

## Thermodynamic Properties of Oxygen Fluoride and Chlorine Fluoride from Spectroscopic Data

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state concentration of  $4 \times 10^{12}$  fluorine atoms per cc for our rate of production of some  $4 \times 10^{12}$  atoms per cc per second. The probable mean life of 5 seconds for diffusion to the walls gives a steady state concentration of  $2 \times 10^{13}$  atoms per cc. Since it is likely that a fluorine atom would have to undergo more than one collision with a fluoride coated wall in order to react we conclude that the termolecular processes determine the steady state concentration over most of the volume of the vessel and that in either case the steady state concentration of fluorine atoms was some  $10^{12}$  atoms per cc. One might well worry about the failure to observe

exchange under these conditions. However, by application of Eq. (3), with viscosity radii and the above concentration of fluorine atoms we are forced to assume that the exchange of fluorine atoms with either HF or  $\text{F}_2$  molecules must have a free energy of activation in the sense of the Eyring rate theory of about 9 Kcal per mole. This seems not an unreasonable value. It seems likely that more intense illumination and/or slightly elevated temperatures will actually accomplish this exchange, and such an investigation would appear to offer real opportunities for studying the reaction of fluorine atoms with HF and  $\text{F}_2$  molecules.

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## Thermodynamic Properties of Oxygen Fluoride and Chlorine Fluoride from Spectroscopic Data\*

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Spectroscopic and electron diffraction data have been combined to make calculations of the free energy, entropy, and heat capacity of  $\text{OF}_2$  to the rigid rotator-harmonic oscillator approximation between  $298.16^\circ$  and  $1500^\circ\text{K}$ . The spectrum of  $\text{ClF}$  is known well enough to calculate these properties to the next approximation from  $298.16^\circ$  to  $2000^\circ\text{K}$ . Thermal data have been combined with these results to give the complete thermodynamic properties of these two fluorine compounds. It is pointed out that the accepted dissociation energy of  $\text{F}_2$  is too high, and calculations show that it must be close to 1.5 ev per molecule.

THE thermodynamic properties of fluorine compounds are difficult to measure directly because of experimental difficulties. However, in cases of gaseous compounds where spectroscopic data are adequate, these properties may be calculated by standard methods of statistical mechanics.

Oxygen fluoride was first reported by Lebeau and Damiens.<sup>1</sup> The molecule is similar to the water molecule and belongs to point group  $\text{C}_{2v}$ . Hence, it has a symmetry number  $\sigma=2$ . A triatomic asymmetric molecule has three non-degenerate fundamentals. The vibrational infra-red spectrum of  $\text{OF}_2$  has been studied by Hettner, Pohlman, and Schumacher<sup>2</sup> and the fundamentals observed by them have been reassigned by Sutherland and Penney.<sup>3</sup> The three fundamentals are  $\gamma_1=833\text{ cm}^{-1}$ ,  $\gamma_2=492\text{ cm}^{-1}$ , and  $\gamma_3=1110\text{ cm}^{-1}$ .

Although no rotational spectrum of  $\text{OF}_2$  has been observed, electron-diffraction measurements have been made which give sufficient information to allow the rotational constants to be calculated. Sutton and

Brockway<sup>4</sup> and Boersch<sup>5</sup> have made these measurements, and Brockway<sup>6</sup> has summarized these electron-diffraction experiments. He gives  $\alpha_{\text{FOF}}=100 \pm 5^\circ$  and  $r_{\text{OF}}=1.41 \pm 0.05\text{ \AA}$  for the bond angle and oxygen-fluorine distance, respectively. With these figures one calculates  $I_1=88.94 \times 10^{-40}\text{ g cm}^2$ ,  $I_2=73.59 \times 10^{-40}\text{ g cm}^2$ , and  $I_3=15.35 \times 10^{-40}\text{ g cm}^2$ . The atomic weights of oxygen and fluorine were taken as 16.000 and 19.000, respectively.<sup>7</sup> The molecule was considered to be a rigid rotator and the vibrations to be those of harmonic oscillators. The method of calculations was adapted from Mayer and Mayer;<sup>8</sup> the physical constants were those of Dumond and Cohen<sup>9</sup> and Birge.<sup>10</sup> The constant in the free energy equation is  $7.2797$  ( $R=1.98646\text{ cal.}$ ), and the second radiation constant  $C_2$  is  $1.4384_{\text{s}}$ . With these values, the thermodynamic properties of  $\text{OF}_2$  may

<sup>4</sup> L. E. Sutton and L. O. Brockway, *J. Am. Chem. Soc.* **57**, 473 (1935).

<sup>5</sup> H. Boersch, *Sitz. ber. Akad. Wiss. Wien.* **144**, 1 (1935); *Monatsch.* **65**, 311 (1935).

<sup>6</sup> L. O. Brockway, *Rev. Mod. Phys.* **8**, 231 (1936).

<sup>7</sup> Thirteenth Report of the Committee on the Atomic Weights of the International Union of Chemistry, *J. Am. Chem. Soc.* **69**, 731 (1947).

<sup>8</sup> Mayer and Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940).

<sup>9</sup> J. W. M. Dumond and E. R. Cohen, *Rev. Mod. Phys.* **20**, 82 (1948).

<sup>10</sup> Raymond T. Birge, *Rev. Mod. Phys.* **13**, 233 (1941).

\* Contribution No. 710 from the Department of Chemistry, University of Pittsburgh.

<sup>1</sup> P. Lebeau and A. Damiens, *Comptes Rendus* **185**, 652 (1927).

<sup>2</sup> Hettner, Pohlman, and Schumacher, *Zeits. f. Physik* **96**, 203 (1935).

<sup>3</sup> G. B. B. M. Sutherland and W. G. Penney, *Proc. Roy. Soc. London A* **156**, 678 (1936).

TABLE I. Thermodynamic functions of OF<sub>2</sub>.

T °K	-(F <sup>0</sup> -H <sub>0</sub> <sup>0</sup> )/T	S <sup>0</sup>	C <sub>p</sub> <sup>0</sup>
	cal./deg.mole	cal./deg.mole	cal./deg.mole
298.16	50.31	58.93	10.08
300	50.36	59.00	10.10
350	51.72	60.60	10.63
400	52.91	62.04	11.08
500	55.00	64.60	11.79
600	56.79	66.79	12.29
700	58.36	68.71	12.65
800	59.76	70.42	12.90
900	61.03	71.95	13.09
1000	62.20	73.34	13.23
1100	63.27	74.61	13.34
1200	64.26	75.77	13.42
1300	65.19	76.85	13.49
1400	66.06	77.85	13.54
1500	66.88	78.79	13.58

be calculated. The values of  $-(F^0-H_0^0)/T$ ,  $S^0$ , and  $C_p^0$  are listed in Table I. It is to be noted that these values do not include nuclear spin and that they refer to OF<sub>2</sub> in the ideal gas state at one atmosphere pressure.

If a reliable heat of formation of OF<sub>2</sub> were known, the complete thermodynamic properties of OF<sub>2</sub> would be available. Ruff and Menzel<sup>11</sup> give  $\Delta H_f = 4.6 \pm 2$  kcal., Von Wartenburg and Klinkott<sup>12</sup> give  $\Delta H_f = 11 \pm 2$  kcal., and later Von Wartenburg<sup>13</sup> gives as an average  $\Delta H_f = 9.0$  kcal. Bichowsky and Rossini<sup>14</sup> give  $\Delta H_f = 5.5$  kcal. from an analysis of these data. Thermodynamic functions of oxygen<sup>15</sup> and of fluorine,<sup>16</sup> when combined with values for OF<sub>2</sub> and the value of  $\Delta H_f$  selected by Bichowsky and Rossini, lead to  $\Delta H_0^0 = 6080$  cal./mole;  $\Delta H_{298.16}^0 = 5500$  cal./mole; and  $\Delta F_{298.16}^0 = 9720$  cal./mole. The determinations of  $\Delta H_f$  were not made at 25°C, but their accuracy is such as to make it senseless to attempt the slight correction to 25°C. These are the best figures available for the thermodynamic properties of OF<sub>2</sub>. The entropy at 298.16°K is in agreement with that given by Kelley.<sup>17</sup>

In 1928, Ruff<sup>18</sup> and co-workers reported a new compound of fluorine, ClF. The rotation-vibration spectrum has been investigated by Wahrhaftig<sup>19</sup> and the vibration spectrum by Schmitz and Schumacher.<sup>20</sup> Wahrhaftig observed the electronic transitions  ${}^3\Pi_0^+ \leftarrow {}^1\Sigma^+$  and from these transitions he has obtained values of the ground state constants. He gives  $\omega_e'' = 793.2$  cm<sup>-1</sup>,

TABLE II. Thermodynamic functions of isotopic ClF.

T °K	-(F <sup>0</sup> -H <sub>0</sub> <sup>0</sup> )/T	S <sup>0</sup>	C <sub>p</sub> <sup>0</sup>
	cal./deg.mole	cal./deg.mole	cal./deg.mole
298.16	44.904	52.045	7.672
300	44.948	52.092	7.680
350	46.056	53.292	7.895
400	47.029	54.358	8.072
500	48.684	56.189	8.348
600	50.067	57.731	8.534
700	51.259	59.057	8.666
800	52.308	60.221	8.762
900	53.246	61.257	8.836
1000	54.094	62.191	8.894
1100	54.870	63.041	8.942
1200	55.584	63.821	8.983
1300	56.245	64.542	9.019
1400	56.862	65.212	9.050
1500	57.440	65.837	9.079
1600	57.983	66.424	9.106
1700	58.496	66.977	9.130
1800	58.982	67.500	9.153
1900	59.444	67.995	9.175
2000	59.883	68.466	9.196

$\omega_e''x_e'' = 9.9$  cm<sup>-1</sup>,  $B_e'' = 0.518$  cm<sup>-1</sup>, and  $\alpha_e'' = 0.006$  cm<sup>-1</sup>. The excited state lies 19,826 cm<sup>-1</sup> above the ground state<sup>20</sup> which is non-degenerate. Schmitz and Schumacher have observed this transition and they give  $\omega_e'' = 780.4$  cm<sup>-1</sup> and  $\omega_e''x_e'' = 4$  cm<sup>-1</sup>. The difference is small and the uncertainty in the thermodynamic properties is negligible at 2000°K and is small at 298.16°K. With an uncertainty of 12.8 cm<sup>-1</sup> in  $\omega_e''$ , the probable error in the free energy is about 0.2 percent over the temperature range from 298.16 to 2000°K. The probable error in the entropy increases from 0.027 percent at 298.16°K to 0.12 percent at 2000°K, while the heat capacity may be in error by 0.15 percent at 298.16°, but the error has decreased to 0.007 percent at 2000°K. For consistency, the data of Wahrhaftig was used for both rotation and vibration.

The procedure outlined by Mayer and Mayer<sup>8</sup> for diatomic molecules was used to calculate the thermodynamic functions. The expansion of their equation 7.42 is not valid for the constants of ClF below 900°K and hence the equation was used without expansion to evaluate the correction terms for the state sum of the molecule considered as a rigid rotator and harmonic oscillator. It is to be noted that Wahrhaftig's data refer to Cl<sup>35</sup>F. The molecular constants were changed to those of Cl<sup>37</sup>F by standard methods.<sup>21</sup> The atomic weights were taken from Hahn, Flügge, and Mattauch<sup>22</sup> as were the abundances of the two isotopes of chlorine. The ratio of chemical to physical atomic weights was taken from Birge.<sup>10</sup> The thermodynamic functions were calculated for both isotopic molecules and the results mixed according to the abundance of the two molecules. The entropy of mixing was omitted. The contribution of the excited state to the state sum is negligible at

<sup>11</sup> O. Ruff and W. Menzel, *Zeits. f. anorg. u. allgem. Chem.* **190**, 257 (1930).

<sup>12</sup> H. Von Wartenburg and G. Klinkott, *Zeits. f. anorg. u. allgem. Chem.* **193**, 409 (1930).

<sup>13</sup> H. Von Wartenburg, *Zeits. f. anorg. u. allgem. Chem.* **200**, 235 (1931).

<sup>14</sup> Bichowsky and Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

<sup>15</sup> H. W. Woolley, *J. Research Nat. Bur. Standards* **40**, 163 (1948).

<sup>16</sup> G. M. Murphy and J. E. Vance, *J. Chem. Phys.* **7**, 806 (1939).

<sup>17</sup> K. K. Kelley, *Bur. Mines Bull.* **434** (1941), IX, "Entropies of Inorganic Substances."

<sup>18</sup> O. Ruff, *Zeits. f. anorg. u. allgem. Chem.* **176**, 258 (1928).

<sup>19</sup> A. Wahrhaftig, *J. Chem. Phys.* **10**, 248 (1942).

<sup>20</sup> H. Schmitz and H. Schumacher, *Zeits. f. Naturforsch.* **2a**, 358 (1947).

<sup>21</sup> Herzberg, *Molecular Spectra* (Prentice-Hall, Inc., New York, 1939).

<sup>22</sup> O. Hahn, S. Flügge, and J. Mattauch, *Physik. Zeits.* **41**, 1 (1940).

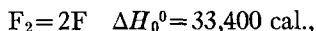
TABLE III. Molecular constants.

OF <sub>2</sub>	Cl <sup>35</sup> F
$\nu_1 = 833 \text{ cm}^{-1}$	$\omega_e = 793.2 \text{ cm}^{-1}$
$\nu_2 = 492 \text{ cm}^{-1}$	$\omega_e x_e = 9.9 \text{ cm}^{-1}$
$\nu_3 = 1100 \text{ cm}^{-1}$	$B_e = 0.518 \text{ cm}^{-1}$
	$\alpha_e = 0.006 \text{ cm}^{-1}$
$I_1 = I_2 + I_3 = 88.947 \times 10^{-40} \text{ g cm}^2$	
$I_2 = 73.592 \times 10^{-40} \text{ g cm}^2$	
$I_3 = 15.353 \times 10^{-40} \text{ g cm}^2$	

2000°K. The free energy, entropy, and heat capacity are shown in Table II. These quantities do not include nuclear spin and they refer to the hypothetical ideal gas at one atmosphere pressure.

If a reliable heat of formation of ClF were known, the complete thermodynamic properties of ClF would be known. Ruff<sup>23</sup> gives values of  $\Delta H_f$  ranging from -22 kcal. to -27.4 kcal. Bichowsky and Rossini<sup>14</sup> reviewed these data and they give  $\Delta H_f = -25.7$  kcal. Schmitz and Schumacher<sup>24</sup> give a more recent value of  $\Delta H_f = -15 \pm .5$  kcal./mole. This determination did not involve the formation of HF but that of NaF(s), and as the work of Schmitz and Schumacher on the heat of formation of NaF(s) is in accord with that of Von Wartenburg and Fitzner,<sup>25</sup> the  $\Delta H_f$  of ClF was taken as -15.0 kcal. This heat of formation was obtained at 18°C, but was used at 25°C without correction because of the uncertainty of 500 cal. which would make any such correction worthless. The thermodynamic functions of Cl<sub>2</sub> were taken from Giauque and Overstreet<sup>26</sup> and those of F<sub>2</sub> from Murphy and Vance.<sup>16</sup> These lead to the values of  $\Delta H_0^0 = -15,000$  cal./mole,  $\Delta H_{298.16}^0 = -15,000$  cal./mole, and  $\Delta F_{298.16}^0 = -15,330$  cal./mole.

Both Wahrhaftig<sup>19</sup> and Schmitz and Schumacher<sup>20</sup> report the dissociation energy of ClF. If the products of dissociation are Cl(<sup>2</sup>P<sub>3/2</sub>) and F(<sup>2</sup>P<sub>3/2</sub>), then  $\Delta H_0^0$  for the dissociation of ClF into normal atoms is 60.31 kcal./mole. The dissociation energy of Cl<sub>2</sub> into normal atoms is 2.481 ev according to Herzberg.<sup>21</sup> Hence the dissociation energy for the reaction



or the dissociation energy of F<sub>2</sub> into normal atoms would be 1.45 ev. If the heat of formation given by Bichowsky and Rossini<sup>14</sup> for ClF is used, the dissociation energy of F<sub>2</sub> would be 0.52 ev. If the products of dissociation of

ClF are both normal atoms, then the dissociation energy of F<sub>2</sub> would be raised to 1.55 ev. On the other hand, if the products of dissociation of ClF are two excited atoms, or if only the chlorine is excited, the dissociation energy of F<sub>2</sub> would be smaller. Schmitz and Schumacher<sup>20</sup> give 21,257 cm<sup>-1</sup> for the predissociation limit of ClF, and this gives an upper limiting value of the dissociation energy of ClF. This is still too low to raise the dissociation energy of F<sub>2</sub> to a value such as 2.8 ev given by Herzberg.<sup>21</sup>

If the heat of dissociation of HF into atoms were known, another path would be available from which the dissociation energy of F<sub>2</sub> could be obtained. (This has been considered by Murphy and Vance.<sup>16</sup>) Kirkpatrick and Salant<sup>27</sup> have estimated the dissociation energy of HF to be 140,000 cal./mole from their values of  $\omega_e$  and  $\omega_e x_e$ , assuming a Morse function. Usually a Morse function gives an upper limiting value to the true dissociation energy. Combining this value with the heat of dissociation of HF into molecules<sup>16</sup> and with the dissociation energy of H<sub>2</sub>,<sup>28</sup> one finds 2.08 ev for the dissociation energy of F<sub>2</sub>. If the calculation is reversed assuming the heat of dissociation of F<sub>2</sub> obtained from the ClF data (33,400 cal./mole), one obtains 132,500 cal./mole for the dissociation energy of HF into atoms.

The dissociation energy of F<sub>2</sub> from the two paths is 1.45 ev and 2.08 ev, and both of these are smaller than the corresponding value for chlorine and they bracket the dissociation energy of bromine. It has been assumed in the past that the dissociation energy of F<sub>2</sub> is greater than that of chlorine, but in view of the irregular behavior of the first row elements, it is not inconceivable that these values may be closer to the true value of the heat of dissociation of F<sub>2</sub> than the value 2.75 ev selected by Murphy and Vance.<sup>16</sup>

In order to obtain a heat of dissociation of F<sub>2</sub>, of the order of magnitude that Herzberg<sup>21</sup> and Murphy and Vance<sup>16</sup> quote, it would be necessary to have the heat of formation of ClF close to zero. Unless Schmitz and Schumacher<sup>24</sup> made some gross error in their heat of formation of ClF, or unless the spectrum of ClF has been misinterpreted, it is apparent that the heat of dissociation of F<sub>2</sub> is smaller than hitherto thought. Until another path is investigated, it seems that the best value for the heat of dissociation of F<sub>2</sub> is 1.5 ev.

The thermodynamic functions of OF<sub>2</sub>(g) and ClF(g) in the ideal gas state are presented in Tables I and II, respectively, while the molecular constants used are collected in Table III. The standard entropy of OF<sub>2</sub>(g) can be taken as  $S_{298.16}^0 = 58.9 \pm 0.2 \text{ E.U.}$ ; and the standard entropy of ClF(g) can be taken as  $S_{298.16}^0 = 52.05 \pm 0.01 \text{ E.U.}$

<sup>27</sup> D. E. Kirkpatrick and E. O. Salant, Phys. Rev. **48**, 945 (1935).

<sup>28</sup> H. Beutler, Zeits. f. physik. Chemie **B29**, 315 (1935).

<sup>23</sup> O. Ruff, Zeits. f. angew. Chem. **42**, 806 (1929); O. Ruff and F. Laass, Zeits. f. anorg. u. allgem. Chem. **183**, 214 (1929); O. Ruff and W. Menzel, *ibid.* **198**, 375 (1931).

<sup>24</sup> H. Schmitz and H. Schumacher, Zeits. f. Naturforsch. **2a**, 362 (1947).

<sup>25</sup> H. Von Wartenburg and O. Fitzner, Zeits. f. anorg. u. allgem. Chem. **151**, 313 (1926).

<sup>26</sup> W. F. Giauque and R. Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).