THE OXYGEN FLUORIDES

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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.	$3.21–5.23 \times 10^{-5}$	(5)
K_α, dyne/cm.	$0.05–1.67 \times 10^{-5}$	(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. $\delta = 8.22\ (\text{cal./cc.})^{1/2}$	(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 $E_{O-F} \simeq 58$ 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 χ 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	

	cal. mole⁻¹ deg.⁻¹			
Temp., °K.	C_p^0	S^0	$-(F^0 - H_{298}^0)/T$	
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	

	kcal. mole⁻¹			
	$H^0 - H_{298}^0$	H_f^0	F_f^0	Log K_p
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: 4210 Å., 23,800 cm.⁻¹ 3580 Å., 28,000 cm.⁻¹ 2940 Å., 34,000 cm.⁻¹ 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	$10^5\epsilon$	
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 1740 929 909 840 826 461	(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	
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 $I(OF) = 13.0 \pm 0.2$ e.v.	
O^+	4.3	...	Indeterminate threshold	
F^+	0.5	...	Immeasurably small	
F^-	63	1.2 ± 0.2	$KE(F^-) = 1.3$ e.v. $KE(F^- + OF)$ 2.0 e.v. $D(FO-F) = = 2.8$ e.v., $D(O-F) = 1.1$ 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 γ-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 ± 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 Pale brown gas (dec.) Orange-red liquid at 110°K. Orange-yellow solid below 110°K.	
Molecular weight 70.000	
Molecular structure Nonplanar atomic chain, F—O—O—F	(41, 47, 55, 56)
Molecular constants Interatomic distance r(O—O) = 1.217 ± 0.003 Å. Interatomic distance r(F—O) = 1.575 ± 0.003 Å. OOF angle = 109°30′ ± 30′ Dihedral angle = 87°30′ ± 30′ Dipole moment = 1.44 ± 0.04 D.	(41)
Ground-state rotational constants and moments of inertia	

	$\mathrm{O_2{}^{16}F_2}$	$\mathrm{O^{18}O^{16}F_2}$	$\mathrm{O_2{}^{18}F_2}$
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. $K_{O-F} = 5.2 \times 10^{-5}$ $K_{O-O} = 2.9 \times 10^{-5}$	(47)
Melting point 109.7°K., −163.5°C.	(76)
Boiling point 216°K., −57°C. dec.	(76)
Vapor pressure $\log P_{mm.} = 7.515 - 1000/T$ (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 Liquid, over the temperature range of 117–186°K. $d = 2.074 - 0.00291T$ g./cc. 1.736 g./cc. at 116°K.	(77)
Molar volume 40.4 cc./mole at 116°K.	(77)
Activation energy of thermal decomposition 17.3 kcal./mole	(24, 25, 85)
Rate of thermal decomposition $\frac{-\mathrm{d}[\mathrm{O_2F_2}]}{\mathrm{d}t} = [\mathrm{O_2F_2}] \times 10^{12.4} \exp(-1700/4.57T)$ 4.3% per day at 195°K. 96.5% per day at 214.5°K. Half-life at 223°K. = 220 min., increasing sevenfold for a 10° drop of temperature	(21, 22, 24, 46, 85)
Heat of vaporization $\Delta H_{vap.} = 4.583 \pm 0.100$ kcal./mole, at 216.2°K.	(46)
Entropy of vaporization (Trouton's constant) 21.22 cal./°K. mole	
Hildebrand's solubility parameter at b.p. 9.26 (cal./cc.)$^{1/2}$	
Heat of formation (from the elements) $\Delta H_{298} = 4.73 \pm 0.30$ kcal./mole	(47)
Heat of atomization 151.5 kcal./mole	(47)
Heat of decomposition For the reaction: $\mathrm{O_2F_2}_{\text{liq.}} \rightarrow \mathrm{O_2}_{\text{gas}} + \mathrm{F_2}_{\text{gas}}$, at 190°K., $\Delta E = -1120 \pm 100$ cal./mole For the reaction: $\mathrm{O_2F_2}_{\text{gas}} \rightarrow \mathrm{O_2}_{\text{gas}} + \mathrm{F_2}_{\text{gas}}$, at 298°K., $\Delta E = -5324 \pm 300$ cal./mole	(47)
Bond energy $E_{O-O} = 62.1$ kcal./bond	(47)
Specific heat Gas, $C_v = 10 \pm 1$ cal./mole °K. (estimated) Liquid, over the temperature range of 121–186°K. $C_v = 24.5 \pm 0.7$ kcal./mole	(47)
Infrared spectrum bands, cm.$^{-1}$ 1024 628 463	(46)
Molar extinction coefficients[a] Gas, at 195°K.	(12)

28.1	at 340 mμ
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

Properties	References
Liquid, dissolved in a mixture of 23% (by volume) Freon 12 + 77% Freon 13, at 77°K.	(48, 93)

13.13	at 350 mμ
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_2 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]	
$\log P_{\text{mm.}} = 6.1343 - 675.57/T$	
(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	
3.6×10^{-5}/hr. at 77.3°K.	(46)
6.2×10^{-5}/hr. at 77.8°K.	
8.3×10^{-5}/hr. at 79.4°K.	
1.6×10^{-3}/hr. at 89.6°K.	
7.2×10^{-2}/hr. at 113.8°K.	
Heat of vaporization	
$\Delta H_{\text{vap.}} = 4.581 \pm 0.200$ 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 $(\text{cal./cc.})^{1/2}$ (10.7, at 90°K.)	
Heat of formation (from the elements)	
$\Delta H_{298} = 6.24 \pm 0.75$ kcal./mole	(47)

Properties	References
Heat of decomposition	
For the reaction:	
$O_3F_{2\,\text{liq.}} \rightarrow O_2F_{2\,\text{liq.}} + 0.5O_{2\,\text{gas}}$, at 121°K.,	(47)
$\Delta E = -2040 \pm 150$ cal./mole	
For the reaction:	
$O_3F_{2\,\text{liq.}} \rightarrow 1.5O_{2\,\text{gas}} + F_{2\,\text{gas}}$, at 121°K.,	
$\Delta E = -2160 \pm 250$ cal./mole	
For the reaction:	
$O_3F_{2\,\text{gas}} \rightarrow 1.5O_{2\,\text{gas}} + F_{2\,\text{gas}}$, at 121°K.,	
$\Delta E = -6500 \pm 450$ cal./mole	
For the reaction:	
$O_3F_{2\,\text{gas}} \rightarrow 1.5O_{2\,\text{gas}} + F_{2\,\text{gas}}$, at 298°K.,	
$\Delta E = -7130 \pm 750$ cal./mole	
Bond energy	
$E_{\text{O–O}} = 61.1$ 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 3.6×10^{-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 ($\sim$0.1% O_3F_2) is poured onto absorbent cotton, the cotton bursts into flame and explodes. When similar liquid mixtures of small amounts of F_2 in O_2 and of O_3 in O_2 are used, no visible reaction takes place. This phenomenon, which is unique for O_3F_2, is best explained as follows. After the liquid oxygen has evaporated, the temperature of the cotton soaked with the concentrated O_3F_2 increases. When the temperature rises to about 120°K., the O_3F_2 starts to decompose with heat evolution and initiates the reaction. When the liquid solutions of F_2 in O_2 and O_3 in O_2 are used, no spontaneous combustion occurs, since F_2 cannot decompose and O_3 evaporates completely (b.p. 161°K.), long before its decomposition temperature ($\sim$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.

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.

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.^{3} 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.

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 $2.05 \pm 0.03:1$ 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 $F_2 = 1.95 \pm 0.03$; 55.6 cm.^{3} gas gave 66.5 mole % O_2 and 33.4 mole % F_2, ratio $O_2:F_2 = 1.98 \pm 0.05$%. 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.

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