

Thermodynamic Properties of Dioxygen Difluoride (O₂F₂) and Dioxygen Fluoride (O₂F)

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Recent spectroscopic and chemical kinetic studies have provided sufficient data for construction of reliable thermodynamic tables for both dioxygen difluoride (O₂F₂; Chemical Abstracts Registry Number, 7783-44-0) and dioxygen fluoride (O₂F; Chemical Abstracts Registry Number, 15499-23-7). This paper contains those tables for these species in both SI units (0.1 MPa standard state) and cal K mol units (1.0 atm standard state). The experimental basis includes three recent assignments of the fundamental vibrational frequencies for O₂F₂, a new set of rotational constants for O₂F, an enthalpy change for dissociation of O₂F, and an updated standard enthalpy of formation for O₂F₂.

Key words: oxygen fluoride; dioxygen difluoride; dioxygen fluoride; entropy; enthalpy of formation; heat capacity; Gibbs energy function; equilibrium constant; spectroscopic constants; thermochemical functions.

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1. Introduction

The *JANAF Thermochemical Tables*¹ have a listing for the thermochemical properties of O₂F, but not for O₂F₂. Additional thermodynamic and spectroscopic data relating to both of these species has recently become available. These new data make possible the calculation of a thermochemical table for O₂F₂ and a more reliable table for O₂F. Furthermore, interest in these species as fluorinating agents is growing. Accurate thermochemical properties are desirable for the development of techniques for synthesis of the oxygen fluorides and for their use in fluorination procedures.

The experimental quantities required for calculation of the thermochemical properties are the enthalpy of formation at some temperature, the fundamental vibrational frequen-

cies, the three rotational constants, and the degeneracies and energies of electronic states. This information is now available for both of these species.

The procedures used were to take the experimental quantities mentioned above and calculate the thermochemical properties for a range of temperatures by using the statistical mechanics methods described in the introduction to the *JANAF tables*.¹ The temperatures and properties are the same as those in the 1985 *JANAF* edition. The calculations are for the gas phase. Earlier *JANAF* editions and most thermochemical data are based on a standard state pressure of 1.0 atm with the energy unit being the caloric. The third edition¹ changed the standard state pressure to 0.1 MPa with all quantities in SI units. I have included two tables for each species. One of these is in SI units and the other is in cal K mol atm units.

Both species are nonlinear polyatomic molecules. I have followed the *JANAF* assumptions: (i) an ideal gas equation of state; (ii) rigid rotator and high-temperature limit for properties derived from the rotational spectroscop-

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ic constants; (iii) harmonic oscillator for all properties derived from molecular vibrations.

2. Experimental Basis for Calculations

2.1. Heat Capacity and Entropy for O₂F₂

Table 1 shows the spectroscopic constants necessary for calculation of the heat capacity and entropy for O₂F₂. Three recent assignments²⁻⁴ of the fundamental vibrational frequencies for O₂F₂ all agree to within a few percent. The assignment taken from gas-phase spectra² is the one used for calculation of the thermochemical quantities because some distortion of the vibrational frequencies occurs in condensed phases.^{3,4} The gas-phase assignment still, however, agrees well with both the assignment from the matrix-isolation study³ and the one from condensed-phase Raman spectra.⁴ The latter also has a complete vibrational analysis with experimental spectra of three isotopic forms of the molecule. Because of the excellent agreement among the three assignments, thermochemical quantities such as entropy calculated from any of the assignments agree to within better than 0.2% (0.04% at 298.15%). Table 1 shows all three assignments. The assignments from Refs. 3 and 4 are in parenthesis.

The structure^{5,6} of O₂F₂ is a nonlinear FOOF chain with an OOF angle of 109°30', a dihedral angle of 87°30', an O-O bond length of 1.217 Å, and an F-O bond length of

1.575 Å. The molecular point group is C₂. The ground-electronic-state symmetry number (σ) follows from the published structure,⁶ and Ref. 5 gives the degeneracy (g_0). The published⁷⁻¹⁰ absorption spectra of O₂F₂ indicate no electronic states at energies below the dissociation energy of the molecule. Therefore, inclusion of excited electronic states in the partition functions was not necessary.

2.2. Heat Capacity and Entropy for O₂F

Measurements since the JANAF tables have resulted in minor changes in some of the spectroscopic constants necessary for calculation of thermodynamic functions related to heat capacity and entropy. Table 2 shows the spectroscopic constants used in the JANAF Tables and in this work.

The JANAF tables used the vibrational frequencies obtained by Pimentel's^{13,14} group in matrix-isolation studies. Arkell¹⁵ also measured the spectrum in a cryogenic matrix. One additional matrix-isolation study³ and two gas-phase studies^{11,12} since the JANAF entry have refined these frequencies somewhat. I have used the gas-phase values where available. One of these papers¹² is a diode-laser spectrum of O₂F. This gave precise values of the rotational constants and hence, the moments of inertia for the molecule. These also differ somewhat from those used in the JANAF entry. The structure¹² of the molecule is that of a bent FOO triatomic with a bond angle of 111.2°, an O-O bond length of 1.20 Å, and an F-O bond length of 1.649 Å. The molecular point

Table 1. Spectroscopic Constants for O₂F₂

Constant	Values	Ref.
ν_1^a	1210 (1250, 1281) cm ⁻¹	2, (3, 4)
ν_2	625 (612, 607)	
ν_3	350 (366, 373)	
ν_4	202 (195, 197)	
ν_5	614 (627, 623)	
ν_6	471 (466, 461)	
I_A	4.1409x10 ⁻³⁹ g cm ²	5, 6
I_B	1.6747x10 ⁻³⁸ g cm ²	5, 6
I_C	1.9247x10 ⁻³⁸ g cm ²	5, 6
$I_A I_B I_C$	1.3348x10 ⁻¹¹⁴ g ³ cm ⁶	5
g_0	1	5
σ	2	5

^a The first number is from Ref. 2. The numbers in parenthesis are from Refs. 3 and 4.

Table 2. Spectroscopic Constants for O₂F

	JANAF	Current Values	Ref.
ν_1	1495.0	1490.0 cm ⁻¹	11
ν_2	584.5	579.3 cm ⁻¹	12
ν_3	376.0	376.0 cm ⁻¹	3, 13
I_A	1.1104x10 ⁻³⁹ g cm ²	1.0688x10 ⁻³⁹ g cm ²	12
I_B	7.8188x10 ⁻³⁹ g cm ²	8.3810x10 ⁻³⁹ g cm ²	12
I_C	8.9292x10 ⁻³⁹ g cm ²	9.4775x10 ⁻³⁹ g cm ²	12
$I_A I_B I_C$	7.7523x10 ⁻¹¹⁶ g ³ cm ⁶	8.4896x10 ⁻¹¹⁶ g ³ cm ⁶	12
g_0	2	2	1
σ	1	1	1

group is C_s. The ground state degeneracy (g_0), and the symmetry number (σ) are those used in the JANAF tables.

The published^{10,16} absorption spectra of O₂F indicate no electronic states at energies below the dissociation energy of the molecule. Therefore, inclusion of excited electronic states in the partition functions was not necessary.

2.3. Enthalpy of Formation for O₂F₂

A critical measurement for calculation of the thermodynamic functions for both O₂F and O₂F₂ is the standard enthalpy of formation of O₂F₂ by Kirshenbaum *et al.*¹⁷ These authors made a calorimetric measurement at 190 K for decomposition of O₂F₂ into O₂ and F₂. Conversion of that measurement from 190 K to the standard enthalpy of formation at 298 K required knowledge of the difference in constant-volume heat capacity between the reactant (O₂F₂) and the products (O₂ and F₂). The authors assumed that difference to be zero over the entire range. With the published¹ heat capacities for fluorine and oxygen, plus that for O₂F₂ reported here, we find that the average heat capacity difference over the 190 to 298 K temperature range to be 1.41 cal K⁻¹ mol⁻¹. The standard heat of formation that Kirshenbaum *et al.*¹⁷ reported was

$$\Delta_f H^0(\text{O}_2\text{F}_2, 298.15) = +4.73 \pm 0.30 \text{ kcal/mol}, \quad (1)$$

with the heat-capacity correction it becomes

$$\Delta_f H^0(\text{O}_2\text{F}_2, 298.15) = +4.58 \pm 0.20 \text{ kcal/mol}, \quad (2)$$

I used this value for the enthalpy-related functions for both of the species.

2.4. Enthalpy of Formation for O₂F

The JANAF value of the enthalpy of formation of gas-phase O₂F at 298.15 K is based on two experimental results, neither of which was a direct measurement of the enthalpy of formation.

The first result is the activation energy of 17.3 kcal/mol that Schumacher and Frisch¹⁸ obtained for the decomposition of O₂F₂. The most likely rate-limiting step for this decomposition is



Levy and Copeland¹⁹ assumed that the reverse of Reaction (3) has no activation energy, which gave 17.3 kcal/mol for the enthalpy change for this reaction.

The second experimental result is the measurement¹⁷ of the heat of formation for O₂F₂ that was discussed in the previous section [Eqs. (1) and (2)]. Levy and Copeland¹⁹ used the initial value [Eq. (1)], along with the heat of formation for atomic fluorine and the above enthalpy change for Reaction (3) to obtain

$$\Delta_f H^0(\text{O}_2\text{F}, 298.15) = +3.5 \text{ kcal/mol}, \quad (4)$$

Another approach¹ was to assume that Reaction (3) has half the enthalpy change of the dissociation to oxygen plus two fluorine atoms. This assumption, with Eq. (1), gave

$$\Delta_f H^0(\text{O}_2\text{F}, 298.15) = +2.4 \text{ kcal/mol}. \quad (5)$$

The JANAF authors used this information [Eqs. (4) and (5)] to conclude that

$$\Delta_f H^0(\text{O}_2\text{F}, 298.15) = +3 \pm 5 \text{ kcal/mol}. \quad (6)$$

Information since the JANAF compilation includes an enthalpy change for the reaction



of

$$\Delta H^0(298.15) = -13.48 \pm 0.33 \text{ kcal/mol}, \quad (8)$$

that Lyman and Holland²⁰ obtained. They obtained this value by using the expression for the equilibrium constant

$$\begin{aligned} K_{\text{eq}}(T) &= k_f/k_r \\ &= RT \exp[-\Delta S^0(T)/R + \Delta H^0(T)/RT]. \end{aligned} \quad (9)$$

All of the quantities in this expression were known but the enthalpy change $[\Delta H^0(T)]$. They had measured the ratio of the rate constants for the forward (k_f) and reverse (k_r) of Reaction (7) at 298 K (1.1×10^{-15} molecules⁻¹ cm³). The published¹ entropies of the reactants and products gave the entropy change $[\Delta S^0(T)]$ for the reaction at the same temperature. These quantities, with Eq. (9), gave the enthalpy change for Reaction (7), which in turn gave²⁰

$$\Delta_f H^0(\text{O}_2\text{F}, 298.15) = +5.49 \pm 0.40 \text{ kcal/mol}, \quad (10)$$

for the standard enthalpy of formation of O₂F. The O–F bond is by far the weaker of the two bonds in O₂F. From this work and the JANAF Tables¹ the O–O bond strength is 80 kcal/mol.

Preliminary analysis²¹ of experiments similar to those described in Ref. 20 gave another value for the enthalpy of formation for O₂F. These were direct measurements of the temperature dependence of the forward and reverse rates of Reaction (7). The enthalpy change for Reaction (7) derived from these experiments was

$$\Delta H^0(298.15) = -13.2 \text{ kcal/mol}. \quad (11)$$

With this value we obtain

$$\Delta_f H^0(\text{O}_2\text{F}, 298.15) = +5.77 \text{ kcal/mol}, \quad (12)$$

The measured^{11,22} activation energy for Reaction (7) is -1.8 kcal/mol (-1.7 kcal/mol for Ref. 23). Derivation of Eq. (11) required the assumption that the reverse of Reaction (3) had that same activation energy. One would expect a small, negative activation energy for this type of recombination reaction. Note that Levy and Copeland¹⁹ assumed that that activation energy was zero. If we assume that the activation energy for the reverse of Reaction (3) is -1.8 kcal/mol, use Eq. (2) for the standard enthalpy of formation for O₂F₂, and use the slightly modified¹ formation enthalpies for fluorine and oxygen, then Eq. (4) becomes

$$\Delta_f H^0(\text{O}_2\text{F}, 298.15) = +5.16 \text{ kcal/mol}, \quad (13)$$

These three values [Eqs. (10), (12), and (13)] of the standard enthalpy of formation for O₂F all fall within the 0.4 kcal/mol of Eq. (10). Their mean gives the value used to calculate the tables,

$$\Delta_f H^0(\text{O}_2\text{F}, 298.15) = +5.47 \pm 0.40 \text{ kcal/mol}, \quad (14)$$

This is somewhat greater than the JANAF value [Eq. (6)], but it is still well within the stated error limits.

3. Thermochemical Tables for O₂F₂ and O₂F

Tables 3–6 are the thermochemical tables for O₂F₂ (Tables 3,4) and for O₂F (Tables 5,6) over the temperature range of 0 to 6000 K. Tables 3 and 5 are for an enthalpy reference temperature (T_r) of 298.15 K and a standard state pressure (p_0) of 0.1 MPa. The units for C_p^0 , S^0 , and $-[G^0 - H^0(T_r)]/T$ are J K⁻¹ mol⁻¹, and kJ mol⁻¹ for $H^0 - H^0(T_r)$, $\Delta_f H^0$, and $\Delta_f G^0$. The quantity $\text{Log } K_f$ is the base-10 logarithm of the equilibrium constant. The last three columns are all relative to the elements (F₂ and O₂) in their standard states.¹

For convenience in working with older data sets Tables 4 and 6 tabulate the thermochemical quantities for a standard state pressure (p_0) of 1.0 atm. The units for C_p^0 , S^0 , and $-[G^0 - H^0(T_r)]/T$ are cal K⁻¹ mol⁻¹ (Gibbs mol⁻¹), and kcal mol⁻¹ for $H^0 - H^0(T_r)$, $\Delta_f H^0$, and $\Delta_f G^0$.

The differences between the values in Table 5 and those in the JANAF tables¹ are very minor for C_p^0 , S^0 , and $-[G^0 - H^0(T_r)]/T$ and $H^0 - H^0(T_r)$. For example S^0 is about 0.5 J K⁻¹ mol⁻¹ higher in Table 5 than in the JANAF Tables over the entire temperature range. These small differences reflect the minor changes in the spectroscopic constants (Table 2). The differences for $\Delta_f H^0$, $\Delta_f G^0$, and $\text{Log } K_f$ are somewhat greater. The values in Table 5 for $\Delta_f H^0$ and $\Delta_f G^0$ exceed those in the JANAF Tables by about 10 kJ mol⁻¹. These differences reflect the change in the enthalpy of formation for O₂F.

4. Conclusions

The thermochemical properties in this paper are a significant improvement over what was previously available. The lack of spectroscopic data for O₂F₂ until recently had prevented calculation of properties for that species. The three published sets of vibrational frequencies agree to within a few percent. This agreement gives high confidence in the entropy and heat capacity for O₂F₂. The standard enthalpy of formation for O₂F₂ is based on a direct measurement. The minor adjustment made here removes the main uncertainty in the measurement.

The most significant uncertainty in the JANAF tables for O₂F was in the enthalpy of formation. Two additional experiments and a re-evaluation of a third have reduced the uncertainty in the standard enthalpy of formation for O₂F by an order of magnitude. Changes in the spectroscopic constants for O₂F were minor.

This pair of oxygen fluorides is somewhat unique. The corresponding chlorides are possible analogs, but the monochloride has a different structure¹ (C_{2v}) and the dichloride has not been studied sufficiently for comparison. The dinitrogen difluoride molecule exists as a stable species in both a *cis* and *trans* forms.¹ The nitrogen compound is more stable than the corresponding oxide. Isomerization of the nitrogen compound occurs more rapidly than dissociation (isomerization activation energy¹ = 27.5 kcal/mol). The nitrogen difluoride does, however, have a higher heat of formation

Table 3. Dioxygen Difluoride (O₂F₂), Ideal Gas

Enthalpy Ref. Temp. = 298.15 K		Standard State Pres. = 0.1 MPa					
-----J K ⁻¹ mol ⁻¹ -----		-----kJ mol ⁻¹ -----					
T/K	C _p ^o	S ^o	-[G ^o -H ^o (T _r)]/T	H ^o -H ^o (T _r)	Δ _f H ^o	Δ _f G ^o	Log K _f
0	0.	0.	INFINITE	-13.803	22.868	22.868	INFINITE
100	39.558	222.863	325.879	-10.302	20.558	32.640	-17.049
200	52.759	254.411	282.778	-5.673	19.346	45.292	-11.829
250	58.065	266.775	278.367	-2.898	19.161	51.803	-10.824
298.15	62.155	277.365	277.365	0.000	19.163	58.092	-10.177
300	62.294	277.750	277.366	0.115	19.166	58.277	-10.147
350	65.656	287.615	278.138	3.317	19.302	64.853	-9.679
400	68.347	296.564	279.890	6.670	19.530	71.342	-9.316
450	70.518	304.744	282.204	10.143	19.819	77.806	-9.031
500	72.283	312.268	284.839	13.715	20.150	84.232	-8.800
600	74.925	325.696	290.557	21.083	20.886	96.980	-8.443
700	76.753	337.391	296.430	28.673	21.668	109.600	-8.178
800	78.056	347.730	302.209	36.417	22.467	122.109	-7.973
900	79.011	356.981	307.790	44.272	23.262	134.514	-7.807
1000	79.726	365.345	313.134	52.211	24.049	146.834	-7.670
1100	80.275	372.970	318.232	60.212	24.822	159.076	-7.554
1200	80.704	379.974	323.089	68.262	25.577	171.247	-7.454
1300	81.046	386.448	327.717	76.350	26.312	183.356	-7.367
1400	81.321	392.464	332.129	84.469	27.029	195.412	-7.291
1500	81.546	398.083	336.341	92.613	27.718	207.413	-7.223
1600	81.732	403.352	340.366	100.777	28.387	219.369	-7.162
1700	81.888	408.312	344.219	108.958	29.031	231.286	-7.106
1800	82.020	412.996	347.911	117.154	29.651	243.166	-7.056
1900	82.132	417.434	351.454	125.361	30.247	255.012	-7.011
2000	82.228	421.649	354.859	133.580	30.822	266.828	-6.969
2100	82.312	425.663	358.136	141.807	31.376	278.614	-6.930
2200	82.384	429.494	361.293	150.042	31.914	290.373	-6.894
2300	82.448	433.157	364.339	158.283	32.437	302.111	-6.861
2400	82.503	436.667	367.280	166.531	32.948	313.826	-6.830
2500	82.553	440.036	370.123	174.784	33.451	325.515	-6.801
2600	82.597	443.275	372.875	183.041	33.950	337.190	-6.774
2700	82.636	446.393	375.540	191.303	34.449	348.845	-6.749
2800	82.671	449.399	378.125	199.568	34.948	360.479	-6.725
2900	82.703	452.301	380.633	207.837	35.455	372.097	-6.702
3000	82.732	455.105	383.068	216.109	35.969	383.696	-6.681
3100	82.758	457.818	385.436	224.383	36.492	395.277	-6.660
3200	82.781	460.446	387.739	232.660	37.029	406.841	-6.641
3300	82.803	462.993	389.981	240.939	37.581	418.393	-6.623
3400	82.822	465.466	392.165	249.221	38.150	429.920	-6.605
3500	82.840	467.867	394.294	257.504	38.739	441.436	-6.588
3600	82.857	470.201	396.370	265.789	39.345	452.933	-6.572
3700	82.872	472.471	398.397	274.075	39.973	464.415	-6.556
3800	82.886	474.681	400.375	282.363	40.622	475.877	-6.541
3900	82.899	476.834	402.308	290.652	41.293	487.327	-6.527
4000	82.911	478.933	404.198	298.943	41.986	498.752	-6.513
4100	82.922	480.981	406.045	307.234	42.699	510.162	-6.499
4200	82.933	482.979	407.853	315.527	43.437	521.556	-6.486
4300	82.942	484.931	409.623	323.821	44.196	532.931	-6.474
4400	82.951	486.837	411.357	332.116	44.975	544.285	-6.461
4500	82.960	488.702	413.055	340.411	45.777	555.624	-6.449
4600	82.968	490.525	414.719	348.708	46.597	566.944	-6.438
4700	82.975	492.310	416.351	357.005	47.438	578.249	-6.426
4800	82.982	494.056	417.952	365.303	48.296	589.532	-6.415
4900	82.988	495.768	419.522	373.601	49.173	600.797	-6.404
5000	82.995	497.444	421.064	381.900	50.065	612.049	-6.394
5100	83.000	499.088	422.578	390.200	50.972	623.279	-6.384
5200	83.006	500.700	424.065	398.500	51.893	634.493	-6.373
5300	83.011	502.281	425.526	406.801	52.826	645.685	-6.364
5400	83.016	503.832	426.962	415.102	53.769	656.866	-6.354
5500	83.020	505.356	428.373	423.404	54.723	668.024	-6.344
5600	83.025	506.852	429.761	431.707	55.683	679.173	-6.335
5700	83.029	508.321	431.127	440.009	56.650	690.295	-6.326
5800	83.033	509.765	432.470	448.312	57.620	701.401	-6.317
5900	83.037	511.185	433.792	456.616	58.595	712.488	-6.308
6000	83.040	512.580	435.094	464.920	59.568	723.563	-6.299

Table 4. Dioxygen Difluoride (O₂F₂), Ideal Gas, cal-K-mol units

T/K	Enthalpy Ref. Temp. -298.15 K			Standard State Pres. -1.0 atm			
	C _p ⁰	S ⁰	-[G ⁰ -H ⁰ (T _r)]/T	H ⁰ -H ⁰ (T _r)	Δ _f H ⁰	Δ _f G ⁰	Log K _f
0	0.	0.	INFINITE	-3.299	5.466	5.466	INFINITE
100	9.455	53.239	77.861	-2.462	4.914	7.798	-17.043
200	12.610	60.779	67.559	-1.356	4.624	10.820	-11.823
250	13.878	63.735	66.505	-0.693	4.580	12.375	-10.818
298.15	14.855	66.266	66.266	0.000	4.580	13.877	-10.172
300	14.889	66.358	66.266	0.028	4.581	13.921	-10.141
350	15.692	68.715	66.450	0.793	4.613	15.491	-9.673
400	16.335	70.854	66.869	1.594	4.668	17.041	-9.310
450	16.854	72.809	67.422	2.424	4.737	18.584	-9.026
500	17.276	74.608	68.052	3.278	4.816	20.119	-8.794
600	17.907	77.817	69.419	5.039	4.992	23.163	-8.437
700	18.344	80.612	70.822	6.853	5.179	26.177	-8.173
800	18.656	83.083	72.204	8.704	5.370	29.164	-7.967
900	18.884	85.294	73.537	10.581	5.560	32.126	-7.801
1000	19.055	87.293	74.815	12.479	5.748	35.068	-7.664
1100	19.186	89.116	76.033	14.391	5.933	37.991	-7.548
1200	19.289	90.790	77.194	16.315	6.113	40.898	-7.448
1300	19.370	92.337	78.300	18.248	6.289	43.789	-7.362
1400	19.436	93.775	79.355	20.189	6.460	46.668	-7.285
1500	19.490	95.118	80.361	22.135	6.625	49.534	-7.217
1600	19.535	96.377	81.323	24.086	6.785	52.389	-7.156
1700	19.572	97.563	82.244	26.042	6.939	55.234	-7.101
1800	19.603	98.682	83.126	28.000	7.087	58.071	-7.051
1900	19.630	99.743	83.973	29.962	7.229	60.900	-7.005
2000	19.653	100.750	84.787	31.926	7.367	63.721	-6.963
2100	19.673	101.710	85.570	33.893	7.499	66.535	-6.924
2200	19.690	102.625	86.325	35.861	7.628	69.343	-6.889
2300	19.705	103.501	87.053	37.831	7.753	72.146	-6.855
2400	19.719	104.340	87.756	39.802	7.875	74.943	-6.824
2500	19.731	105.145	88.435	41.774	7.995	77.735	-6.795
2600	19.741	105.919	89.093	43.748	8.114	80.522	-6.768
2700	19.751	106.664	89.730	45.722	8.233	83.305	-6.743
2800	19.759	107.383	90.348	47.698	8.353	86.083	-6.719
2900	19.766	108.076	90.947	49.674	8.474	88.857	-6.696
3000	19.773	108.746	91.529	51.651	8.597	91.627	-6.675
3100	19.780	109.395	92.095	53.629	8.722	94.392	-6.655
3200	19.785	110.023	92.646	55.607	8.850	97.154	-6.635
3300	19.790	110.632	93.182	57.586	8.982	99.912	-6.617
3400	19.795	111.223	93.704	59.565	9.118	102.664	-6.599
3500	19.799	111.797	94.212	61.545	9.259	105.414	-6.582
3600	19.803	112.354	94.709	63.525	9.404	108.159	-6.566
3700	19.807	112.897	95.193	65.506	9.554	110.901	-6.551
3800	19.810	113.425	95.666	67.486	9.709	113.638	-6.536
3900	19.813	113.940	96.128	69.468	9.869	116.372	-6.521
4000	19.816	114.442	96.579	71.449	10.035	119.100	-6.507
4100	19.819	114.931	97.021	73.431	10.205	121.824	-6.494
4200	19.821	115.409	97.453	75.413	10.382	124.545	-6.481
4300	19.824	115.875	97.876	77.395	10.563	127.261	-6.468
4400	19.826	116.331	98.290	79.378	10.749	129.972	-6.456
4500	19.828	116.776	98.696	81.360	10.941	132.680	-6.444
4600	19.830	117.212	99.094	83.343	11.137	135.383	-6.432
4700	19.831	117.639	99.484	85.326	11.338	138.082	-6.421
4800	19.833	118.056	99.867	87.309	11.543	140.776	-6.410
4900	19.835	118.465	100.242	89.293	11.753	143.466	-6.399
5000	19.836	118.866	100.611	91.276	11.966	146.152	-6.388
5100	19.838	119.259	100.972	93.260	12.183	148.834	-6.378
5200	19.839	119.644	101.328	95.244	12.403	151.511	-6.368
5300	19.840	120.022	101.677	97.228	12.626	154.184	-6.358
5400	19.841	120.393	102.020	99.212	12.851	156.854	-6.348
5500	19.842	120.757	102.357	101.196	13.079	159.518	-6.339
5600	19.843	121.114	102.689	103.180	13.309	162.180	-6.329
5700	19.844	121.466	103.016	105.165	13.540	164.835	-6.320
5800	19.845	121.811	103.337	107.149	13.772	167.487	-6.311
5900	19.846	122.150	103.653	109.134	14.004	170.134	-6.302
6000	19.847	122.483	103.964	111.118	14.237	172.779	-6.293

Table 5. Dioxygen Fluoride (O₂F), Ideal Gas

Enthalpy Ref. Temp. = 298.15 K		Standard State Pres. = 0.1 MPa					
-----J K ⁻¹ mol ⁻¹ -----		-----kJ mol ⁻¹ -----					
T/K	C _p ⁰	S ⁰	-[G ⁰ -H ⁰ (T _r)]/T	H ⁰ -H ⁰ (T _r)	Δ _r H ⁰	Δ _r G ⁰	Log K _r
0	0.	0.	INFINITE	-11.256	24.726	24.726	INFINITE
100	34.494	216.955	296.034	-7.908	23.717	27.870	-14.558
200	40.259	242.614	263.475	-4.172	23.077	32.316	-8.440
250	42.625	251.862	260.253	-2.098	22.942	34.643	-7.238
298.15	44.449	259.531	259.531	0.000	22.886	36.903	-6.465
300	44.512	259.806	259.532	0.082	22.886	36.961	-6.435
350	46.073	266.788	260.079	2.348	22.880	39.341	-5.871
400	47.408	273.029	261.315	4.686	22.909	41.690	-5.444
450	48.572	278.682	262.935	7.086	22.957	44.037	-5.112
500	49.595	283.854	264.772	9.541	23.022	46.376	-4.845
600	51.282	293.052	268.738	14.588	23.173	51.033	-4.443
700	52.582	301.059	272.795	19.784	23.338	55.663	-4.154
800	53.584	308.148	276.780	25.095	23.508	60.270	-3.935
900	54.360	314.506	280.624	30.494	23.673	64.854	-3.764
1000	54.969	320.266	284.305	35.961	23.834	69.421	-3.626
1100	55.450	325.529	287.817	41.483	23.987	73.973	-3.513
1200	55.837	330.371	291.164	47.048	24.130	78.511	-3.417
1300	56.150	334.853	294.354	52.648	24.262	83.037	-3.336
1400	56.406	339.024	297.398	58.276	24.383	87.556	-3.267
1500	56.619	342.923	300.304	63.928	24.486	92.062	-3.206
1600	56.797	346.583	303.083	69.599	24.576	96.564	-3.152
1700	56.947	350.031	305.745	75.286	24.649	101.060	-3.105
1800	57.075	353.289	308.296	80.987	24.705	105.554	-3.063
1900	57.184	356.378	310.746	86.701	24.742	110.045	-3.025
2000	57.279	359.314	313.102	92.424	24.763	114.535	-2.991
2100	57.361	362.110	315.369	98.156	24.765	119.023	-2.960
2200	57.433	364.780	317.555	103.896	24.753	123.511	-2.932
2300	57.496	367.335	319.664	109.642	24.724	128.001	-2.907
2400	57.551	369.783	321.702	115.395	24.682	132.493	-2.884
2500	57.601	372.133	323.672	121.152	24.627	136.984	-2.862
2600	57.645	374.393	325.580	126.914	24.562	141.482	-2.842
2700	57.684	376.570	327.429	132.681	24.488	145.980	-2.824
2800	57.719	378.668	329.221	138.451	24.407	150.481	-2.807
2900	57.751	380.694	330.961	144.225	24.321	154.986	-2.792
3000	57.780	382.652	332.652	150.001	24.230	159.493	-2.777
3100	57.806	384.547	334.296	155.781	24.136	164.002	-2.763
3200	57.830	386.383	335.895	161.562	24.040	168.514	-2.751
3300	57.852	388.163	337.452	167.347	23.946	173.033	-2.739
3400	57.872	389.890	338.969	173.133	23.852	177.550	-2.728
3500	57.890	391.568	340.448	178.921	23.761	182.073	-2.717
3600	57.907	393.199	341.891	184.711	23.672	186.597	-2.707
3700	57.922	394.786	343.299	190.502	23.587	191.125	-2.698
3800	57.937	396.331	344.674	196.295	23.506	195.655	-2.689
3900	57.950	397.836	346.018	202.090	23.430	200.189	-2.681
4000	57.962	399.303	347.332	207.885	23.359	204.720	-2.673
4100	57.973	400.735	348.617	213.682	23.292	209.254	-2.666
4200	57.984	402.132	349.875	219.480	23.232	213.792	-2.659
4300	57.994	403.496	351.106	225.279	23.177	218.330	-2.652
4400	58.003	404.829	352.312	231.079	23.126	222.867	-2.646
4500	58.012	406.133	353.493	236.879	23.081	227.406	-2.640
4600	58.020	407.408	354.651	242.681	23.039	231.947	-2.634
4700	58.027	408.656	355.787	248.483	23.003	236.491	-2.628
4800	58.034	409.878	356.901	254.286	22.968	241.031	-2.623
4900	58.041	411.074	357.995	260.090	22.937	245.574	-2.618
5000	58.047	412.247	359.068	265.894	22.907	250.119	-2.613
5100	58.053	413.397	360.122	271.700	22.879	254.666	-2.608
5200	58.059	414.524	361.158	277.505	22.851	259.209	-2.604
5300	58.064	415.630	362.175	283.311	22.822	263.755	-2.599
5400	58.069	416.715	363.175	289.118	22.790	268.302	-2.595
5500	58.074	417.781	364.158	294.925	22.756	272.847	-2.591
5600	58.078	418.827	365.125	300.733	22.717	277.401	-2.587
5700	58.083	419.855	366.076	306.541	22.673	281.947	-2.584
5800	58.087	420.865	367.012	312.349	22.621	286.495	-2.580
5900	58.090	421.858	367.933	318.158	22.562	291.041	-2.577
6000	58.094	422.835	368.840	323.967	22.492	295.592	-2.573

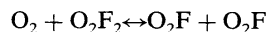
Table 6. Dioxygen Fluoride (O₂F), Ideal Gas, cal-K-mol units

Enthalpy Ref. Temp.=298.15 K				Standard State Pres.=1.0 atm			
----cal K ⁻¹ mol ⁻¹ -----				-----kcal mol ⁻¹ -----			
T/K	C _p ^o	S ^o	-[G ^o -H ^o (T _r)]/T	H ^o -H ^o (T _r)	Δ _f H ^o	Δ _f G ^o	Log K _f
0	0.	0.	INFINITE	-2.690	5.910	5.910	INFINITE
100	8.244	51.827	70.728	-1.890	5.668	6.660	-14.555
200	9.622	57.960	62.946	-0.997	5.515	7.721	-8.437
250	10.188	60.170	62.176	-0.501	5.483	8.277	-7.235
298.15	10.624	62.003	62.003	0.000	5.470	8.816	-6.462
300	10.639	62.069	62.003	0.020	5.470	8.830	-6.433
350	11.012	63.738	62.134	0.561	5.468	9.398	-5.868
400	11.331	65.229	62.430	1.120	5.475	9.959	-5.441
450	11.609	66.580	62.817	1.694	5.487	10.519	-5.109
500	11.853	67.816	63.256	2.280	5.502	11.078	-4.842
600	12.257	70.015	64.204	3.487	5.538	12.189	-4.440
700	12.567	71.929	65.174	4.729	5.578	13.295	-4.151
800	12.807	73.623	66.126	5.998	5.618	14.394	-3.932
900	12.992	75.143	67.045	7.288	5.658	15.489	-3.761
1000	13.138	76.519	67.924	8.595	5.696	16.579	-3.623
1100	13.253	77.777	68.764	9.915	5.733	17.666	-3.510
1200	13.345	78.934	69.564	11.245	5.767	18.749	-3.415
1300	13.420	80.006	70.326	12.583	5.799	19.829	-3.334
1400	13.481	81.002	71.054	13.928	5.828	20.908	-3.264
1500	13.532	81.934	71.748	15.279	5.852	21.984	-3.203
1600	13.575	82.809	72.413	16.635	5.874	23.058	-3.150
1700	13.611	83.633	73.049	17.994	5.891	24.132	-3.102
1800	13.641	84.412	73.658	19.356	5.905	25.205	-3.060
1900	13.667	85.150	74.244	20.722	5.913	26.277	-3.022
2000	13.690	85.852	74.807	22.090	5.918	27.348	-2.988
2100	13.710	86.520	75.349	23.460	5.919	28.420	-2.958
2200	13.727	87.158	75.871	24.832	5.916	29.491	-2.930
2300	13.742	87.769	76.375	26.205	5.909	30.563	-2.904
2400	13.755	88.354	76.862	27.580	5.899	31.635	-2.881
2500	13.767	88.916	77.333	28.956	5.886	32.707	-2.859
2600	13.777	89.456	77.789	30.333	5.870	33.781	-2.840
2700	13.787	89.976	78.231	31.712	5.853	34.855	-2.821
2800	13.795	90.478	78.660	33.091	5.833	35.929	-2.804
2900	13.803	90.962	79.076	34.471	5.813	37.005	-2.789
3000	13.810	91.430	79.480	35.851	5.791	38.080	-2.774
3100	13.816	91.883	79.872	37.232	5.769	39.157	-2.761
3200	13.822	92.322	80.255	38.614	5.746	40.234	-2.748
3300	13.827	92.747	80.627	39.997	5.723	41.313	-2.736
3400	13.832	93.160	80.989	41.380	5.701	42.391	-2.725
3500	13.836	93.561	81.343	42.763	5.679	43.471	-2.714
3600	13.840	93.951	81.688	44.147	5.658	44.551	-2.705
3700	13.844	94.330	82.024	45.531	5.637	45.632	-2.695
3800	13.847	94.699	82.353	46.916	5.618	46.713	-2.687
3900	13.850	95.059	82.674	48.301	5.600	47.795	-2.678
4000	13.853	95.410	82.988	49.686	5.583	48.877	-2.670
4100	13.856	95.752	83.295	51.071	5.567	49.959	-2.663
4200	13.859	96.086	83.596	52.457	5.553	51.043	-2.656
4300	13.861	96.412	83.890	53.843	5.539	52.126	-2.649
4400	13.863	96.730	84.178	55.229	5.527	53.209	-2.643
4500	13.865	97.042	84.461	56.615	5.517	54.292	-2.637
4600	13.867	97.347	84.738	58.002	5.507	55.377	-2.631
4700	13.869	97.645	85.009	59.389	5.498	56.461	-2.625
4800	13.871	97.937	85.275	60.776	5.490	57.545	-2.620
4900	13.872	98.223	85.537	62.163	5.482	58.629	-2.615
5000	13.874	98.503	85.793	63.550	5.475	59.715	-2.610
5100	13.875	98.778	86.045	64.938	5.468	60.800	-2.605
5200	13.876	99.047	86.293	66.325	5.462	61.885	-2.601
5300	13.878	99.312	86.536	67.713	5.455	62.970	-2.597
5400	13.879	99.571	86.775	69.101	5.447	64.055	-2.592
5500	13.880	99.826	87.010	70.489	5.439	65.140	-2.588
5600	13.881	100.076	87.241	71.877	5.430	66.227	-2.585
5700	13.882	100.322	87.468	73.265	5.419	67.312	-2.581
5800	13.883	100.563	87.692	74.653	5.406	68.398	-2.577
5900	13.884	100.800	87.912	76.042	5.392	69.483	-2.574
6000	13.885	101.034	88.129	77.430	5.376	70.570	-2.570

than the oxygen difluoride by about 11 kcal/mol for the *cis* isomer and about 15 kcal/mol for the *trans* isomer.

Note added in proof

Recent experimental evidence (K. D. Abney, P. G. Eller, M. P. Eastman, W. H. Woodruff, C. F. Pace, S. A. Kinkead, and R. J. Kissane, unpublished data) suggests that the values for $\Delta_f H^0(T)$ [and $\Delta_f G^0(T)$] for O_2F_2 in this paper are low by 5.65 kJ mol^{-1} ($1.35 \text{ kcal mol}^{-1}$). The basis of this conclusion is an experimental study of the equilibrium



at 297 K. The discrepancy may be due to errors in the calorimetric study of Ref. 6, to errors in the enthalpy of formation of O_2F , or to the lack of attainment of equilibrium. Adjustment of the thermochemical tables is probably premature at this point. The authors are continuing their research over a range of temperatures. Analysis of these data will help resolve the discrepancy.

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6. References

- ¹M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, "JANAF Thermochemical Tables, Third Edition," J. Phys. Chem. Ref. Data Suppl. 1 **14**, (1985).
- ²K. C. Kim and G. M. Campbell, J. Mol. Struct. **129**, 263 (1985).
- ³M. E. Jacox, J. Mol. Spectrosc. **84**, 74 (1980).
- ⁴W. H. Woodruff, E. M. Larson, B. I. Swanson, S. A. Kinkead, L. H. Jones, and P. G. Eller, "Raman Spectroscopic studies of $F^{16}O^{16}OF$, $F^{18}O^{18}OF$, and $F^{18}O^{16}OF$," paper presented at the American Chemical Society National Meeting, Denver, CO, April 1987.
- ⁵A. G. Streng, Chem. Rev. **63**, 607 (1963).
- ⁶R. H. Jackson, J. Chem. Soc. **1962**, 4585.
- ⁷P. H. Brodersen, P. Frisch, and H. J. Schumacher, Z. phys. Chem. Abt. B **37**, 25 (1937).
- ⁸A. D. Kirshenbaum and A. G. Streng, J. Chem. Phys. **35**, 1440 (1961).
- ⁹A. G. Streng and L. V. Streng, J. Phys. Chem. **69**, 1079 (1965).
- ¹⁰N. M. Matchuk, V. I. Tupikov, A. I. Malkova, and S. Ya. Pshchetskii, Opt. Spectrosc. (USSR) **40**, 7 (1976).
- ¹¹K. C. Kim and G. M. Campbell, Chem. Phys. Lett. **116**, 236 (1985).
- ¹²C. Yamada and E. Hirota, J. Chem. Phys. **80**, 4694 (1984).
- ¹³P. N. Noble and G. C. Pimentel, J. Chem. Phys. **44**, 3641 (1966).
- ¹⁴R. D. Spratley, J. J. Turner, and G. C. Pimentel, J. Chem. Phys. **44**, 2063 (1966).
- ¹⁵A. Arkell, J. Amer. Chem. Soc. **87**, 4057 (1965).
- ¹⁶A. Glissman and H. J. Schumacher, Z. physik. Chem. Abt. B **24**, 328 (1934).
- ¹⁷A. D. Kirshenbaum, A. V. Grosse, and J. G. Aston, J. Am. Chem. Soc. **81**, 6398 (1959).
- ¹⁸H. J. Schumacher and P. Frisch, Z. physik. Chem. Abt. B **37**, 1 (1937).
- ¹⁹J. B. Levy and B. K. W. Copeland, J. Phys. Chem. **69**, 408 (1965).
- ²⁰J. L. Lyman and R. Holland, "Oxygen Fluoride Chemical Kinetics," J. Phys. Chem. **92**, 7232 (1988).
- ²¹R. Holland, G. L. Loge, and J. L. Lyman (unpublished).
- ²²N. F. Shamonima and A. G. Kotov, Kinet. Katal. **20**, 233 (1979).
- ²³P. P. Chegodaev, V. I. Tupikov, E. G. Strukov, and S. Ya. Pshchetskii, Khim. Vys. Energ. **12**, 116 (1978).