$ will cause a significant difference. The handling hazards, however, would be much greater with 35% $F_2$ than with 0.05% $O_3F_2$. The $O_3F_2$–$O_2$ solutions present a greater hazard upon spilling than liquid oxygen alone presents, but again much smaller than that of $F_2$–$O_2$ mixtures.

Experiments with gaseous $H_2$ and a saturated solution of $O_3F_2$ in liquid $O_2$ (both at 77°K.) carried out in a hypergolic ignition test apparatus of the Pratt and Whitney Co. showed that hypergolic ignition occurs with delays of up to 1200 msec. At 195°K. starting temperature for $H_2$, the time to ignition was shortened. The ignition delay decreased also with the increase of the chamber pressure (58).

One satisfactory run, achieved in a series of tests performed with liquid $H_2$ and a saturated solution of $O_3F_2$ in $O_2$ in a 500-lb. thrust engine utilizing a 90° injector, showed "an apparently well behaved hypergolic ignition 0.5 sec. after the full LOX injector pressure was reached" (1).

### I. METHOD OF ANALYSIS OF $O_3F_2$

$O_3F_2$ is decomposed to $F_2$ and $O_2$ by warming slowly to room temperature. The simplest way to determine fluorine in the obtained gas mixture is the classical method of H. Moissan: absorption by mercury in a gas buret. The residual gas is then analyzed for $O_2$ by any desired method (absorption in an alkaline pyrogallol solution, for example) (46).

## V. Tetraoxygen Difluoride, $O_4F_2$

The latest known member of the series, tetraoxygen difluoride, $O_4F_2$, was synthesized by Grosse, Kirshenbaum, and Streng (1960) (28, 93). Since the name oxozone has been used to denote $O_4$, $O_4F_2$ may also be called *oxozone fluoride*.

### A. PREPARATION

Tetraoxygen difluoride is produced by an electrical discharge in a $2O_2 + F_2$ gas mixture at a temperature of 60–77°K. and 5–15 mm. pressure. The electrical discharge applied is 4.5–4.8 ma. at 840–1280 v. The discharge vessel is made of Pyrex glass with copper electrodes. In form and dimensions it is similar to the discharge vessel used in the preparation of $O_3F_2$.

The composition of $O_4F_2$ was established both by (a) synthesis and (b) analysis. In a synthetic test, 355 cm.³ (at S.T.P.), of a 2.05 ± 0.03:1 $O_2/F_2$ mixture reacted at 77°K. in a discharge vessel. The gas mixture was admitted at a rate of 2.0 cm.³/min. The mixture was converted quantitatively to the solid reaction product, except for 15.4 cm.³ of gas which was pumped off periodically in order to keep the gas phase composition constant. Even if the 15.4 cm.³ is pure $O_2$, the composition of the product should equal $O_{4.00}F_{2.06}$.

Typical analyses of the gas produced from the solid product, using Moissan's absorption buret for $F_2$ and an Orsat apparatus for $O_2$, were as follows: 96.9 cm.³ contained 66.3 mole % $O_2$ and 33.7 mole % $F_2$, ratio $O_2$ $F_2$ = 1.95 ± 0.03; 55.6 cm.³ gas gave 66.5 mole % $O_2$ and 33.4 mole % $F_2$, ratio $O_2:F_2$ = 1.98 ± 0.05%. Theory for $O_4F_2$ is 2.00.

The vapor pressures of $O_3F_2$, $O_2F_2$, and $O_2$ differ widely, and $O_2$ can be pumped off easily; thus, the elementary composition, $O_4F_2$, cannot be due to dissolved $O_2$. The proof that it is *not* due to $O_3$ is more difficult. This proof was necessary, however, because $O_2$-gas alone, under the pressure, temperature, and discharge conditions, is converted into liquid $O_3$. Furthermore, liquid $O_3$ and liquid $O_3F_2$ mix homogeneously in all proportions at 90°K., and the $O_3 + 3O_3F_2$ mixture, on cooling to 77°K., forms a brown mass very similar in appearance to $O_4F_2$. Attempts to distinguish $O_4F_2$ from the $O_3 + O_3F_2$ mixtures by visible spectra could not be made because the molecular extinction coefficients for $O_3F_2$ and $O_4F_2$ were not known.

A simple means of differentiation, however, is provided by the solubility behavior in liquid $O_2$. It was found that the samples of $O_4F_2$ extracted at 77°K. gave no visible trace of $O_3$. On analysis, this particular sample, after liquid $O_2$ extraction and pumping off all $O_2$, had the composition $O_{4.00}F_{2.04}$. In contrast, the $O_3 + 3O_3F_2$ mixture prepared from pure $O_3$ and $O_3F_2$ immediately gave a deep blue extract of $O_3$ in liquid $O_2$ (28, 93).

### B. PROPERTIES

Tetraoxygen difluoride is one of the most potent oxidizers known.

At 77°K., $O_4F_2$ is a reddish brown *solid*, depositing on the walls of the discharge vessel between the electrodes. It differs in color from $O_3F_2$ and sometimes forms clusters of long needle-like brown crystals.

Tetraoxygen difluoride has a vapor pressure of less than 1 mm. at 90°K. It is liquid and stable, at least for a few hours, at 90°K., since no noticeable rise in pressure occurs. Between 90 and 110°K. it decomposes slowly into $O_3F_2$ and $O_2$, and the former at 110°K., to $O_2$ and $O_2F_2$. Since $O_2F_2$ in turn forms $O_2 + F_2$ at about 200°K., all the $O_4F_2$ is decomposed finally into $O_2$ and $F_2$ gas.

Tetraoxygen difluoride is only slightly soluble in liquid $O_2$ (pale brown solution) at 77°K., *viz.*, of the same order of magnitude as that of $O_3F_2$ (0.05 mole %) (28, 93).

## VI. Concluding Remarks

The knowledge gained during the synthesis of $O_4F_2$ suggests that under certain conditions higher members of the oxygen–fluoride series, namely, $O_5F_2$ and $O_6F_2$, should be obtainable.

The general rule in the preparation of oxygen fluorides is that the less stable the given member of the oxygen–fluoride series, the milder or more delicate must be the preparation conditions. For a synthesis in an electrical-discharge vessel, the more sensitive the oxygen fluoride compound to be prepared, the less must be the energy per time unit, the lower the temperature, and the more effective the cooling provided. The shape of the reaction vessel, its surface–volume ratio, and the wall thickness also play a very important role. The most suitable forms of the reaction vessels known are described above (for details, see ref. 47 and 94). Some investigators are using U-shape reaction vessels for the preparation of $O_2F_2$ and $O_3F_2$. This practice is not recommended because in such tubes ozone is also formed (94); it condenses on the walls and sometimes causes explosions when it mixes with the oxygen fluorides at temperatures above 120°K.

The author wishes to express his deep appreciation to his wife and assistant, Mrs. Lucia V. Streng, for help in the systematization of the material, to Dr. A. V. Grosse for advice and important suggestions, to Dr. W. F. Faragher for reading and commenting on the manuscript, and to Messrs. A. D. Kirshenbaum and C. S. Stokes for the data on the sensitivity of $O_2F_2$ and on the specific impulses of the $OF_2$–fuel systems.

This review was written in connection with the research work performed for the Office of Naval Research, Contract Nonr 3085 (01).

## VII. REFERENCES

(1) Amster, A. B., Neff, J. A., and Aitken, A. J., "Preparation and Properties of Ozone Fluoride," Final Report. Stanford Research Institute, Menlo Park, Calif., November 1, 1962.
(2) Anderson, R., Schnitzlein, J. G., Toole, R. C., and O'Brien, T. D., *J. Phys. Chem.*, **56**, 473 (1952).
(3) Aoyama, S., and Sakuraba, S., *J. Chem. Soc. Japan*, **59**, 1321 (1938).
(4) Aoyama, S., and Sakuraba, S., *J. Chem. Soc. Japan*, **62**, 208 (1941).
(5) Bernstein, H. J., and Powling, J., *J. Chem. Phys.*, **18**, 685 (1950).
(6) Boersch, H., *Monatsh. Chem.*, **65**, 311 (1935).
(7) Boersch, H., *Sitzungsber. Akad. Wiss. Wien.*, **144**, 1 (1935).
(8) Bollbuhler, R. J., and Straight, D. M., "Ignition of a Hydrogen-Oxygen Rocket Engine by Addition of Fluorine to the Oxidant," N.A.S.A. Report TN-D-1308, July, 1962. See reference 1.
(9) Bransford, J. W., Kunkel, A. C., and Jache, A. W., *J. Inorg. Nucl. Chem.*, **14**, 159 (1960).
(10) Brauer, G., "Handbuch der Preparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, 1954.
(11) Brockway, L. O., *Rev. Mod. Phys.*, **8**, 231 (1936).
(12) Brodersen, P. H., Frisch, P., and Schumacher, H. J., *Z. physik. Chem.*, **B37**, 25 (1937).
(13) Burg, A. B., "Volatile Inorganic Fluorides." "Fluorine Chemistry," Vol. 1, Simmons, J. H., Ed., Academic Press, Inc., New York, N. Y., 1950.
(14) Cady, G. H., *J. Am. Chem. Soc.*, **56**, 1431 (1934).
(15) Cady, G. H., *J. Am. Chem. Soc.*, **56**, 1647 (1934).
(16) Cady, G. H., *J. Am. Chem. Soc.*, **57**, 246 (1935).
(17) Dibeler, V. H., Reese, R. M., and Franklin, J. L., *J. Chem. Phys.*, **27**, 1296 (1957).
(18) Dodd, R. E., and Little, R., *Nature*, **188**, 737 (1960).
(19) Engelbrecht, A., and Nachbaur, E., *Monatsh. Chem.*, **90**, 367 (1959).
(20) Evans, W. H., Munson, T. R., and Wagman, D. D., *J. Res. Natl. Bur. Std.*, **55**, 147 (1955).
(21) Frisch, P., and Schumacher, H. J., *Z. physik. Chem.*, **B34**, 322 (1936).
(22) Frisch, P., and Schumacher, H. J., *Z. anorg. allgem. Chem.*, **229**, 423 (1936).
(23) Frisch, P., and Schumacher, H. J., *Z. physik. Chem.*, **B37**, 1 (1937).
(24) Frisch, P., and Schumacher, H. J., *Z. physik. Chem.*, **B37**, 18 (1937).
(25) Frisch, P., and Schumacher, H. J., *Z. Elektrochem.*, **43**, 807 (1937).
(26) Glissman, A., and Schumacher, H. J., *Z. physik. Chem.*, **B24**, 328 (1934).
(27) Gmelin, "Handbuch der Anorganischen Chemie, Fluor, System-Nummer 5," Verlag Chemie, GMBH, Weinheim, Bergstrasse, 1959.
(28) Grosse, A. V., Streng, A. G., and Kirshenbaum, A. D., *J. Am. Chem. Soc.*, **83**, 1004 (1961).
(29) Hettner, G., Pohlman, R., and Schumacher, H. J., *Z. Physik*, **96**, 203 (1935).
(30) Hettner, G., Pohlman, R., and Schumacher, H. J., *Naturwissenschaften*, **23**, 114 (1935).
(31) Hettner, G., Pohlman, R., and Schumacher, H. J., *Z. Elektrochem.*, **41**, 524 (1935).
(32) Hildebrand, J. H., and Scott, R. L., "The Solubility of Nonelectrolytes," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, p. 424.
(33) Hilton, A. P., Jr., Jache, A. W., Beal, J. B., Jr., Henderson, W. D., and Robinson, R. J., *J. Chem. Phys.*, **34**, 1137 (1961).
(34) Holzmann, R. T., and Cohen, M. S., *Inorg. Chem.*, **1**, 972 (1962).
(35) Huff, V. N., Calvert, C. S., and Erdmann, V. C., NASA Memo RM-E8117a, 1949.
(36) Huff, V. N., and Gordon, S., NASA Memo RM-E52H14, 1952; NASA Memo RM-E51L11, 1952; NASA Memo RM-E52GO9, 1952.
(37) Ibers, J. A., and Schomaker, V., *J. Phys. Chem.*, **57**, 699 (1953).
(38) Ishikawa, F., Murooka, T., and Hagisawa, H., *Bull. Inst. Phys. Chem. Res.* (Tokyo), **12**, 742 (1933).
(39) Ishikawa, F., Murooka, T., and Hagisawa, H., *Sci. Rept. Tohoku Univ.*, **23**, 431 (1934).
(40) Ishikawa, F., and Takai, T., *Sci. Rept. Tohoku Univ.*, **24**, 98 (1935).
(41) Jackson, R. H., *J. Chem. Soc.*, 4585 (1962).
(42) JANAF Thermochemical Data, 1960–1962.
(43) Jones, E. A., Kirby-Smith, J. S., Woltz, P. J. H., and Nielsen, A. H., *J. Chem. Phys.*, **19**, 337 (1951).
(44) Judge, J. F., *Missiles Rockets*, **9**, 22 (1961).
(45) Kanarek, I. A., U. S. Patent 2,968,145 (January 17, 1961).
(46) Kirshenbaum, A. D., and Grosse, A. V., *J. Am. Chem. Soc.*, **81**, 1277 (1959).
(47) Kirshenbaum, A. D., Grosse, A. V., and Aston, J. G., *J. Am. Chem. Soc.*, **81**, 6398 (1959).

(48) Kirshenbaum, A. D., and Streng, A. G., *J. Chem. Phys.*, **35**, 1440 (1961).

(49) Koblitz, W., and Schumacher, H. J., *Z. physik. Chem.*, **B25**, 283 (1934).

(50) Lagemann, R. T., *J. Chem. Phys.*, 14, 743 (1946).

(51) Lange, W., *Chem. Ztg.*, **59**, 393 (1935).

(52) Lebeau, P., and Damiens, A., *Compt. rend.*, **185**, 652 (1927).

(53) Lebeau, P., and Damiens, A., *Compt. rend.*, **188**, 1253 (1929).

(54) Leech, H. R., "Compounds of Fluorine with Oxygen," "Mellor's Comprehensive Treatis eon Inorganic and Theoretical Chemistry, Supplement II, Part I," Longmans, Green and Co., London, New York, Toronto, 1956, pp. 186–193.

(55) Maguire, R. G., ARL Technical Report 60–287, 1960.

(56) Maguire, R. G., private communication, March 30, 1962.

(57) Mann, D. J., and Smith, D. S., "Evaluation of Oxygen Difluoride as a High Energy Space Storable Propellant," paper presented at the 142nd National A.C.S. Meeting, September 9–14, 1962, Atlantic City, N. J.

(58) McAnally, W. J., III, "Hypergolic Ignition Studies," Short Memorandum Report FR-384, March, 1962, Pratt and Whitney Aircraft, Division of United Aircraft Corp. See reference 1.

(59) McKenna, F. E., "Methods of Fluorine and Fluoride Analysis," McGraw-Hill Publishing Co., New York, N. Y., 1951.

(60) Nielsen, A. H., *J. Chem. Phys.*, **19**, 379 (1951).

(61) Pauling, L., *J. Am. Chem. Soc.*, **54**, 3570 (1932).

(62) Petat, F., *Z. Elektrochem.*, 42, 85 (1936); 42, 94 (1936).

(63) Pierce, L., and Jackson, R., *J. Chem. Phys.*, **35**, 2240 (1961).

(64) Pohlman, R., and Schumacher, H. J., *Z. physik. Chem.*, **102**, 678 (1936).

(65) Potter, L. R., *J. Chem. Phys.*, **17**, 957 (1949).

(66) Riehl, W. A., Perkins, H., Stokes, C. S., and Kirshenbaum, A. D., *ARS J.*, **32**, 384 (1962).

(67) Rohzbach, G. H., and Cady, G. H., *J. Am. Chem. Soc.*, **69**, 677 (1947).

(68) Ruff, O., "Die Chemie des Fluores," Verlag von J. Springer, Berlin, 1920.

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

(70) Ruff, O., *Z. anorg. allgem. Chem.*, **197**, 273 (1931).

(71) Ruff, O., and Clusius, K., *Z. anorg. allgem. Chem.*, **190**, 267 (1930).

(72) Ruff, O., and Menzel, W., *Z. anorg. allgem. Chem.*, **190**, 257 (1930).

(73) Ruff, O., and Menzel, W., *Z. anorg. allgem. Chem.*, **198**, 39 (1931).

(74) Ruff, O., and Menzel, W., *Z. anorg. allgem. Chem.*, **198**, 375 (1931).

(75) Ruff, O., and Menzel, W., *Z. anorg. allgem. Chem.*, **229**, 423 (1932).

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

(77) Ruff, O., and Menzel, W., *Z. anorg. allgem. Chem.*, **217**, 85 (1934).

(78) Ruff, O., Menzel, W., and Neumann, W., *Z. anorg. allgem. Chem.*, **208**, 293 (1932).

(79) Ruff, O., and Zedner, J., *Ber.*, 42, 1037 (1909).

(80) Schnitzlein, J. G., Sheard, J. L., Toole, R. C., and O'Brien, T. D., *J. Phys. Chem.*, **56**, 233 (1952).

(81) Schomaker, V., and Stevenson, D. P., *J. Am. Chem. Soc.*, **63**, 37 (1941).

(82) Schumacher, H. J., *Congr. Intern. Quim. Pura Apl., 9 Madrid 1934*, **2**, 485 (1935).

(83) Schumacher, H. J., *Z. Physik*, **96**, 203 (1935).

(84) Schumacher, H. J., *An. Argent.*, **38**, 209 (1950).

(85) Schumacher, H. J., and Frisch, P., *Z. physik. Chem.*, **B37**, 1 (1937).

(86) Simons, E., Willson, T. P., and Schuman, S. C., *Natl. Nucl. Energy Ser., Div. II*, **16**, 1922 (1949).

(87) Simons, J. H., "Fluorine Chemistry," Vol. I and II, Academic Press, Inc., New York, N. Y., 1950 and 1954.

(88) Skinner, H. A., *Trans. Faraday Soc.*, 41, 645 (1945).

(88a) Solomon, I. J., "Research on Chemistry of $O_3F_2$ and $O_2F_2$," Technical Summary Reports, Nov. 8, 1962, and Feb. 13, 1963, Armour Research Foundation, Chicago, Ill.

(89) Stokes, C. S., "The Use of Ozone Fluoride as a Hypergolic Additive to Liquid Oxygen," Research Institute of Temple University, Philadelphia, Pa., March 1, 1961.

(90) Streng, A. G., *J. Am. Chem. Soc.*, **85**, 1380 (1963).

(91) Streng, A. G., "The Miscibility and Solubility of Liquified and Solidified Gases," Research Institute of Temple University, Philadelphia, Pa., 1962.

(92) Streng, A. G., and Grosse, A. V., *J. Inorg. Nucl. Chem.*, **9**, 315 (1959).

(93) Streng, A. G., and Grosse, A. V., "Addition and Substitution Compounds of Oxygen Fluorides," First Annual Progress Report for the Office of Naval Research, Contract Nonr 3085(01), Research Institute of Temple University, Philadelphia, Pa., January 3, 1961.

(94) Streng, A. G., and Grosse, A. D., "Addition and Substitution Compounds of Oxygen Fluorides," Second Annual Progress Report for the Office of Naval Research, Contract Nonr 3085(01), Research Institute of Temple University, Philadelphia, Pa., January 19, 1962.

(95) Streng, A. G., and Grosse, A. V., "Free Radicals in Inorganic Chemistry," Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p. 159.

(96) Streng, A. G., Kirshenbaum, A. D., and Grosse, A. V., Third Annual Progress Report for the Office of Naval Research, Contract Nonr 3085(01), Research Institute of Temple University, Philadelphia, Pa., January 15, 1963.

(97) Stuart, H. A., *Z. physik. Chem.*, **B36**, 155 (1937).

(98) Sutherland, G. B. B. M., and Penny, W. G., *Proc. Roy. Soc.* (London), **A156**, 678 (1936).

(99) Sutton, L. E., and Brockway, L. O., *J. Am. Chem. Soc.*, **57**, 473 (1935).

(100) Warhurst, E., *Trans. Faraday Soc.*, **45**, 461 (1949).

(101) Wartenberg, H., *Z. anorg. allgem. Chem.*, **200**, 235 (1931).

(102) Wartenberg, H., and Klinkott, G., *Z. anorg. allgem. Chem.*, **193**, 418 (1930).

(103) Wicke, E., *Nature*, **33**, 132 (1946).

(104) Willard, H. H., *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933).

(105) Willard, H. H., and Horton, C. A., *Anal. Chem.*, **22**, 1190 (1950).

(106) Willard, H. H., and Horton, C. A., *Anal. Chem.*, 24, 862 (1952).

(107) Wulfman, C. E., *J. Chem. Phys.*, **33**, 1567 (1960).

(108) Yost, D. M., *Inorg. Syn.* **1**, 109 (1939).

(109) Yost, D. M., and Hetcher, J. B., *J. Chem. Educ.*, **10**, 330 (1933).