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THE THERMODYNAMIC PROPERTIES OF SOME CHALCOGEN FLUORIDES

by

P. A. G. O'Hare

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Chemistry

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9700 South Cass Avenue
Argonne, Illinois 60439

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P. A. G. O'Hare

Chemical Engineering Division

July 1968

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GLOSSARY OF TERMS

GLOSSARY OF TERMS

P = pressure (atm or Torr)

V = gas volume

T = temperature in °K (in vapor-pressure tables, T is in °C)

t = temperature in °C

$(G^\circ - H_0^\circ)/T$ = Gibbs energy function

$(H^\circ - H_0^\circ)/T$ = enthalpy function

S° = standard entropy

C_p° = standard heat capacity at constant pressure (1 atm)

ΔHf = enthalpy of formation

ΔGf = Gibbs energy of formation

Kf = equilibrium constant of formation ($e^{-\Delta Gf/RT}$)

ΔHv° = standard enthalpy of vaporization

ΔHm° = standard enthalpy of melting (fusion)

ΔHs° = standard enthalpy of sublimation (= $\Delta Hv^\circ + \Delta Hm^\circ$)

ΔHa° = standard enthalpy of atomization

$D(A\text{-}B)$ = dissociation energy of the bond A-B

$E(A\text{-}B)$ = bond-energy term for the bond A-B

$k(A\text{-}B)$ = stretching-force constant of the bond A-B (in dyne cm^{-1})

M = molecular weight

σ = symmetry number

$r(A\text{-}B)$ = length of the bond A-B (in Ångstrom units)

I = moment of inertia (diatomic molecule)

$I_A I_B I_C$ = product of principal moments of inertia (polyatomic molecule)

β = $2.799076 \times 10^{-39}/I$

ω = fundamental wave number of harmonic oscillator (in cm^{-1})

Z = ground-state quantum weight

Z = 2 for OF, SF, SeF, TeF, SF_5, SeF_5 and TeF_5

Z = 1 for all other molecules dealt with in this report

(g) = gaseous state

(l) = liquid state

(c) = crystalline or solid state

u = $(1.43879/T)\,\omega$

THE THERMODYNAMIC PROPERTIES OF SOME CHALCOGEN FLUORIDES

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P. A. G. O'Hare

ABSTRACT

Physical and thermodynamic data are presented for 24 gaseous fluorides of the oxygen-group elements. Data are also included for the liquid and solid states where enthalpies of vaporization and fusion are available. The thermodynamic functions $-(G^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, S°, C_p°, $H^\circ - H_{298}^\circ$, ΔHf, ΔGf, and log Kf are tabulated from 0 to 2000°K.

I. INTRODUCTION

For many of the simple fluorides of the oxygen (chalcogen) group, thermodynamic data are sparse and in many cases nonexistent. The need for thermodynamic and structural information on many simple molecules containing selenium, tellurium, and polonium was emphasized by Bagnall.[1]

This report represents an initial effort to respond to this need. Many values in the present report are estimated, and an attempt has been made to attach meaningful uncertainties to them. In most instances, the accuracy of the data do not warrant five or six significant figures, but the tables were set up in this way for the sake of convenience.

II. CALCULATIONS

The thermodynamic functions C_p°, S°, $-(G^\circ - H_0^\circ)/T$, and $(H^\circ - H_0^\circ)/T$ for the chalcogen fluorides in the ideal gas state were obtained by means of the rigid-rotator, harmonic-oscillator approximation[2] over the range 0-2000°K. A computer program (see appendix) was used to calculate the functions according to the equations[2] shown in Table I and to derive values for $H^\circ - H_{298}^\circ$, ΔHf, ΔGf, and log Kf. Where appropriate enthalpies of vaporization and fusion were available, thermodynamic functions for the liquid and solid states were also computed. (The computer program is also able to fit a polynomial equation to the high-temperature enthalpy data over the range 298.15-2000°K.) Tables of vapor pressure versus temperature are included for the chalcogen fluorides whose vapor pressures have been measured.

TABLE I. Equations for Thermodynamic Functions of Ideal Gaseous Chalcogen Fluorides

Translation Plus Rotation

Diatomic Molecules

$C_p^\circ = 6.955079 + 0.0914148(\beta/T)^2$

$(H^\circ - H_0^\circ)/T = 6.955079 - 0.953038(\beta/T) - 0.0914148(\beta/T)^2$

$-(G^\circ - H_0^\circ)/T = 6.863426 \log M + 11.439043 \log T - 4.575617 \log (\beta\sigma/T) + 0.953038(\beta/T) + 0.0457074(\beta/T)^2 - 8.005804$

$S^\circ = 6.863426 \log M + 11.439043 \log T - 4.575617 \log (\beta\sigma/T) - 0.0457074(\beta/T)^2 - 1.050725$

Nonlinear Polyatomic Molecules

$C_p^\circ = 7.948662$

$(H^\circ - H_0^\circ)/T = 7.948662$

$-(G^\circ - H_0^\circ)/T = 6.863426 \log M + 18.302469 \log T - 4.575617 \log \sigma + 2.287809 \log (I_A I_B I_C \times 10^{117}) - 10.297926$

$S^\circ = 6.863426 \log M + 18.302469 \log T - 4.575617 \log \sigma + 2.287809 \log (I_A I_B I_C \times 10^{117}) - 2.349265$

Vibration (All Molecules)

$C_p^\circ = 1.98717u^2e^{-u}/(1 - e^{-u})^2$

$(H^\circ - H_0^\circ)/T = 1.98717ue^{-u}/(1 - e^{-u})$

$-(G^\circ - H_0^\circ)/T = -4.575617 \log (1 - e^{-u})$

$S^\circ = 1.98717ue^{-u}/(1 - e^{-u}) - 4.575617 \log (1 - e^{-u})$

Electronic (All Molecules)

$-(G^\circ - H_0^\circ)/T = S^\circ = R \ln Z$

All molecular weights used in the calculations are based on the 1961 Table of Atomic Weights. Additional constants and auxiliary thermodynamic data are listed in Tables II and III.

Unless otherwise noted, thermochemical data given in the text refer to 298.15°K (25°C).

TABLE II. Constants Used in the Calculations[3]

Constant	Symbol	Value
Ice point	0°C	273.15°K
Thermochemical calorie	cal	4.1840 abs J
Velocity of light in vacuo	c	2.997925×10^{10} cm sec^{-1}
Avogadro number	N_A	6.02252×10^{23} mol^{-1}
Planck constant	h	6.6256×10^{-27} erg sec
Gas constant	R	1.98717 cal deg^{-1} mol^{-1}
Boltzmann constant	k	1.38054×10^{-16} erg deg^{-1}

TABLE III. Auxiliary Thermodynamic Data Used in the Calculations

M	$\Delta Hf°(M_2,g)$, kcal mol^{-1}	$D°(M_2,g)$, kcal mol^{-1}	$\Delta Hf°(M,g)$,[a] kcal mol^{-1}
O	0	119.12[4]	59.6
F	0	37.72[4]	18.9
S	30.68[3]	101.2[5]	65.9
Se	34.90[3]	75.7[6]	55.3
Te	40.20[3]	60.85[5]	50.5

[a] $\Delta Hf°(M,g) = \frac{1}{2}[D°(M_2,g) + \Delta Hf°(M_2,g)]$.

III. PROPERTIES OF CHALCOGEN FLUORIDES

A. Sulfur Fluorides

1. SF_6 Gas

a. Compressibility. MacCormack and Schneider[7] measured the compressibility of SF_6 from 0 to 250°C at pressures up to 50 atm. The following equation is applicable at 273.15°K:

$$PV \text{ (Amagat units)} = 1.015317 - 15.114 \times 10^{-3}P - 20.25 \times 10^{5}P^{2} - 6.81 \times 10^{-7}P^{4}.$$

b. Virial Coefficients. The values in Table IV for the second (B) and third (C) virial coefficients in the relationship $V[(PV/RT) - 1] = B + C/V\ldots$ are taken from Clegg *et al.*[8]

TABLE IV. Virial Coefficients for $SF_6(g)$

t, °C	34.19	49.86	74.86	97.18	131.3
B, $cm^3\ mol^{-1}$(a)	-259	-230	-191	-164	-131
C, $cm^6\ mol^{-2}$(a)	19,920	18,710	15,720	13,910	12,390

(a) Other values for B and C have been given by MacCormack and Schneider[7] and by Hamann *et al.*[9]

c. Critical-state Properties. The critical-state properties (P_c, t_c, V_c) have been extensively investigated. Table V summarizes the best modern values.

TABLE V. Critical-state Properties for $SF_6(g)$

P_c, atm	t_c, °C	V_c, cm^3	ρ_c, g cm^{-3}	Ref.
36.76	45.5	-	0.727	10
38.27	45.55	-	-	11
37.10	45.58	199	-	8
37.113	45.547	200	-	7

d. Thermochemical Data. For the reactions

(1) $S(rh) + 3F_2(g) \rightarrow SF_6(g)$:[12]

$\Delta Ef° = -290.59 \pm 0.24$ kcal mol^{-1};

$\Delta Hf° = -291.77 \pm 0.24$ kcal mol^{-1};

$\Delta Sf° = -83.36$ cal deg^{-1} mol^{-1};

$\Delta Gf° = -266.92$ kcal mol^{-1};

$\log Kf° = 195.6$.

(2) $\frac{1}{2}S_2(g) + 3F_2(g) \rightarrow SF_6(g)$:

$\Delta Hf = -307.11 \pm 0.25$ kcal mol^{-1}.

Additional thermodynamic functions calculated by statistical mechanical methods are given in Table VI.

e. Data Used in the Statistical Calculations

$M = 146.0544$.

$r(S-F) = 1.564 \pm 0.010$ Å.[13]

Symmetry $= O_h$;[13] $\sigma = 24$.[13]

$I_A I_B I_C = 29{,}405 \times 10^{-117}$ g^3 cm^6.

$\omega = 775, 644(2), 947(3), 615(3), 524(3)$, and $354(3)$ cm^{-1}.[14]

2. SF_6 Liquid

a. Vapor Pressure. The vapor pressure of liquid SF_6 from 0 to 45.58°C is represented by the following equation:[8]

$\log P$ (atm) $= 4.38846 - 899.46/T$.

The vapor pressures calculated from this equation are given in Table VII.

TABLE VI. Thermodynamic Properties of Sulfur Hexafluoride

T (DEG.K.)	$-(G^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	45.112	8.1716	53.283	9.1942
200.00	51.330	10.3572	61.688	16.3807
273.15	54.900	12.6988	67.599	21.6277
298.15	56.047	13.5116	69.559	23.1303
300.00	56.131	13.5712	69.702	23.2353
400.00	60.460	16.5993	77.060	27.7859
500.00	64.447	19.1455	83.593	30.6574
600.00	68.128	21.2291	89.357	32.5074
700.00	71.533	22.9342	94.467	33.7439
800.00	74.690	24.3422	99.033	34.6016
900.00	77.627	25.5181	103.145	35.2169
1000.00	80.369	26.5118	106.881	35.6714
1100.00	82.937	27.3608	110.297	36.0157
1200.00	85.349	28.0936	113.443	36.2823
1300.00	87.624	28.7319	116.356	36.4927
1400.00	89.774	29.2925	119.067	36.6615
1500.00	91.812	29.7885	121.601	36.7988
1600.00	93.749	30.2303	123.979	36.9121
1700.00	95.594	30.6262	126.220	37.0065
1800.00	97.355	30.9829	128.338	37.0859
1900.00	99.039	31.3060	130.345	37.1535
2000.00	100.652	31.5998	132.252	37.2114

T (DEG.K.)	$(H^\circ - H^\circ_{298})$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG K_f
0.00	-4.0285	303.74	303.74	INF
100.00	-3.2113	305.35	296.14	647.22
200.00	-1.9570	306.55	286.41	312.98
273.15	-0.5598	307.03	279.07	223.28
298.15	0.0000	307.11	276.39	202.60
300.00	0.0429	307.12	276.20	201.21
400.00	2.6113	307.26	265.86	145.26
500.00	5.5443	307.16	255.52	111.69
600.00	8.7090	306.91	245.22	89.32
700.00	12.0255	306.58	234.96	73.36
800.00	15.4453	306.19	224.76	61.40
900.00	18.9378	305.77	214.60	52.11
1000.00	22.4833	305.32	204.50	44.69
1100.00	26.0684	304.85	194.44	38.63
1200.00	29.6839	304.37	184.42	33.59
1300.00	33.3230	303.89	174.44	29.33
1400.00	36.9810	303.40	164.50	25.68
1500.00	40.6543	302.90	154.60	22.52
1600.00	44.3400	302.41	144.73	19.77
1700.00	48.0361	301.92	134.88	17.34
1800.00	51.7408	301.43	125.08	15.19
1900.00	55.4529	300.94	115.29	13.26
2000.00	59.1712	300.45	105.53	11.53

TABLE VII. Vapor Pressure of Liquid Sulfur Hexafluoride

T(C)	P(TORR)	LOGP(TORR)	1/T(K)
0,00	12.46	1,09554	3.661-003
2,00	13.17	1,11948	3.634-003
4,00	13.90	1,14307	3.608-003
6,00	14.67	1,16632	3.582-003
8,00	15.46	1,18924	3.557-003
10,00	16.29	1,21184	3.532-003
12,00	17.14	1,23412	3.507-003
14,00	18.03	1,25609	3.483-003
16,00	18.96	1,27776	3.458-003
18,00	19.91	1,29912	3.435-003
20,00	20.90	1,32020	3.411-003
22,00	21.93	1,34099	3.388-003
24,00	22.99	1,36150	3.365-003
26,00	24.08	1,38174	3.343-003
28,00	25.22	1,40171	3.321-003
30,00	26.39	1,42141	3.299-003
32,00	27.60	1,44086	3.277-003
34,00	28.84	1,46005	3.256-003
36,00	30.13	1,47900	3.235-003
38,00	31.46	1,49770	3.214-003
40,00	32.82	1,51616	3.193-003
42,00	34.23	1,53439	3.173-003
44,00	35.68	1,55239	3.153-003

b. Thermochemical Data. For the reactions

(1) $SF_6(l) \rightarrow SF_6(g)$:

$\Delta Hv^\circ = 4.1$ kcal mol^{-1};[15]

$\Delta Sv^\circ = 19.58$ cal deg^{-1} mol^{-1}.

(2) $S(rh) + 3F_2(g) \rightarrow SF_6(l)$:

$\Delta Hf^\circ = -295.87 \pm 0.3$ kcal mol^{-1}.

3. SF_6 Crystal

a. Sublimation Point. -63.8°C.[16]

b. Melting Point. -50.65 ± 0.2°C.[17]

c. Vapor Pressure. The following vapor pressure-temperature relationships give calculated results in reasonable agreement with each other:

$$\log P\ (\text{Torr}) = -1224.8/T + 8.7360;^{18} \quad (1)$$

$$\log P\ (\text{Torr}) = -1231.3/T + 8.7648;^{19} \quad (2)$$

$$\log P\ (\text{Torr}) = -624.69/T + 2.78753 + 0.014731T.^{20} \quad (3)$$

Equation 2 was arbitrarily chosen to generate the data (from -100 to -64°C) in Table VIII.

d. Thermochemical Data

(1) Heat Capacity. Eucken and Schröder[21] measured the heat capacity of SF_6 from 13 to 230°K. The smoothed results are given in Table IX.

(2) Enthalpy of Fusion. 1.390 kcal mol^{-1}.[19]

(3) Enthalpy of Sublimation. 5.46 kcal mol^{-1}.[15]

(4) For the reaction

$S(rh) + 3F_2(g) \rightarrow SF_6(c)$:

$\Delta Hf^\circ = -297.23 \pm 0.41$ kcal mol^{-1}.

TABLE VIII. Vapor Pressure of Solid Sulfur Hexafluoride

T(C)	P(TORR)	LOGP(TORR)	1/T(K)
-100,00	45,04	1,65362	5.775-003
-98,00	54,30	1,73483	5.709-003
-96,00	65,19	1,81419	5.645-003
-94,00	77,95	1,89179	5.582-003
-92,00	92,83	1,96767	5.520-003
-90,00	110,13	2,04190	5.460-003
-88,00	130,17	2,11452	5.401-003
-86,00	153,32	2,18559	5.343-003
-84,00	179,95	2,25515	5.287-003
-82,00	210,50	2,32326	5.231-003
-80,00	245,45	2,38996	5.177-003
-78,00	285,30	2,45529	5.124-003
-76,00	330,60	2,51930	5.072-003
-74,00	381,96	2,58202	5.021-003
-72,00	440,05	2,64350	4.971-003
-70,00	505,55	2,70376	4.922-003
-68,00	579,23	2,76285	4.874-003
-66,00	661.91	2,82080	4.827-003
-64,00	754,46	2,87764	4.781-003

TABLE IX. Heat Capacity of SF_6 from 13 to 230°K

T, °K	C_p°, cal deg^{-1} mol^{-1}	T, °K	C_p°, cal deg^{-1} mol^{-1}	T, °K	C_p°, cal deg^{-1} mol^{-1}
13	2.68	65	12.94	140	17.06
15	3.47	70	13.39	150	17.96
20	5.41	75	13.90	160	18.95
25	7.09	80	14.49	170	20.11
30	8.41	85	15.22	180	21.43
35	9.42	90	16.15	190	22.98
40	10.26	95	13.63	200	24.88
45	10.93	100	13.94	210	27.85
50	11.52	110	14.65	220	44.0
55	12.03	120	15.40	225	26.50
60	12.51	130	16.20	230	28.56

4. SF_5 Gas

a. Thermochemical Data. The sulfur pentafluoride free radical is a product of the dissociation of SF_6. For the electron-impact reaction,

$$SF_6(g) + e^- \rightarrow SF_5(g) + F^-,$$

Curran[22] measured the kinetic energy, $\phi_{kin} = 0.23 \pm 0.05$ eV, and the F^- appearance potential,

$$A_0(F^-) = 0^{+0.05}_{-0.00} \text{ eV}.$$

These values, combined with the electron-affinity value $E_a(F) = 3.448 \pm 0.005$ eV (Ref. 23) and the plausible assumption that the internal excitation energy of the SF_5 fragment is small, yield D_1, the primary bond-dissociation energy in SF_6:

$$D_1 = D(SF_5\text{-}F) = 3.218 \pm 0.071 \text{ eV} = 74.21 \pm 1.61 \text{ kcal mol}^{-1}.$$

We take $\Delta Hf°(SF_6,g) = -291.77 \pm 0.24$ kcal mol^{-1}, and $\Delta Hf°(F,g) = 18.9 \pm 0.1$ kcal mol^{-1}, and thus obtain

$$\Delta Hf°(SF_5,g) = -236.44 \pm 1.66 \text{ kcal mol}^{-1}.$$

For the reaction

$$\tfrac{1}{2}S_2(g) + \tfrac{5}{2}F_2(g) \rightarrow SF_5(g):$$

$$\Delta Hf = -251.78 \pm 1.67 \text{ kcal mol}^{-1}.$$

Additional thermodynamic functions calculated by statistical mechanical methods are given in Table X.

b. Data Used in the Statistical Calculations

$M = 127.056.$

$r(S\text{-}F) = 1.56$ Å (estimated by analogy with SF_6).

Symmetry* $= C_{4v}$; $\sigma = 4.$

$I_A I_B I_C = 14{,}706 \times 10^{-117}$ g^3 cm^6.

$\omega = 947(2), 775, 644(2), 615(2), 524(2)$, and $354(3)$ cm^{-1}.
(Values estimated by analogy with SF_6.[14])

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*D_{3h} symmetry, by analogy with PF_5,[24] is also plausible.

TABLE X. Thermodynamic Properties of Sulfur Pentafluoride

T (DEG.K.)	$-(G^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0,00	0,000	0.0000	0.000	0.0000
100,00	48,944	8,1610	57,105	9,1113
200,00	55,092	10,0589	65,151	15,1193
273,15	58,511	11,9976	70,509	19,3089
298,15	59,591	12,6613	72,252	20,4944
300,00	59,669	12,7098	72,379	20,5771
400,00	63,670	15,1562	78,826	24,1353
500,00	67,278	17,1915	84,469	26,3592
600,00	70,564	18,8466	89,410	27,7840
700,00	73,574	20,1955	93,769	28,7329
800,00	76,345	21,3061	97,651	29,3896
900,00	78,910	22,2318	101,142	29,8600
1000,00	81,294	23,0128	104,307	30,2070
1100,00	83,519	23,6793	107,199	30,4697
1200,00	85,605	24,2539	109,859	30,6730
1300,00	87,566	24,7541	112,321	30,8333
1400,00	89,417	25,1931	114,610	30,9619
1500,00	91,169	25,5813	116,750	31,0665
1600,00	92,831	25,9269	118,758	31,1527
1700,00	94,412	26,2365	120,649	31,2245
1800,00	95,920	26,5153	122,435	31,2850
1900,00	97,361	26,7677	124,128	31,3364
2000,00	98,740	26,9973	125,737	31,3804

T (DEG.K.)	$(H^\circ - H^\circ_{298})$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG K_f
0,00	-3,7750	249.21	249.21	INF
100,00	-2,9589	250,48	243,68	532,57
200,00	-1,7632	251,39	236,49	258,43
273,15	-0,4978	251.73	231,07	184,89
298,15	0,0000	251,78	229,08	167,92
300,00	0,0380	251,78	228,94	166,79
400,00	2,2875	251,86	221,31	120,92
500,00	4,8208	251,76	213,69	93,40
600,00	7,5330	251,55	206,09	75,07
700,00	10,3619	251,28	198,53	61,98
800,00	13,2699	250,97	191,02	52,18
900,00	16,2336	250,63	183,55	44,57
1000,00	19,2378	250,28	176,11	38,49
1100,00	22,2722	249,92	168,71	33,52
1200,00	25,3298	249,55	161,35	29,39
1300,00	28,4054	249,18	154,01	25,89
1400,00	31,4954	248,80	146,70	22,90
1500,00	34,5970	248,42	139,42	20,31
1600,00	37,7081	248,05	132,17	18,05
1700,00	40,8270	247,67	124,94	16,06
1800,00	43,9526	247,30	117,73	14,29
1900,00	47,0837	246,93	110,54	12,72
2000,00	50,2196	246,57	103,37	11,30

5. SF_4 Gas

a. Critical Temperature. Tullock et al.[25] reported a value of 90.9 ± 0.2°C.

b. Thermochemical Data. Nichols[26] measured the enthalpy of solution of SF_4 in water. From the "best" values[3] for $\Delta Hf°(HF,nH_2O)$ and $\Delta Hf°(H_2SO_3,aq)$, $\Delta Hf°(SF_4,g)$ is calculated to be -178.97 ± 4.0 kcal mol^{-1}. Vaughn and Muetterties[27] reported the enthalpy of reaction of SF_4 with hydrogen; their results have been recalculated to yield $\Delta Hf°(SF_4,g)$ = -185.23 ± 2.3 kcal mol^{-1}. The value selected, $\Delta Hf°(SF_4,g)$ = -182.1 ± 5.0 kcal mol^{-1}, is the mean of the two enthalpies of formation.

For the reaction

$$\tfrac{1}{2}S_2(g) + 2F_2(g) \rightarrow SF_4(g):$$

$$\Delta Hf = -197.44 \pm 4.65 \text{ kcal mol}^{-1}.$$

Additional thermodynamic functions calculated by statistical mechanical methods are given in Table XI.

c. Data Used in the Statistical Calculations. Two investigations[28,29] on the structure of SF_4 gave results in very close agreement. The electron-diffraction data of Kimura and Bauer[28] were arbitrarily selected for use in the statistical calculations.

$M = 108.0576.$

$r(S\text{-}F)_{ax} = 1.643 \pm 0.005$ Å; $r(S\text{-}F)_{eq} = 1.542 \pm 0.005$ Å.

$\widehat{FSF}_{ax} = 177 \pm 2.5°$; $\widehat{FSF}_{eq} = 104 \pm 0.6°$.

Symmetry = C_{2v}; $\sigma = 2$.

$I_A I_B I_C = 7248.9 \times 10^{-117}$ g^3 cm^6.

ω = 891.5, 867, 728, 645, 558.4, 532.2, 353, 226, and 171 cm^{-1}.[30]

6. SF_4 Liquid

a. Boiling Point. -40.4°C.[31]

b. Vapor Pressure. The vapor pressure of liquid SF_4, measured by Brown and Robinson[31] over the range -113 to -49°C, was fitted to the equation

TABLE XI. Thermodynamic Properties of Sulfur Tetrafluoride

T (DEG.K.)	$-(G^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	47.989	8.7435	56.733	10.5011
200.00	54.631	10.6879	65.319	14.7575
273.15	58.181	12.1574	70.339	17.4892
298.15	59.267	12.6378	71.904	18.2703
300.00	59.345	12.6727	72.018	18.3249
400.00	63.235	14.4040	77.639	20.6909
500.00	66.607	15.8217	82.429	22.1809
600.00	69.597	16.9669	86.564	23.1379
700.00	72.285	17.8970	90.182	23.7758
800.00	74.726	18.6610	93.387	24.2173
900.00	76.962	19.2969	96.259	24.5335
1000.00	79.023	19.8328	98.856	24.7667
1100.00	80.936	20.2897	101.225	24.9433
1200.00	82.718	20.6834	103.402	25.0799
1300.00	84.388	21.0259	105.414	25.1876
1400.00	85.957	21.3264	107.284	25.2739
1500.00	87.438	21.5920	109.030	25.3442
1600.00	88.839	21.8283	110.667	25.4021
1700.00	90.169	22.0400	112.209	25.4504
1800.00	91.434	22.2306	113.665	25.4910
1900.00	92.641	22.4032	115.044	25.5255
2000.00	93.794	22.5600	116.354	25.5551

T (DEG.K.)	$(H^\circ - H^\circ_{298})$ (KCAL/MOL)	$-\Delta Hf$ (KCAL/MOL)	$-\Delta Gf$ (KCAL/MOL)	LOG Kf
0.00	-3.7680	195.92	195.92	INF
100.00	-2.8936	196.78	191.98	419.58
200.00	-1.6304	197.27	186.97	204.31
273.15	-0.4472	197.43	183.24	146.61
298.15	0.0000	197.44	181.86	133.31
300.00	0.0339	197.44	181.77	132.42
400.00	1.9937	197.42	176.54	96.46
500.00	4.1429	197.30	171.33	74.89
600.00	6.4122	197.12	166.16	60.52
700.00	8.7599	196.90	161.01	50.27
800.00	11.1609	196.67	155.90	42.59
900.00	13.5993	196.42	150.82	36.62
1000.00	16.0648	196.16	145.77	31.86
1100.00	18.5507	195.91	140.74	27.96
1200.00	21.0522	195.64	135.74	24.72
1300.00	23.5657	195.38	130.76	21.98
1400.00	26.0890	195.12	125.80	19.64
1500.00	28.6200	194.86	120.85	17.61
1600.00	31.1574	194.60	115.93	15.84
1700.00	33.7001	194.34	111.02	14.27
1800.00	36.2472	194.09	106.13	12.89
1900.00	38.7981	193.83	101.25	11.65
2000.00	41.3521	193.58	96.38	10.53

$$\log P\ (\text{Torr}) = 8.8126 - 138/T.$$

Vapor pressures of SF_4, calculated from the above equation, are presented in Table XII.

c. Thermochemical Data. For the reactions

(1) $SF_4(l) \rightarrow SF_4(g)$:

$\Delta Hv^\circ = 6.32$ kcal mol^{-1};[31]

$\Delta Sv^\circ = 27.1$ cal deg^{-1} mol^{-1}.

(2) $S(rh) + 2F_2(g) \rightarrow SF_4(l)$:

$\Delta Hf^\circ = -188.42 \pm 4.7$ kcal mol^{-1}.

7. SF_2 Gas

a. Thermochemical Data. Reese, Dibeler, and Franklin[32] measured the appearance potential of SO_2^+ from SO_2F_2 and derived the value $\Delta Hf^\circ(SO_2F_2,g) = -205.2$ kcal mol^{-1}. If it is assumed that the sums of the S=O bond strengths in SO_2F_2 and SO_2 are approximately equal, an estimate of $\Delta Hf^\circ(SF_2,g)$ according to the reaction

$$S(rh) + F_2(g) \rightarrow SF_2(g)$$

may be obtained by substitution of the appropriate values in the equation

$$\Delta Hf^\circ(SF_2,g) = \Delta Hf^\circ(S,g) + \Delta Hf^\circ(SO_2F_2,g) - \Delta Hf^\circ(SO_2,g).$$

We take $\Delta Hf^\circ(SO_2,g) = -70.94 \pm 0.05$ kcal mol^{-1},[3] and $\Delta Hf^\circ(S,g) = 65.9$ kcal mol^{-1} (see Table III), and thus estimate that

$$\Delta Hf^\circ(SF_2,g) = -68 \pm 5 \text{ kcal mol}^{-1}.$$

For the reaction

$\frac{1}{2}S_2(g) + F_2(g) \rightarrow SF_2(g)$:

$\Delta Hf = -83.34 \pm 5$ kcal mol^{-1}.

Additional thermodynamic functions calculated by statistical mechanical methods are given in Table XIII.

TABLE XII. Vapor Pressure of Liquid Sulfur Tetrafluoride

T(C)	P(TORR)	LOGP(TORR)	1/T(K)
-113,00	1,55	0,18943	6.244-003
-110,00	2,23	0,34800	6.129-003
-107,00	3,17	0,50083	6.019-003
-104,00	4,45	0,64825	5.912-003
-101,00	6,17	0,79053	5.809-003
-98,00	8,47	0,92793	5.709-003
-95,00	11,50	1,06071	5.613-003
-92,00	15,46	1,18908	5.520-003
-89,00	20,57	1,31328	5.430-003
-86,00	27,13	1,43349	5.343-003
-83,00	35,47	1,54991	5.259-003
-80,00	46,00	1,66272	5.177-003
-77,00	59,17	1,77207	5.098-003
-74,00	75,53	1,87813	5.021-003
-71,00	95,73	1,98104	4.947-003
-68,00	120,49	2,08094	4.874-003
-65,00	150,65	2,17796	4.804-003
-62,00	187,17	2,27223	4.736-003
-59,00	231,13	2,36385	4.670-003
-56,00	283,75	2,45294	4.605-003
-53,00	346,42	2,53960	4.542-003
-50,00	420,67	2,62394	4.481-003

TABLE XIII. Thermodynamic Properties of Sulfur Difluoride

T (DEG.K.)	$-(G^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	43.302	7.9565	51.258	8.0109
200.00	48.868	8.1944	57.062	9.0378
273.15	51.474	8.5625	60.037	10.0883
298.15	52.230	8.7043	60.934	10.4154
300.00	52.284	8.7149	60.999	10.4387
400.00	54.870	9.2846	64.154	11.4799
500.00	56.998	9.7970	66.795	12.1646
600.00	58.824	10.2316	69.055	12.6137
700.00	60.429	10.5949	71.024	12.9165
800.00	61.864	10.8990	72.763	13.1277
900.00	63.163	11.1555	74.319	13.2796
1000.00	64.350	11.3738	75.724	13.3921
1100.00	65.443	11.5614	77.005	13.4774
1200.00	66.456	11.7239	78.180	13.5436
1300.00	67.401	11.8660	79.266	13.5958
1400.00	68.285	11.9911	80.276	13.6377
1500.00	69.116	12.1020	81.218	13.6719
1600.00	69.900	12.2011	82.101	13.7000
1700.00	70.642	12.2899	82.932	13.7235
1800.00	71.347	12.3701	83.717	13.7433
1900.00	72.018	12.4429	84.461	13.7601
2000.00	72.658	12.5091	85.167	13.7745

T (DEG.K.)	$(H^\circ - H^\circ_{298})$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG K_f
0.00	-2.5952	82.75	82.75	INF
100.00	-1.7995	83.00	81.73	178.61
200.00	-0.9563	83.21	80.36	87.82
273.15	-0.2563	83.32	79.35	63.49
298.15	0.0000	83.34	78.94	57.86
300.00	0.0193	83.34	78.91	57.49
400.00	1.1187	83.41	77.42	42.30
500.00	2.3033	83.45	75.92	33.18
600.00	3.5438	83.46	74.41	27.10
700.00	4.8212	83.47	72.90	22.76
800.00	6.1240	83.46	71.39	19.50
900.00	7.4448	83.46	69.88	16.97
1000.00	8.7787	83.45	68.38	14.94
1100.00	10.1223	83.44	66.87	13.29
1200.00	11.4735	83.43	65.36	11.90
1300.00	12.8306	83.42	63.86	10.74
1400.00	14.1923	83.41	62.35	9.73
1500.00	15.5579	83.41	60.85	8.87
1600.00	16.9265	83.40	59.35	8.11
1700.00	18.2977	83.40	57.84	7.44
1800.00	19.6711	83.40	56.34	6.84
1900.00	21.0463	83.40	54.84	6.31
2000.00	22.4230	83.40	53.33	5.83

b. Data Used in the Statistical Calculations

$M = 70.0608.$

$r(S\text{-}F) = 1.56$ Å (estimated).

$\widehat{FSF} = 100°$ (estimated).

Symmetry $= C_{2v}$; $\sigma = 2$.

$I_A I_B I_C = 311.64 \times 10^{-117}\ g^3\ cm^6$.

$\omega = 892$, 728, and 523 cm^{-1} (estimated).

8. SF Gas

a. Thermochemical Data. To estimate the standard enthalpy of formation of SF(g), it is assumed, by analogy with similar triatomic molecules, that the primary and secondary bond strengths in SF_2 are approximately equal; i.e., that the energies of the processes

$$SF_2(g) \rightarrow SF(g) + F(g),$$

and

$$SF(g) \rightarrow S(g) + F(g)$$

are the same. Thus,

$$D(SF\text{-}F)_{SF_2} = D(S\text{-}F)_{SF},$$

and

$$\Delta Hf°(SF,g) + \Delta Hf°(F,g) - \Delta Hf°(SF_2,g) = \Delta Hf°(S,g) + \Delta Hf°(F,g) - \Delta Hf°(SF,g).$$

Solving for $\Delta Hf°(SF,g)$, we obtain

$$\Delta Hf°(SF,g) = \tfrac{1}{2}[\Delta Hf°(SF_2,g) + \Delta Hf°(S,g)].$$

Insertion into this equation of the values $\Delta Hf°(SF_2,g) = -68 \pm 5$ kcal mol^{-1} and $\Delta Hf°(S,g) = 65.9$ kcal mol^{-1} (see Table III) yields

$$\Delta Hf°(SF,g) = -1 \pm 5 \text{ kcal mol}^{-1}$$

for the reaction

$$S(rh) + \tfrac{1}{2}F_2(g) \rightarrow SF(g).$$

For the reaction

$\frac{1}{2}S_2(g) + \frac{1}{2}F_2(g) \rightarrow SF(g)$:

$\Delta Ef = \Delta Hf = -16.34 \pm 3.7$ kcal mol^{-1}.

Additional thermodynamic functions calculated by statistical mechanical methods are given in Table XIV.

b. Data Used in the Statistical Calculations

M = 51.0624.

r(S-F) = 1.599 Å.[33]

I = 5.0647×10^{-39} g cm^2.

ω = 898 cm^{-1}.*

9. FS-SF Gas (Disulfur Difluoride)

a. Thermochemical Data. The S-F bond in FSSF and the axial S-F bond in SF_4 are similar, from the point of view of the bond lengths[28,35] and bond stretching-force constants.[36-38] We assume that the bond strengths are also similar in the following derivations of $\Delta Hf°(FSSF,g)$ and $D(S-S)_{FSSF}$.

(1) $FSSF(g) \rightarrow S_2(g) + 2F(g)$:

$$2D(S-F)_{FSSF} = 2D(S-F)_{SF_4(ax)} = 2(76.0) \pm 5 \text{ kcal mol}^{-1}$$

$$= \Delta Hf°(S_2,g) + 2\Delta Hf°(F,g) - \Delta Hf°(FSSF,g);$$

$$\Delta Hf°(FSSF,g) = -83.5 \pm 5 \text{ kcal mol}^{-1}.$$

(2) $FSSF(g) \rightarrow 2SF(g)$

$$D(S-S)_{FSSF} = 2\Delta Hf°(SF) - \Delta Hf°(FSSF,g)$$

$$= 82 \pm 3 \text{ kcal mol}^{-1}.$$

*Calculated by Guggenheimer's rule.[34]

TABLE XIV. Thermodynamic Properties of Sulfur Monofluoride

T (DEG.K.)	$-(G^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	38.308	6.9499	45.258	6.9559
200.00	43.129	6.9726	50.102	7.0852
273.15	45.311	7.0368	52.348	7.3545
298.15	45.929	7.0678	52.996	7.4578
300.00	45.972	7.0702	53.043	7.4655
400.00	48.026	7.2181	55.244	7.8441
500.00	49.653	7.3732	57.027	8.1266
600.00	51.011	7.5162	58.527	8.3243
700.00	52.179	7.6421	59.821	8.4626
800.00	53.207	7.7512	60.958	8.5613
900.00	54.125	7.8454	61.971	8.6335
1000.00	54.956	7.9270	62.883	8.6874
1100.00	55.715	7.9981	63.713	8.7287
1200.00	56.414	8.0604	64.474	8.7609
1300.00	57.061	8.1153	65.176	8.7864
1400.00	57.664	8.1640	65.828	8.8070
1500.00	58.229	8.2074	66.437	8.8238
1600.00	58.760	8.2464	67.007	8.8377
1700.00	59.261	8.2815	67.543	8.8493
1800.00	59.735	8.3134	68.049	8.8591
1900.00	60.186	8.3423	68.528	8.8674
2000.00	60.614	8.3687	68.983	8.8746

T (DEG.K.)	$(H^\circ - H^\circ_{298})$ (KCAL/MOL)	$-\Delta Hf$ (KCAL/MOL)	$-\Delta Gf$ (KCAL/MOL)	LOG Kf
0.00	-2.1073	16.32	16.32	INF
100.00	-1.4123	16.32	16.48	36.02
200.00	-0.7128	16.33	16.64	18.18
273.15	-0.1852	16.34	16.78	13.43
298.15	0.0000	16.34	16.79	12.31
300.00	0.0138	16.34	16.80	12.24
400.00	0.7800	16.36	16.94	9.26
500.00	1.5793	16.38	17.09	7.47
600.00	2.4025	16.39	17.23	6.28
700.00	3.2422	16.41	17.37	5.42
800.00	4.0937	16.42	17.51	4.78
900.00	4.9536	16.44	17.64	4.28
1000.00	5.8198	16.46	17.77	3.88
1100.00	6.6906	16.48	17.90	3.56
1200.00	7.5652	16.49	18.03	3.28
1300.00	8.4426	16.51	18.16	3.05
1400.00	9.3223	16.53	18.28	2.85
1500.00	10.2039	16.56	18.41	2.68
1600.00	11.0870	16.58	18.53	2.53
1700.00	11.9714	16.60	18.65	2.40
1800.00	12.8568	16.63	18.77	2.28
1900.00	13.7431	16.65	18.89	2.17
2000.00	14.6302	16.68	19.01	2.08

For the reaction

$S_2(g) + F_2(g) \rightarrow FSSF(g)$:

$\Delta Hf = -114.18 \pm 5.0$ kcal mol^{-1}.

Additional thermodynamic functions* for FSSF(g) are given in Table XV.

b. Data Used in the Statistical Calculations

M = 102.1248.

FSSF has a nonplanar structure,[35] r(S-S) = 1.888 ± 0.01 Å; r(S-F) = 1.635 ± 0.01 Å; $\widehat{FSS}$ = 108.3 ± 0.5°; the dihedral angle = 87.9 ± 1.5°.

Symmetry = C_2; $\sigma = 2$.

$I_A I_B I_C = 5494.8 \times 10^{-117}$ g^3 cm^6.

ω = 198, 526, 745(2), and 807(2) cm^{-1}.[36]

10. $S{=}SF_2$ Gas (Thiothionyl Fluoride)

a. Thermochemical Data. Since $D(S{=}S)_{S_2}$ = 101 kcal mol^{-1} (Ref. 39) and $D(S{=}S)_{S_2O}$ = 91 kcal mol^{-1},[40] we estimate $D(S{=}S)_{SSF_2}$ = 90 ± 5 kcal mol^{-1}. Consequently, for the reaction

$SSF_2(g) = S(g) + SF_2(g)$:

$\Delta H = 90 \pm 5$ kcal mol^{-1}.

Combination of this value with $\Delta Hf°(S,g) = 65.9$ kcal mol^{-1} and $\Delta Hf°(SF_2,g) = -68 \pm 5$ kcal mol^{-1} yields

$\Delta Hf°(SSF_2,g) = -92 \pm 7$ kcal mol^{-1}.

*In the statistical calculations it was assumed that the barrier to internal rotation in the FSSF molecule was infinitely large. If it is assumed that there is completely free rotation about the S-S bond, the following corrections (in cal deg^{-1} mol^{-1}) must be added to the tabulated values: enthalpy function, +0.9936; heat capacity, +0.9936; free-energy function, -2.2882 log T; entropy, +0.9936 - 2.2882 log T.

TABLE XV. Thermodynamic Properties of Disulfur Difluoride

T (DEG.K.)	$-(G^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	47.395	8.3058	55.701	9.0748
200.00	53.408	9.1910	62.599	11.2564
273.15	56.391	10.0030	66.394	13.1641
298.15	57.279	10.2930	67.573	13.7534
300.00	57.343	10.3145	67.658	13.7951
400.00	60.466	11.4329	71.899	15.6542
500.00	63.125	12.4067	75.532	16.8610
600.00	65.461	13.2190	78.680	17.6449
700.00	67.551	13.8911	81.442	18.1700
800.00	69.444	14.4501	83.894	18.5343
900.00	71.173	14.9192	86.093	18.7956
1000.00	72.766	15.3169	88.083	18.9885
1100.00	74.243	15.6576	89.900	19.1346
1200.00	75.618	15.9523	91.570	19.2477
1300.00	76.905	16.2093	93.115	19.3369
1400.00	78.115	16.4354	94.550	19.4084
1500.00	79.256	16.6356	95.891	19.4666
1600.00	80.335	16.8141	97.149	19.5145
1700.00	81.360	16.9741	98.334	19.5545
1800.00	82.334	17.1184	99.452	19.5881
1900.00	83.263	17.2492	100.512	19.6167
2000.00	84.151	17.3682	101.519	19.6412

T (DEG.K.)	$(H^\circ - H^\circ_{298})$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG K_f
0.00	-3.0689	113.00	113.00	INF
100.00	-2.2383	113.56	110.40	241.27
200.00	-1.2307	113.96	107.07	117.00
273.15	-0.3366	114.15	104.57	83.67
298.15	0.0000	114.18	103.63	75.96
300.00	0.0255	114.18	103.56	75.45
400.00	1.5043	114.27	100.01	54.64
500.00	3.1345	114.28	96.44	42.15
600.00	4.8625	114.23	92.88	33.83
700.00	6.6549	114.15	89.33	27.89
800.00	8.4912	114.05	85.79	23.44
900.00	10.3584	113.93	82.26	19.98
1000.00	12.2480	113.81	78.75	17.21
1100.00	14.1545	113.68	75.25	14.95
1200.00	16.0739	113.55	71.76	13.07
1300.00	18.0033	113.41	68.29	11.48
1400.00	19.9407	113.27	64.82	10.12
1500.00	21.8845	113.13	61.37	8.94
1600.00	23.8336	113.00	57.92	7.91
1700.00	25.7871	112.86	54.48	7.00
1800.00	27.7443	112.72	51.05	6.20
1900.00	29.7046	112.59	47.63	5.48
2000.00	31.6675	112.46	44.21	4.83

For the reaction

$S_2(g) + F_2 \rightarrow SSF_2(g)$:

$\Delta Hf = -122.7 \pm 7.0$ kcal mol^{-1}.

Additional thermodynamic functions calculated by statistical mechanical methods are given in Table XVI.

b. Data Used in the Statistical Calculations

M = 102.1248.

$S{=}SF_2$ has a pyramidal structure,[41] r(S-F) = 1.598 ± 0.012 Å; r(S=S) = 1.860 ± 0.015 Å; $\widehat{SSF}$ = 107.5 ± 1°; $\widehat{FSF}$ = 92.5 ± 1°.

Symmetry = C_{2v}; $\sigma = 2$.

$I_A I_B I_C = 5547.6 \times 10^{-117}$ g^3 cm^6.

ω = 760.5, 718.5, 692.3, 411.2, 364.1, and 337.6 cm^{-1}.[35]

11. $S{=}SF_2$ Liquid (Thiothionyl Fluoride)

a. Freezing Point. -165°C.[42,43]

b. Boiling Point. -10.6°C.[42,43]

c. Thermochemical Data. For the reactions

(1) $SSF_2(l) \rightarrow SSF_2(g)$:

$\Delta Hv° = 5.46$ kcal mol^{-1};[43]

$\Delta Sv° = 20.8$ cal deg^{-1} mol^{-1}.[43]

(2) $2S(rh) + F_2(g) \rightarrow SSF_2(l)$:

$\Delta Hf° = -97.5 \pm 7$ kcal mol^{-1}.

12. S_2F_{10} Gas

a. Thermochemical Data. Electron diffraction experiments have shown that the S_2F_{10} molecule consists of two octahedral SF_5 groups joined together through an S-S bond.[44] Within experimental error, the interatomic distances and stretching-force constants of the S-F bonds in S_2F_{10} are reported to be identical. The S-S bond in S_2F_{10}, however, is

TABLE XVI. Thermodynamic Properties of Thiothionyl Fluoride

T (DEG.K.)	$-(G^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	47.317	8.1136	55.430	8.8202
200.00	53.268	9.3193	62.587	12.2525
273.15	56.332	10.3971	66.729	14.3306
298.15	57.258	10.7512	68.009	14.8972
300.00	57.325	10.7769	68.102	14.9364
400.00	60.604	12.0405	72.645	16.5847
500.00	63.404	13.0566	76.461	17.5761
600.00	65.859	13.8652	79.724	18.1954
700.00	68.047	14.5147	82.562	18.6010
800.00	70.021	15.0439	85.065	18.8784
900.00	71.819	15.4815	87.300	19.0755
1000.00	73.470	15.8485	89.318	19.2200
1100.00	74.995	16.1601	91.155	19.3289
1200.00	76.413	16.4278	92.841	19.4129
1300.00	77.737	16.6601	94.397	19.4789
1400.00	78.980	16.8634	95.843	19.5318
1500.00	80.149	17.0428	97.192	19.5747
1600.00	81.254	17.2022	98.456	19.6100
1700.00	82.302	17.3447	99.646	19.6394
1800.00	83.297	17.4729	100.770	19.6642
1900.00	84.244	17.5888	101.833	19.6852
2000.00	85.149	17.6941	102.843	19.7031

T (DEG.K.)	$(H^\circ - H^\circ_{298})$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG K_f
0.00	-3.2055	121.65	121.65	INF
100.00	-2.3941	122.23	119.05	260.17
200.00	-1.3416	122.59	115.69	126.42
273.15	-0.3655	122.70	113.21	90.58
298.15	0.0000	122.70	112.28	82.30
300.00	0.0276	122.70	112.22	81.75
400.00	1.6107	122.68	108.72	59.40
500.00	3.3228	122.61	105.24	46.00
600.00	5.1137	122.50	101.77	37.07
700.00	6.9548	122.37	98.33	30.70
800.00	8.8296	122.23	94.91	25.93
900.00	10.7279	122.08	91.50	22.22
1000.00	12.6430	121.93	88.11	19.26
1100.00	14.5707	121.78	84.74	16.84
1200.00	16.5079	121.63	81.37	14.82
1300.00	18.4527	121.48	78.03	13.12
1400.00	20.4033	121.33	74.69	11.66
1500.00	22.3587	121.18	71.36	10.40
1600.00	24.3180	121.03	68.05	9.29
1700.00	26.2805	120.89	64.74	8.32
1800.00	28.2457	120.74	61.44	7.46
1900.00	30.2132	120.60	58.15	6.69
2000.00	32.1826	120.46	54.87	6.00

weaker than in typical disulfides, RSSR, as indicated by its greater length [r(S-S) of 2.21 versus 2.05 Å (Ref. 44)] and smaller stretching-force constant [k(S-S) of 1.83×10^5 (Ref. 45) versus 2.5×10^5 dyn cm^{-1} (Ref. 38)].

Various considerations indicate that $\Delta Hf°(S_2F_{10},g)$, knowledge of which would enable calculation of the S-S bond energy in S_2F_{10}, will be extremely difficult to measure experimentally. It is of interest to determine whether consistent estimates of this quantity can be determined by other methods. Three methods of estimating $\Delta Hf°(S_2F_{10},g)$ are compared below: The first, and crudest, involves estimation of the enthalpy of atomization ($\Delta Ha°$) of S_2F_{10} by means of bond energy terms; the second, more refined, uses an empirical equation to derive the dissociation energy of the S-S bond [D(S-S)] in S_2F_{10} which, in turn, is used to derive $\Delta Hf°(S_2F_{10},g)$; the third employs the results of a kinetic study and leads to a limiting value for $\Delta Hf°(S_2F_{10},g)$.

(1) The only published estimate of $\Delta Hf°(S_2F_{10},g)$, -461 kcal mol^{-1}, was calculated by Yost and Russell[46] from

$$\Delta Ha°(S_2F_{10}) = 10E(S\text{-}F) + E(S\text{-}S), \tag{4}$$

and

$$\Delta Hf°(S_2F_{10},g) = 10\Delta Hf°(F,g) + 2\Delta Hf°(S,g) - \Delta Ha°(S_2F_{10}), \tag{5}$$

where E(S-F) and E(S-S) are the bond energy terms for the S-F and S-S bonds, respectively. However, Yost and Russell's value for E(S-F) is based on an incorrect value for $\Delta Hf°(SF_6,g)$. Our revised value[47] for E(S-F), 78.5 kcal mol^{-1}, together with E(S-S) = 66 kcal mol^{-1},[48] yields $\Delta Ha°(S_2F_{10})$ = 851 kcal mol^{-1}. The latter value, when combined in Eq. 5 with $\Delta Hf°(F,g)$ = 18.9 kcal mol^{-1} and $\Delta Hf°(S,g)$ = 65.9 kcal mol^{-1}, yields

$$\Delta Hf°(S_2F_{10},g) = -530 \text{ kcal mol}^{-1}.$$

(2) The enthalpy of formation of $S_2F_{10}(g)$ is given by

$$\Delta Hf°(S_2F_{10},g) = 2\Delta Hf°(SF_5,g) - D(S\text{-}S)_{S_2F_{10}}. \tag{6}$$

The dissociation energy of the S-S bond in S_2F_{10} can be estimated from the empirical equation[49]

$$\frac{D(S\text{-}S)_{S_2F_{10}}}{D(S\text{-}S)_{RSSR}} = \frac{k(S\text{-}S)_{S_2F_{10}}}{k(S\text{-}S)_{RSSR}} \left(\frac{r(S\text{-}S)_{S_2F_{10}}}{r(S\text{-}S)_{RSSR}}\right)^2, \tag{7}$$

where the RSSR terms represent normal or typical values for disulfides. Insertion of the appropriate values and $D(S\text{-}S)_{RSSR} = 65 \pm 1$ kcal mol^{-1} (Ref. 48) into Eq. 7 gives $D(S\text{-}S)_{S_2F_{10}} = 55 \pm 5$ kcal mol^{-1}. (An uncertainty of ±5 kcal mol^{-1} was arbitrarily assigned because of the approximate nature of Eq. 7.) This estimated dissociation energy, together with $\Delta Hf°(SF_5,g) = -236.4 \pm 1.7$ kcal mol^{-1}, was inserted into Eq. 6 to give

$$\Delta Hf°(S_2F_{10},g) = -528 \pm 5 \text{ kcal mol}^{-1}.$$

(3) Trost and McIntosh[50] studied the thermal decomposition of S_2F_{10}. The reaction proceeds according to

$$S_2F_{10}(g) \rightarrow 2SF_5(g) \tag{8}$$

and

$$2SF_5(g) \rightarrow SF_4(g) + SF_6(g). \tag{9}$$

They determined the activation energy to be 49.2 kcal mol^{-1} for the overall process

$$S_2F_{10}(g) \rightarrow SF_4(g) + SF_6(g). \tag{10}$$

The enthalpy of (endothermic) Reaction 10 must be less than (or equal to) its activation energy. Therefore,

$$\Delta Hf°(SF_4,g) + \Delta Hf°(SF_6,g) - \Delta Hf°(S_2F_{10},g) \leq 49 \text{ kcal mol}^{-1}. \tag{11}$$

The values $\Delta Hf°(SF_4,g) = -182 \pm 5$ kcal mol^{-1} and $\Delta Hf°(SF_6,g) = -292 \pm 0.2$ kcal mol^{-1}, when inserted into Eq. 11, yield

$$-\Delta Hf°(S_2F_{10},g) < 528 \text{ kcal mol}^{-1}.$$

The three independent estimates are seen to be consistent, and we are confident that the true value for $\Delta Hf°(S_2F_{10},g)$ lies within the range -523 to -528 kcal mol^{-1}.

For the reactions

(1) $2S(rh) + 5F_2(g) \rightarrow S_2F_{10}(g)$:

$$\Delta Hf° = -526.0 \pm 4.0 \text{ kcal mol}^{-1}.$$

(2) $S_2(g) + 5F_2(g) \rightarrow S_2F_{10}(g)$:

$$\Delta Hf = -556.68 \pm 4.1 \text{ kcal mol}^{-1}.$$

Additional thermodynamic functions calculated by statistical mechanical methods are given in Table XVII.

TABLE XVII. Thermodynamic Properties of Disulfur Decafluoride

T (DEG.K.)	$-(G^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	56.023	12.9051	68.929	17.7802
200.00	66.600	18.4948	85.094	30.9524
273.15	73.046	23.1088	96.155	40.1447
298.15	75.137	24.6489	99.786	42.7619
300.00	75.290	24.7612	100.051	42.9445
400.00	83.204	30.3668	113.570	50.8066
500.00	90.494	34.9826	125.476	55.7065
600.00	97.214	38.7158	135.929	58.8337
700.00	103.417	41.7476	145.165	60.9097
800.00	109.160	44.2377	153.397	62.3429
900.00	114.493	46.3093	160.803	63.3674
1000.00	119.465	48.0547	167.520	64.1223
1100.00	124.117	49.5425	173.660	64.6932
1200.00	128.484	50.8242	179.308	65.1345
1300.00	132.597	51.9389	184.536	65.4823
1400.00	136.483	52.9166	189.400	65.7611
1500.00	140.164	53.7807	193.945	65.9878
1600.00	143.660	54.5497	198.210	66.1746
1700.00	146.988	55.2382	202.226	66.3302
1800.00	150.163	55.8582	206.021	66.4612
1900.00	153.198	56.4192	209.618	66.5725
2000.00	156.106	56.9293	213.035	66.6678

T (DEG.K.)	$(H^\circ-H^\circ_{298})$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG K_f
0.00	-7.3491	551.34	551.34	INF
100.00	-6.0586	554.22	536.10	1171.65
200.00	-3.6501	556.02	517.19	565.16
273.15	-1.0369	556.62	503.06	402.50
298.15	0.0000	556.68	497.96	365.01
300.00	0.0793	556.68	497.59	362.50
400.00	4.7976	556.61	477.89	261.11
500.00	10.1422	556.13	458.26	200.31
600.00	15.8804	555.40	438.75	159.81
700.00	21.8743	554.52	419.37	130.93
800.00	28.0411	553.56	400.14	109.31
900.00	34.3293	552.52	381.02	92.52
1000.00	40.7056	551.45	362.02	79.12
1100.00	47.1477	550.36	343.13	68.17
1200.00	53.6400	549.24	324.34	59.07
1300.00	60.1715	548.11	305.64	51.38
1400.00	66.7342	546.98	287.03	44.81
1500.00	73.3220	545.84	268.50	39.12
1600.00	79.9304	544.70	250.06	34.16
1700.00	86.5559	543.57	231.67	29.78
1800.00	93.1956	542.44	213.37	25.91
1900.00	99.8474	541.31	195.11	22.44
2000.00	106.5096	540.18	176.91	19.33

b. Data Used in the Statistical Calculations

M = 254.1120.

r(S-F) = 1.56 Å; r(S-S) = 2.209 Å.[44]

Symmetry = D_{4d}, with two octahedral SF_5 groups linked through the S-S bond. The equatorial fluorine atoms attached to different sulfur atoms are in the gauche configuration;[44] σ = 8.

$I_A I_B I_C$ = 717,909 x 10^{-117} g^3 cm^6.

ω = 913, 690, 423, 247, 87, 938, 684, 571, 826(2), 544(2), 410(2), 37, 57, 728(2), 624(2), 509(2), 860(2), 634(2), 425(2), and 188(2) cm^{-1}.[45,51]

13. S_2F_{10} Liquid

a. Freezing Point. -52.7 ± 0.3°C.[52]

b. Boiling Point. 26.7°C.[52]

c. Vapor Pressure. Cohen and MacDiarmid[52] fitted the vapor-pressure data for liquid S_2F_{10} to the following equation:

$$\log P\ (\text{Torr}) = -1498.863/T - 5324.074/T^2 + 7.936121\ (-51 \text{ to } 0°C).$$

Vapor pressures calculated from this equation are given in Table XVIII. The equation given by Denbigh and Whytlaw-Gray,[53]

$$\log P\ (\text{Torr}) = 7.950 - 1530.0/T\ (-92 \text{ to } 29°C),$$

was for impure $S_2F_{10}(l)$.

TABLE XVIII. Vapor Pressure of Liquid Disulfur Decafluoride

t, °C	P, Torr	Log P, Torr	$10^3/T$, $°K^{-1}$	t, °C	P, Torr	Log P, Torr	$10^3/T$, $°K^{-1}$
-51.0	11.93	1.07646	4.505	-23.0	71.69	1.85548	4.000
-48.0	14.77	1.16934	4.444	-18.0	94.70	1.97635	3.922
-43.0	20.83	1.31868	4.348	-13.0	123.7	2.09251	3.846
-38.0	28.94	1.46157	4.255	-8.0	160.0	2.20422	3.774
-33.0	39.67	1.59843	4.167	-3.0	205.0	2.31174	3.704
-28.0	53.66	1.72962	4.082	0.0	238.5	2.37744	3.661

d. Thermochemical Data. For the reactions

(1) $S_2F_{10}(l) \rightarrow S_2F_{10}(g)$:

$\Delta Hv^\circ = 7.07$ kcal mol^{-1};[52]

$\Delta Sv^\circ = 23.6$ cal deg^{-1} mol^{-1}.[52]

(2) $2S(rh) + 5F_2(g) = S_2F_{10}(l)$:

$\Delta Hf^\circ = -533.07 \pm 4.1$ kcal mol^{-1}.

B. Selenium Fluorides

1. SeF_6 Gas

a. Critical Temperature. 72.35°C.[54]

b. Thermochemical Data. The energy of fluorination of hexagonal selenium to $SeF_6(g)$ has been measured calorimetrically.[12] The value given below for $\Delta Hf^\circ(SeF_6,g)$ should now supersede the earlier datum of Yost and Claussen.[55]

For the reactions

(1) $Se(hex) + 3F_2(g) \rightarrow SeF_6(g)$:

$\Delta Ef^\circ = -265.77$ kcal mol^{-1};

$\Delta Hf^\circ = -266.95 \pm 0.14$ kcal mol^{-1};

$\Delta Sf^\circ = -80.47$ cal deg^{-1} mol^{-1};

$\Delta Gf^\circ = -242.96$ kcal mol^{-1};

$\log Kf^\circ = 178.1$.

(2) $\frac{1}{2}Se_2(g) + 3F_2(g) \rightarrow SeF_6(g)$:

$\Delta Hf = -284.40 \pm 0.2$ kcal mol^{-1}.

Other thermodynamic data for $SeF_6(g)$ are given in Table XIX.

TABLE XIX. Thermodynamic Properties of Selenium Hexafluoride

T (DEG.K.)	$-(G^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	46.528	8.6686	55.196	11.1144
200.00	53.528	12.1741	65.702	20.0912
273.15	57.746	15.0019	72.748	25.0877
298.15	59.099	15.9046	75.003	26.4170
300.00	59.197	15.9697	75.167	26.5085
400.00	64.241	19.1228	83.363	30.3170
500.00	68.786	21.6065	90.392	32.5776
600.00	72.905	23.5607	96.466	33.9813
700.00	76.658	25.1192	101.777	34.8975
800.00	80.098	26.3829	106.481	35.5230
900.00	83.267	27.4245	110.692	35.9669
1000.00	86.203	28.2958	114.499	36.2921
1100.00	88.935	29.0343	117.970	36.5370
1200.00	91.490	29.6678	121.157	36.7258
1300.00	93.886	30.2166	124.103	36.8743
1400.00	96.144	30.6966	126.840	36.9930
1500.00	98.276	31.1196	129.396	37.0895
1600.00	100.297	31.4953	131.792	37.1688
1700.00	102.217	31.8310	134.048	37.2348
1800.00	104.045	32.1328	136.178	37.2904
1900.00	105.789	32.4056	138.195	37.3375
2000.00	107.458	32.6532	140.111	37.3779

T (DEG.K.)	$(H^\circ-H^\circ_{298})$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG K_f
0.00	-4.7419	281.53	281.53	INF
100.00	-3.8751	283.24	273.98	598.78
200.00	-2.3071	284.16	264.28	288.79
273.15	-0.6442	284.40	257.07	205.68
298.15	0.0000	284.40	254.45	186.52
300.00	0.0490	284.40	254.27	185.23
400.00	2.9072	284.28	244.23	133.44
500.00	6.0613	283.99	234.25	102.39
600.00	9.3945	283.59	224.34	81.71
700.00	12.8415	283.14	214.49	66.97
800.00	16.3644	282.66	204.72	55.93
900.00	19.9401	282.16	195.01	47.35
1000.00	23.5538	281.65	185.36	40.51
1100.00	27.1958	281.13	175.75	34.92
1200.00	30.8594	280.61	166.20	30.27
1300.00	34.5397	280.09	156.68	26.34
1400.00	38.2332	279.57	147.21	22.98
1500.00	41.9375	279.06	137.77	20.07
1600.00	45.6506	278.55	128.37	17.53
1700.00	49.3708	278.04	118.99	15.30
1800.00	53.0972	277.55	109.66	13.31
1900.00	56.8286	277.05	100.35	11.54
2000.00	60.5645	276.56	91.05	9.95

c. Data Used in the Statistical Calculations

$M = 192.9504.$

$r(Se\text{-}F) = 1.688 \pm 0.01$ Å.[13]

Symmetry = O_h;[13] $\sigma = 24.$

$I_A I_B I_C = 46{,}476 \times 10^{-117}\ g^3\ cm^6.$

ω = 778.5(3), 710, 662(2), 436(3), 405(3), and 260(3) cm^{-1}.[14,56]

2. SeF_6 Crystal

a. Melting Point. -34.8 ± 0.5°C.[57]

b. Sublimation Point. -45.8°C.[57]

c. Vapor Pressure. The vapor pressure-temperature behavior of solid SeF_6 was found by Yost and Claussen[19] to obey the equation

$$\log P\ (\text{Torr}) = -1440.8/T + 9.2417\ (-100 \text{ to } -35°C).$$

This equation was used to calculate the vapor pressures given in Table XX.

d. Thermochemical Data. For the reactions

(1) $SeF_6(c) \rightarrow SeF_6(l)$:

$\Delta Hm° = 2.01$ kcal mol^{-1}.[58]

(2) $SeF_6(c) \rightarrow SeF_6(g)$:

$\Delta Hs° = 6.27$ kcal mol^{-1}.[16]

(3) $Se(hex) + 3F_2(g) \rightarrow SeF_6(c)$:

$\Delta Hf° = -273.22 \pm 0.21$ kcal mol^{-1}.

3. SeF_5 Gas

a. Thermochemical Data. The energies of the primary and secondary bond dissociations of SF_6 are equal, within experimental error.[59] We assume that this is also true for SeF_6; thus

$$D(SeF_5\text{-}F) = \tfrac{1}{2}[\Delta Hf°(SeF_4,g) + 2\Delta Hf°(F,g) - \Delta Hf°(SeF_6,g)].$$

TABLE XX. Vapor Pressure of Solid Selenium Hexafluoride

T(C)	P(TORR)	LOGP(TORR)	1/T(K)
-100.00	8.33	0.92059	5.775-003
-97.00	11.54	1.06231	5.677-003
-94.00	15.82	1.19928	5.582-003
-91.00	21.47	1.33174	5.490-003
-88.00	28.83	1.45990	5.401-003
-85.00	38.37	1.58398	5.315-003
-82.00	50.60	1.70416	5.231-003
-79.00	66.17	1.82063	5.151-003
-76.00	85.81	1.93356	5.072-003
-73.00	110.43	2.04310	4.996-003
-70.00	141.06	2.14940	4.922-003
-67.00	178.90	2.25261	4.851-003
-64.00	225.35	2.35286	4.781-003
-61.00	282.02	2.45028	4.714-003
-58.00	350.73	2.54498	4.648-003
-55.00	433.58	2.63707	4.584-003
-52.00	532.92	2.72666	4.522-003
-49.00	651.42	2.81386	4.461-003

The appropriate thermochemical data from this report are inserted in the above equation to yield

$$D(SeF_5\text{-}F) = 61 \text{ kcal mol}^{-1},$$

and from this is obtained

$$\Delta Hf^\circ(SeF_5, g) = -224.8 \pm 3.5 \text{ kcal mol}^{-1}.$$

For the reaction

$$\tfrac{1}{2}Se_2(g) + \tfrac{5}{2}F_2(g) \rightarrow SeF_5(g):$$

$$\Delta Hf = -242.25 \pm 3.6 \text{ kcal mol}^{-1}.$$

Other thermodynamic data for $SeF_5(g)$ are given in Table XXI.

b. Data Used in Statistical Calculations

$M = 173.9520.$

$r(Se\text{-}F) = 1.69$ Å (estimated).

Symmetry $= C_{4v}$; $\sigma = 4$.

$I_A I_B I_C = 24{,}446 \times 10^{-117}$ g^3 cm^6.

$\omega = 710, 662(2), 778.5(2), 436(2), 405(2)$, and $260(3)$ cm^{-1} (estimated by analogy with SeF_6 (Refs. 14 and 56)).

4. SeF_4 Gas

a. Thermochemical Data. Nichols[26] measured the heat of hydrolysis of liquid SeF_4 to form $HF \cdot nH_2O$ and $H_2SeO_3 \cdot nH_2O$; his data have been recalculated on the basis of the "best" values[3] for $\Delta Hf^\circ(HF \cdot nH_2O)$ and $\Delta Hf^\circ(H_2SeO_3 \cdot nH_2O)$ to yield $\Delta Hf^\circ(SeF_4, l) = -194.02 \pm 4.0$ kcal mol^{-1}. Peacock[60] reported $\Delta Hv^\circ(SeF_4, l) = 11.24$ kcal mol^{-1}. Therefore,

$$\Delta Hf^\circ(SeF_4, g) = -182.78 \pm 4.1 \text{ kcal mol}^{-1}.$$

For the reaction

$$\tfrac{1}{2}Se_2(g) + 2F_2(g) \rightarrow SeF_4(g):$$

$$\Delta Hf = -200.23 \pm 4.2 \text{ kcal mol}^{-1}.$$

Other thermodynamic data for $SeF_4(g)$ are given in Table XXII.

TABLE XXI. Thermodynamic Properties of Selenium Pentafluoride

T (DEG.K.)	$-(G^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	50.509	8.6105	59.119	10.7630
200.00	57.312	11.5175	68.830	17.9073
273.15	61.242	13.7846	75.027	21.8337
298.15	62.481	14.5043	76.985	22.8792
300.00	62.570	14.5562	77.127	22.9512
400.00	67.115	17.0628	84.178	25.9474
500.00	71.143	19.0323	90.175	27.7257
600.00	74.755	20.5801	95.336	28.8293
700.00	78.024	21.8134	99.837	29.5494
800.00	81.004	22.8130	103.817	30.0410
900.00	83.740	23.6365	107.377	30.3897
1000.00	86.267	24.3252	110.593	30.6451
1100.00	88.614	24.9089	113.523	30.8375
1200.00	90.803	25.4094	116.213	30.9858
1300.00	92.855	25.8430	118.698	31.1023
1400.00	94.784	26.2221	121.006	31.1956
1500.00	96.605	26.5563	123.161	31.2713
1600.00	98.328	26.8530	125.181	31.3336
1700.00	99.964	27.1181	127.082	31.3854
1800.00	101.521	27.3564	128.878	31.4290
1900.00	103.006	27.5718	130.578	31.4661
2000.00	104.425	27.7673	132.193	31.4977

T (DEG.K.)	$(H^\circ - H^\circ_{298})$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG K_f
0.00	-4.3245	240.01	240.01	INF
100.00	-3.4634	241.39	234.55	512.61
200.00	-2.0210	242.08	227.38	248.47
273.15	-0.5592	242.25	222.06	177.67
298.15	0.0000	242.25	220.11	161.35
300.00	0.0424	242.25	219.98	160.25
400.00	2.5006	242.15	212.56	116.14
500.00	5.1917	241.91	205.19	89.69
600.00	8.0236	241.60	197.87	72.08
700.00	10.9449	241.25	190.61	59.51
800.00	13.9259	240.88	183.41	50.10
900.00	16.9484	240.49	176.24	42.80
1000.00	20.0008	240.10	169.13	36.96
1100.00	23.0753	239.71	162.05	32.20
1200.00	26.1668	239.31	155.01	28.23
1300.00	29.2714	238.91	148.00	24.88
1400.00	32.3865	238.52	141.02	22.01
1500.00	35.5100	238.13	134.07	19.53
1600.00	38.6403	237.74	127.15	17.37
1700.00	41.7763	237.36	120.24	15.46
1800.00	44.9171	236.99	113.37	13.76
1900.00	48.0619	236.62	106.51	12.25
2000.00	51.2101	236.26	99.67	10.89

TABLE XXII. Thermodynamic Properties of Selenium Tetrafluoride

T (DEG.K.)	$-(G^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	49.326	8.2178	57.544	9.0188
200.00	55.369	9.5226	64.892	12.9518
273.15	58.533	10.8675	69.400	16.0470
298.15	59.505	11.3404	70.845	16.9543
300.00	59.575	11.3753	70.951	17.0179
400.00	63.097	13.1584	76.256	19.7900
500.00	66.202	14.6733	80.875	21.5426
600.00	68.991	15.9186	84.909	22.6685
700.00	71.524	16.9399	88.464	23.4184
800.00	73.843	17.7840	91.627	23.9372
900.00	75.979	18.4894	94.469	24.3086
1000.00	77.959	19.0857	97.045	24.5825
1100.00	79.803	19.5952	99.398	24.7897
1200.00	81.527	20.0351	101.562	24.9499
1300.00	83.146	20.4182	103.564	25.0763
1400.00	84.672	20.7546	105.426	25.1776
1500.00	86.114	21.0523	107.166	25.2600
1600.00	87.481	21.3175	108.799	25.3279
1700.00	88.781	21.5551	110.336	25.3845
1800.00	90.019	21.7692	111.788	25.4321
1900.00	91.201	21.9631	113.165	25.4726
2000.00	92.333	22.1395	114.472	25.5072

T (DEG.K.)	$(H^\circ-H^\circ_{298})$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG K_f
0.00	-3.3812	198.11	198.11	INF
100.00	-2.5594	199.17	194.21	424.45
200.00	-1.4766	199.87	188.94	206.46
273.15	-0.4127	200.18	184.96	147.99
298.15	0.0000	200.23	183.48	134.50
300.00	0.0314	200.23	183.38	133.59
400.00	1.8822	200.35	177.74	97.11
500.00	3.9555	200.33	172.09	75.22
600.00	6.1700	200.22	166.45	60.63
700.00	8.4768	200.06	160.83	50.21
800.00	10.8461	199.87	155.24	42.41
900.00	13.2593	199.65	149.67	36.35
1000.00	15.7045	199.43	144.13	31.50
1100.00	18.1736	199.19	138.62	27.54
1200.00	20.6609	198.95	133.12	24.24
1300.00	23.1625	198.70	127.64	21.46
1400.00	25.6753	198.46	122.19	19.07
1500.00	28.1974	198.21	116.74	17.01
1600.00	30.7269	197.98	111.32	15.21
1700.00	33.2626	197.74	105.91	13.62
1800.00	35.8035	197.50	100.52	12.21
1900.00	38.3487	197.27	95.14	10.94
2000.00	40.8978	197.04	89.77	9.81

b. Data Used in the Statistical Calculations

$M = 154.9536.$

$r(Se\text{-}F) = 1.70 \pm 0.25$ Å (mean value).[13]

$\widehat{FSeF}_{ax} = 180°$; $\widehat{FSeF}_{eq} = 100 \pm 2°$.[13]

Symmetry = C_{2v}; $\sigma = 2$ (SeF_4 structure similar to SF_4).

$I_A I_B I_C = 11{,}513 \times 10^{-117}\ g^3\ cm^6$.

ω = 889, 867, 725, 715, 645, 557, 532, 463, and 235 cm^{-1}.[61,62]

5. SeF_4 Liquid

a. Freezing Point. -9.5°C.[63]

b. Boiling Point. 101.6°C[60]; 107.7°C.[64]

c. Vapor Pressure. The following vapor-pressure equations for $SeF_4(l)$ were given by Peacock[60] and Dagron,[64] respectively:

log P (Torr) (Ref. 60) = 9.44 - 2457/T (-9 to 46°C);

log P (Torr) (Ref. 64) = 8.88 - 2284/T (40 to 107°C).

Vapor pressures calculated from these equations are given in Tables XXIII and XXIV, respectively.

d. Thermochemical Data. For the reactions

(1) $SeF_4(l) \rightarrow SeF_4(g)$:

$\Delta Hv° = 11.24$ kcal mol^{-1};

$\Delta Sv° = 30.0$ cal deg^{-1} mol^{-1}.

(2) $Se(hex) + 2F_2(g) \rightarrow SeF_4(l)$:

$\Delta Hf° = -194.02 \pm 4.0$ kcal mol^{-1}.

6. SeF_2 Gas

a. Thermochemical Data. The enthalpy of formation of $SeF_2(g)$ was estimated by assuming that

$$D(F_2Se{=}O) = D(OSe{=}O) = \Delta Hf°(SeO,g) + \Delta Hf°(O,g) - \Delta Hf°(SeO_2,g).$$

TABLE XXIII. Vapor Pressure of Liquid Selenium Tetrafluoride, -9 to 45°C

T(C)	P(TORR)	LOGP(TORR)	1/T(K)
40,00	38.58	1,58637	3.193-003
43,00	45,25	1,65558	3.163-003
46,00	52,90	1,72349	3.133-003
49,00	61,68	1,79014	3.104-003
52,00	71,71	1,85555	3.076-003
55,00	83,13	1,91977	3.047-003
58,00	96,12	1,98282	3.020-003
61,00	110,85	2,04475	2.993-003
64,00	127,52	2,10557	2.966-003
67,00	146,32	2,16532	2.940-003
70,00	167.50	2,22402	2.914-003
73,00	191,30	2,28170	2.889-003
76,00	217,97	2,33840	2.864-003
79,00	247,81	2,39413	2.840-003
82,00	281,13	2,44891	2.816-003
85,00	318.26	2,50278	2.792-003
88,00	359,55	2,55576	2.769-003
91,00	405,38	2,60786	2.746-003
94,00	456,15	2,65911	2.724-003
97,00	512.30	2,70953	2.702-003
100,00	574.30	2,75914	2.680-003
103,00	642.62	2,80795	2.659-003
106,00	717.79	2,85600	2.637-003

TABLE XXIV. Vapor Pressure of Liquid Selenium Tetrafluoride, 40 to 106°C

T(C)	P(TORR)	LOGP(TORR)	1/T(K)
-9,00	1,38	0,13847	3.786-003
-6,00	1,75	0,24292	3.743-003
-3,00	2,21	0,34505	3.702-003
0,00	2,79	0,44494	3.661-003
3,00	3,49	0,54266	3.621-003
6,00	4,35	0,63828	3.582-003
9,00	5,39	0,73187	3.544-003
12,00	6,66	0,82348	3.507-003
15,00	8,19	0,91319	3.470-003
18,00	10.02	1,00105	3.435-003
21,00	12,22	1,08712	3.400-003
24,00	14,84	1,17145	3.365-003
27,00	17.95	1,25409	3.332-003
30,00	21.63	1,33510	3.299-003
33,00	25,97	1,41452	3.266-003
36,00	31,07	1,49240	3.235-003
39,00	37,05	1,56878	3.204-003
42,00	44,03	1,64371	3.173-003
45,00	52.15	1,71723	3.143-003

By inserting into this equation the values $\Delta Hf°(SeO_2,g) = -30.96$ kcal mol^{-1},[3,65] $\Delta Hf°(SeO,g) = 14.35$ kcal mol^{-1},[66] and $\Delta Hf°(O,g) = 59.6$ kcal mol^{-1}, we obtain

$$D(F_2Se{=}O) = 104.9 \pm 5.1 \text{ kcal mol}^{-1}.$$

Insertion of this value and the value $\Delta Hf°(SeOF_2,g) = -115.4$ kcal mol^{-1} (Refs. 26 and 64) into the equation

$$D(F_2Se{=}O) = \Delta Hf°(SeF_2,g) + \Delta Hf°(O,g) - \Delta Hf°(SeOF_2,g)$$

yields

$$\Delta Hf°(SeF_2,g) = -70.1 \pm 5.2 \text{ kcal mol}^{-1}.$$

For the reaction

$\frac{1}{2}Se_2(g) + F_2(g) \rightarrow SeF_2(g)$:

$\Delta Hf = -87.55 \pm 5.5$ kcal mol^{-1}.

Other thermodynamic data for $SeF_2(g)$ are given in Table XXV.

b. Data Used in the Statistical Calculations

$M = 116.9568$.

$r(Se-F) = 1.69$ Å; $\widehat{FSeF} = 100°$ (both values estimated).

Symmetry $= C_{2v}$; $\sigma = 2$.

$I_A I_B I_C = 828.63 \times 10^{-117}$ g^3 cm^6.

$\omega = 780$, 437, and 405 cm^{-1} (estimated by analogy with SeF_4).

7. SeF Gas

a. Thermochemical Data. The enthalpy of formation of SeF(g) was estimated by assuming that the bonds in SeF_2 were of equal strength (cf., SCl_2, $SeCl_2$, and SF_2) and thus equal to 82 ± 3 kcal mol^{-1}. Therefore for the reactions

(1) $Se(hex) + \frac{1}{2}F_2(g) \rightarrow SeF(g)$:

$\Delta Hf° = -7.4 \pm 3.0$ kcal mol^{-1}.

(2) $\frac{1}{2}Se_2(g) + \frac{1}{2}F_2(g) \rightarrow SeF(g)$:

$\Delta Ef = \Delta Hf = -24.85 \pm 3.2$ kcal mol^{-1}.

Other thermodynamic data for SeF(g) are given in Table XXVI.

b. Data Used in the Statistical Calculations

$M = 97.9584$.

$r(Se-F) = 1.69$ Å (estimated).

$I = 7.2624 \times 10^{-39}$ g cm^2.

$\omega = 735$ cm^{-1}.[34]

TABLE XXV. Thermodynamic Properties of Selenium Difluoride

T (DEG.K.)	$-(G^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	45.810	8.0065	53.816	8.2986
200.00	51.515	8.6034	60.119	10.1278
273.15	54.280	9.1633	63.443	11.1978
298.15	55.091	9.3461	64.437	11.4817
300.00	55.148	9.3593	64.508	11.5013
400.00	57.933	10.0054	67.938	12.3143
500.00	60.223	10.5195	70.742	12.7976
600.00	62.178	10.9261	73.104	13.0983
700.00	63.888	11.2514	75.139	13.2949
800.00	65.408	11.5157	76.924	13.4292
900.00	66.777	11.7339	78.511	13.5247
1000.00	68.023	11.9167	79.940	13.5946
1100.00	69.167	12.0717	81.238	13.6474
1200.00	70.223	12.2048	82.428	13.6880
1300.00	71.204	12.3202	83.525	13.7200
1400.00	72.121	12.4211	84.542	13.7456
1500.00	72.981	12.5101	85.491	13.7664
1600.00	73.791	12.5892	86.380	13.7835
1700.00	74.557	12.6599	87.217	13.7977
1800.00	75.282	12.7234	88.006	13.8097
1900.00	75.972	12.7809	88.752	13.8199
2000.00	76.629	12.8330	89.462	13.8286

T (DEG.K.)	$(H^\circ - H^\circ_{298})$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG K_f
0.00	-2.7865	86.94	86.94	INF
100.00	-1.9859	87.33	86.07	188.11
200.00	-1.0658	87.50	84.72	92.58
273.15	-0.2836	87.55	83.74	67.00
298.15	0.0000	87.55	83.34	61.09
300.00	0.0213	87.55	83.31	60.69
400.00	1.2156	87.56	81.90	44.75
500.00	2.4732	87.54	80.49	35.18
600.00	3.7692	87.52	79.08	28.80
700.00	5.0895	87.49	77.67	24.25
800.00	6.4261	87.47	76.27	20.84
900.00	7.7740	87.44	74.87	18.18
1000.00	9.1302	87.42	73.48	16.06
1100.00	10.4924	87.40	72.08	14.32
1200.00	11.8592	87.38	70.69	12.87
1300.00	13.2297	87.36	69.30	11.65
1400.00	14.6030	87.35	67.91	10.60
1500.00	15.9787	87.34	66.52	9.69
1600.00	17.3562	87.34	65.14	8.90
1700.00	18.7353	87.34	63.75	8.20
1800.00	20.1156	87.35	62.36	7.57
1900.00	21.4971	87.35	60.97	7.01
2000.00	22.8796	87.36	59.58	6.51

TABLE XXVI. Thermodynamic Properties of Selenium Monofluoride

T (DEG.K.)	$-(G^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	40.965	6.9519	47.917	6.9608
200.00	45.794	7.0066	52.800	7.2387
273.15	47.993	7.1174	55.110	7.6021
298.15	48.618	7.1630	55.781	7.7188
300.00	48.662	7.1664	55.829	7.7271
400.00	50.750	7.3562	58.106	8.0994
500.00	52.411	7.5309	59.942	8.3418
600.00	53.797	7.6800	61.477	8.4989
700.00	54.991	7.8050	62.796	8.6038
800.00	56.040	7.9097	63.950	8.6765
900.00	56.977	7.9979	64.975	8.7286
1000.00	57.824	8.0730	65.897	8.7670
1100.00	58.596	8.1375	66.734	8.7960
1200.00	59.307	8.1933	67.500	8.8185
1300.00	59.965	8.2421	68.207	8.8362
1400.00	60.577	8.2851	68.862	8.8504
1500.00	61.150	8.3232	69.473	8.8619
1600.00	61.688	8.3571	70.045	8.8715
1700.00	62.196	8.3876	70.583	8.8794
1800.00	62.676	8.4151	71.091	8.8861
1900.00	63.132	8.4401	71.572	8.8917
2000.00	63.565	8.4628	72.028	8.8966

T (DEG.K.)	$(H^\circ-H^\circ_0)$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG K_f
0.00	-2.1356	24.65	24.65	INF
100.00	-1.4404	24.80	24.98	54.59
200.00	-0.7343	24.82	25.13	27.47
273.15	-0.1915	24.85	25.28	20.22
298.15	0.0000	24.85	25.28	18.53
300.00	0.0143	24.85	25.28	18.42
400.00	0.8069	24.87	25.42	13.89
500.00	1.6298	24.89	25.56	11.17
600.00	2.4724	24.90	25.69	9.36
700.00	3.3279	24.92	25.82	8.06
800.00	4.1921	24.93	25.95	7.09
900.00	5.0625	24.95	26.08	6.33
1000.00	5.9373	24.96	26.20	5.73
1100.00	6.8156	24.98	26.32	5.23
1200.00	7.6963	25.00	26.45	4.82
1300.00	8.5791	25.02	26.56	4.47
1400.00	9.4635	25.04	26.68	4.17
1500.00	10.3491	25.07	26.80	3.90
1600.00	11.2358	25.10	26.92	3.68
1700.00	12.1233	25.13	27.03	3.47
1800.00	13.0116	25.17	27.14	3.30
1900.00	13.9005	25.20	27.25	3.13
2000.00	14.7899	25.24	27.35	2.99

C. Tellurium Fluorides

1. TeF_6 Gas

a. Critical Temperature. 83.25°C.[58]

b. Thermochemical Data. The standard enthalpy of formation of $TeF_6(g)$ was derived from measurement of the energy of combustion of Te(c) in fluorine in a bomb calorimeter.[12]

For the reactions

(1) $Te(c) + 3F_2(g) \rightarrow TeF_6(g)$:

$\Delta Ef° = -326.02$ kcal mol^{-1};

$\Delta Hf° = -327.20 \pm 0.56$ kcal mol^{-1};

$\Delta Sf° = -76.9$ cal deg^{-1} mol^{-1};

$\Delta Gf° = -304.26$ kcal mol^{-1};

$\log Kf° = 223.0$.

(2) $\frac{1}{2}Te_2(g) + 3F_2(g) \rightarrow TeF_6(g)$:

$\Delta Hf = -347.30 \pm 0.58$ kcal mol^{-1}.

Additional thermodynamic functions for $TeF_6(g)$ are given in Table XXVII.

c. Data Used in the Statistical Calculations

$M = 241.5904$.

$r(Te\text{-}F) = 1.84 \pm 0.02$ Å.[67]

Symmetry = O_h;[67] $\sigma = 24$.

$I_A I_B I_C = 77{,}966 \times 10^{-117}$ g^3 cm^6.

$\omega = 752(3), 697, 672(2), 325(3), 315(3)$, and $197(3)$ cm^{-1}.[14]

2. TeF_6 Liquid

a. Vapor Pressure. The following vapor-pressure equation[58] applies over the narrow range -38.6 to -37.7°C:

$\log P\ (Torr) = 7.091 - 988/T$.

TABLE XXVII. Thermodynamic Properties of Tellurium Hexafluoride

T (DEG.K.)	$-(G^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	48.021	9.5639	57.585	13.7544
200.00	56.034	14.0695	70.103	22.6850
273.15	60.862	16.9847	77.847	26.9640
298.15	62.388	17.8699	80.258	28.0936
300.00	62.499	17.9332	80.432	28.1714
400.00	68.088	20.9333	89.021	31.4089
500.00	73.018	23.2369	96.255	33.3344
600.00	77.419	25.0270	102.446	34.5316
700.00	81.388	26.4444	107.832	35.3136
800.00	84.996	27.5885	112.585	35.8478
900.00	88.302	28.5284	116.830	36.2269
1000.00	91.349	29.3128	120.662	36.5048
1100.00	94.175	29.9766	124.151	36.7141
1200.00	96.808	30.5450	127.353	36.8754
1300.00	99.273	31.0370	130.310	37.0023
1400.00	101.589	31.4669	133.056	37.1038
1500.00	103.773	31.8455	135.619	37.1862
1600.00	105.839	32.1815	138.021	37.2541
1700.00	107.800	32.4816	140.281	37.3105
1800.00	109.664	32.7512	142.415	37.3580
1900.00	111.441	32.9948	144.436	37.3983
2000.00	113.140	33.2158	146.355	37.4328

T (DEG.K.)	$(H^\circ - H^\circ_{298})$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG K_f
0.00	-5.3279	345.11	345.11	INF
100.00	-4.3715	346.62	337.43	737.46
200.00	-2.5140	347.26	327.89	358.31
273.15	-0.6885	347.34	320.88	256.74
298.15	0.0000	347.30	318.34	233.35
300.00	0.0520	347.30	318.16	231.78
400.00	3.0454	347.05	308.48	168.54
500.00	6.2905	346.67	298.88	130.64
600.00	9.6883	346.21	289.36	105.40
700.00	13.1832	345.72	279.92	87.40
800.00	16.7428	345.20	270.56	73.91
900.00	20.3476	344.67	261.26	63.44
1000.00	23.9849	344.13	252.02	55.08
1100.00	27.6463	343.59	242.84	48.25
1200.00	31.3261	343.05	233.71	42.56
1300.00	35.0202	342.51	224.61	37.76
1400.00	38.7257	341.97	215.56	33.65
1500.00	42.4404	341.44	206.55	30.09
1600.00	46.1625	340.91	197.58	26.99
1700.00	49.8908	340.38	188.63	24.25
1800.00	53.6243	339.86	179.73	21.82
1900.00	57.3622	339.34	170.84	19.65
2000.00	61.1038	338.83	161.99	17.70

b. Thermochemical Data. For the reactions

(1) $TeF_6(l) \rightarrow TeF_6(g)$:

$\Delta Hv° = 4.23$ kcal mol^{-1};[58]

$\Delta Sv° = 18.01$ cal deg^{-1} mol^{-1}.

(2) $Te(c) + 3F_2(g) \rightarrow TeF_6(l)$:

$\Delta Hf° = -331.43 \pm 0.61$ kcal mol^{-1}.

3. TeF_6 Crystal

a. Melting Point. $-37.6 \pm 0.5°C$.[57]

b. Sublimation Point. $-38.3°C$.[57]

c. Vapor Pressure. The following equations represent the vapor pressure of $TeF_6(c)$:

$$\log P\ (\text{Torr}) = -1471.4/T + 9.1605\ (100 \text{ to } -37°C),^{19} \tag{12}$$

and

$$\log P\ (\text{Torr}) = -1342/T + 8.5940\ (100 \text{ to } -37°C).^{58} \tag{13}$$

Equation 12 was used to calculate the data in Table XXVIII.

d. Thermochemical Data. For the reactions

(1) $TeF_6(c) \rightarrow TeF_6(l)$:

$\Delta Hm° = 1.9$ kcal mol^{-1}.[58]

(2) $Te(c) + 3F_2(g) \rightarrow TeF_6(c)$:

$\Delta Hf° = -333.33 \pm 0.65$ kcal mol^{-1}.

4. TeF_5 Gas

a. Thermochemical Data. The standard enthalpy of formation of $TeF_5(g)$ was estimated by assuming that the primary and secondary bond dissociation energies of TeF_6 were equal (see Section B.3).

TABLE XXVIII. Vapor Pressure of Solid Tellurium Hexafluoride

T(C)	P(TORR)	LOGP(TORR)	1/T(K)
-100.00	4.60	0.66267	5.775-003
-97.00	6.42	0.80739	5.677-003
-94.00	8.86	0.94727	5.582-003
-91.00	12.09	1.08254	5.490-003
-88.00	16.35	1.21343	5.401-003
-85.00	21.88	1.34014	5.315-003
-82.00	29.03	1.46288	5.231-003
-79.00	38.18	1.58182	5.151-003
-76.00	49.79	1.69715	5.072-003
-73.00	64.42	1.80901	4.996-003
-70.00	82.71	1.91758	4.922-003
-67.00	105.43	2.02298	4.851-003
-64.00	133.46	2.12536	4.781-003
-61.00	167.82	2.22484	4.714-003
-58.00	209.68	2.32155	4.648-003
-55.00	260.38	2.41560	4.584-003
-52.00	321.44	2.50710	4.522-003
-49.00	394.59	2.59615	4.461-003
-46.00	481.77	2.68284	4.402-003
-43.00	585.16	2.76728	4.345-003
-40.00	707.20	2.84954	4.289-003

For the reactions

(1) $Te(c) + \frac{5}{2}F_2(g) \rightarrow TeF_5(g)$:

$\Delta Hf^\circ = -277.2 \pm 5.0$ kcal mol^{-1}.

(2) $\frac{1}{2}Te_2(g) + \frac{5}{2}F_2(g) \rightarrow TeF_5(g)$:

$\Delta Hf = -297.3 \pm 5.1$ kcal mol^{-1}.

Additional thermodynamic functions for $TeF_5(g)$ are given in Table XXIX.

TABLE XXIX. Thermodynamic Properties of Tellurium Pentafluoride

T (DEG,K,)	$-(G^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0,00	0,000	0,0000	0,000	0,0000
100,00	52,046	9,3782	61,424	12,8887
200,00	59,670	13,0038	72,674	19,8206
273,15	64,074	15,3077	79,382	23,1938
298,15	65,445	16,0073	81,452	24,0902
300,00	65,544	16,0574	81,601	24,1519
400,00	70,504	18,4315	88,935	26,7291
500,00	74,821	20,2573	95,079	28,2651
600,00	78,646	21,6775	100,323	29,2206
700,00	82,075	22,8027	104,878	29,8449
800,00	85,181	23,7112	108,892	30,2713
900,00	88,018	24,4578	112,476	30,5740
1000,00	90,628	25,0811	115,710	30,7958
1100,00	93,044	25,6085	118,653	30,9629
1200,00	95,292	26,0603	121,353	31,0917
1300,00	97,394	26,4514	123,846	31,1929
1400,00	99,367	26,7931	126,160	31,2740
1500,00	101,226	27,0941	128,320	31,3398
1600,00	102,984	27,3612	130,345	31,3939
1700,00	104,650	27,5997	132,249	31,4389
1800,00	106,233	27,8141	134,047	31,4768
1900,00	107,742	28,0078	135,750	31,5090
2000,00	109,184	28,1835	137,367	31,5366

T (DEG,K,)	$(H^\circ-H^\circ_{298})$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG K_f
0,00	-4,7726	295,61	295,61	INF
100,00	-3,8348	296,79	290,02	633,84
200,00	-2,1718	297,27	282,98	309,22
273,15	-0,5913	297,33	277,81	222,28
298,15	0,0000	297,30	275,92	202,25
300,00	0,0446	297,30	275,79	200,91
400,00	2,6000	297,11	268,64	146,78
500,00	5,3561	296,81	261,55	114,33
600,00	8,2339	296,46	254,54	92,71
700,00	11,1893	296,07	247,58	77,30
800,00	14,1964	295,68	240,68	65,75
900,00	17,2395	295,27	233,83	56,78
1000,00	20,3085	294,86	227,02	49,62
1100,00	23,3968	294,44	220,26	43,76
1200,00	26,4998	294,03	213,54	38,89
1300,00	29,6142	293,62	206,84	34,77
1400,00	32,7377	293,21	200,18	31,25
1500,00	35,8685	292,80	193,55	28,20
1600,00	39,0053	292,40	186,95	25,54
1700,00	42,1470	292,00	180,36	23,19
1800,00	45,2928	291,61	173,82	21,11
1900,00	48,4422	291,22	167,28	19,24
2000,00	51,5945	290,83	160,77	17,57

b. Data Used in Statistical Calculations

M = 222.5920.

r(Te-F) = 1.84 Å (estimated).

Symmetry = C_{4v}; σ = 4.

$I_A I_B I_C$ = 41,399 x 10^{-117} g^3 cm^6.

ω = 697, 672(2), 752(2), 325(2), 315(2), and 197(3) cm^{-1}.
(Values estimated by analogy with $TeF_6(g)$.[14])

5. TeF_4 Gas

a. Thermochemical Data. A value for $\Delta Hf°(TeF_4,g)$ was calculated on the basis of the heat of hydrolysis of $TeF_4(c)$, measured by Nichols,[26] and a heat of sublimation of 14.5 kcal mol^{-1}.[68]

For the reactions

(1) $Te(c) + 2F_2(g) \rightarrow TeF_4(g)$:

$\Delta Hf°$ = -227.3 ± 2.1 kcal mol^{-1}.

(2) $\frac{1}{2}Te_2(g) + 2F_2(g) \rightarrow TeF_4(g)$:

ΔHf = -247.4 ± 2.3 kcal mol^{-1}.

Additional thermodynamic functions for $TeF_4(g)$ are presented in Table XXX.

b. Data Used in Statistical Calculations

M = 203.5936.

r(Te-F) = 1.85 Å (mean value).

$\widehat{FTeF}_{eq}$ = 100°; $\widehat{FTeF}_{ax}$ = 180°.

Symmetry = C_{2v}; σ = 2 (SF_4 structure assumed).

$I_A I_B I_C$ = 18,362 x 10^{-117} g^3 cm^6.

ω = 880, 420, 250, 100, 580, 700, 480, 610, and 200 cm^{-1}.
(Values estimated by analogy with SF_4 and SeF_4.)

TABLE XXX. Thermodynamic Properties of Tellurium Tetrafluoride

T (DEG,K,)	$-(G^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0,00	0.000	0,0000	0,000	0,0000
100,00	51.247	9,4301	60,677	11,7446
200,00	58.500	11,7634	70,263	16,3459
273,15	62.407	13,3593	75,766	18,9588
298,15	63.599	13,8590	77,458	19,6636
300,00	63.685	13,8950	77,580	19,7123
400,00	67.929	15,6264	83,555	21,7526
500,00	71.568	16,9842	88,552	22,9784
600,00	74.763	18,0519	92,814	23,7454
700,00	77.612	18,9035	96,515	24,2486
800,00	80.183	19,5945	99,777	24,5935
900,00	82.524	20,1643	102,689	24,8388
1000,00	84.674	20,6412	105,315	25,0188
1100,00	86.661	21,0456	107,707	25,1547
1200,00	88.508	21,3926	109,900	25,2595
1300,00	90.232	21,6933	111,925	25,3419
1400,00	91.849	21,9564	113,806	25,4080
1500,00	93.372	22,1883	115,561	25,4616
1600,00	94.811	22,3943	117,205	25,5057
1700,00	96.174	22,5785	118,753	25,5425
1800,00	97.470	22,7440	120,214	25,5734
1900,00	98.703	22,8937	121,597	25,5997
2000,00	99.881	23,0295	122,911	25,6222

T (DEG,K,)	$(H^\circ - H^\circ_{298})$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG K
0,00	-4,1321	246,12	246,12	INF
100,00	-3,1891	246,96	242,14	529,20
200,00	-1,7794	247,34	237,12	259,11
273,15	-0,4830	247,41	233,42	186,76
298,15	0,0000	247,40	232,05	170,10
300,00	0,0364	247,40	231,95	168,98
400,00	2,1185	247,30	226,82	123,93
500,00	4,3600	247,11	221,72	96,91
600,00	6,6991	246,88	216,66	78,92
700,00	9,1004	246,63	211,64	66,08
800,00	11,5435	246,36	206,67	56,46
900,00	14,0158	246,08	201,72	48,98
1000,00	16,5091	245,81	196,80	43,01
1100,00	19,0181	245,53	191,92	38,13
1200,00	21,5390	245,25	187,06	34,07
1300,00	24,0693	244,97	182,22	30,63
1400,00	26,6069	244,69	177,40	27,69
1500,00	29,1505	244,42	172,60	25,15
1600,00	31,6989	244,15	167,83	22,92
1700,00	34,2514	243,87	163,06	20,96
1800,00	36,8072	243,61	158,33	19,22
1900,00	39,3659	243,35	153,59	17,67
2000,00	41,9270	243,09	148,87	16,27

6. TeF_4 Liquid

a. Boiling Point. 193°C (dec).[68]

b. Vapor Pressure. The following vapor-pressure equation for liquid TeF_4 (130-193°C) was given by Junkins, Bernhardt, and Barber:[68]

$$\log P\ (\text{Torr}) = 5.6397 - 1786.4/T.$$

This equation was used to calculate the vapor pressures given in Table XXXI.

c. Thermochemical Data. For the reactions

(1) $TeF_4(l) \rightarrow TeF_4(g)$:

$\Delta Hv° = 8.17$ kcal mol^{-1};[68]

$\Delta Sv° = 12.62$ cal deg^{-1} mol^{-1}.[68]

(2) $Te(c) + 2F_2(g) \rightarrow TeF_4(l)$:

$\Delta Hf° = -235.5 \pm 2.1$ kcal mol^{-1}.

7. TeF_4 Crystal

a. Melting Point. 129.6°C.[68]

b. Vapor Pressure. The vapor pressure of $TeF_4(c)$ from 25 to 130°C is given by the equation[68]

$$\log P\ (\text{Torr}) = 9.0934 - (3174.3/T).$$

The vapor pressures in Table XXXII have been calculated from this equation.

c. Thermochemical Data. For the reactions

(1) $TeF_4(c) \rightarrow TeF_4(l)$:

$\Delta Hm° = 6.35$ kcal mol^{-1};[68]

$\Delta Sm° = 15.77$ cal deg^{-1} mol^{-1}.[68]

(2) $Te(c) + 2F_2(g) \rightarrow TeF_4(c)$:

$\Delta Hf° = -241.8 \pm 2.1$ kcal mol^{-1}.[26]

TABLE XXXI. Vapor Pressure of Liquid Tellurium Tetrafluoride

T(C)	P(TORR)	LOGP(TORR)	1/T(K)
130,00	16,17	1,20859	2.480-003
133,00	17,43	1,24133	2.462-003
136,00	18,77	1,27358	2.444-003
139,00	20,20	1,30536	2.426-003
142,00	21,71	1,33668	2.409-003
145,00	23,31	1,36755	2.391-003
148,00	25,00	1,39798	2.374-003
151,00	26,79	1,42798	2.358-003
154,00	28,68	1,45756	2.341-003
157,00	30,67	1,48673	2.325-003
160,00	32,77	1,51549	2.309-003
163,00	34,98	1,54386	2.293-003
166,00	37,31	1,57184	2.277-003
169,00	39,76	1,59944	2.262-003
172,00	42,33	1,62667	2.246-003
175,00	45,03	1,65353	2.231-003
178,00	47,87	1,68004	2.217-003
181,00	50,84	1,70620	2.202-003
184,00	53,95	1,73201	2.187-003
187,00	57,21	1,75749	2.173-003
190,00	60,62	1,78263	2.159-003
193,00	64,19	1,80746	2.145-003

TABLE XXXII. Vapor Pressure of Solid Tellurium Tetrafluoride

T(C)	P(TORR)	LOGP(TORR)	1/T(K)
25,00	0,03	-1,55325	3.354-003
30,00	0,04	-1,37765	3.299-003
35,00	0,06	-1,20775	3.245-003
40,00	0,09	-1,04328	3.193-003
45,00	0,13	-0,88397	3.143-003
50,00	0,19	-0,72959	3.095-003
55,00	0,26	-0,57992	3.047-003
60,00	0,37	-0,43474	3.002-003
65,00	0,51	-0,29385	2.957-003
70,00	0,70	-0,15707	2.914-003
75,00	0,95	-0,02422	2.872-003
80,00	1,27	0,10487	2.832-003
85,00	1,70	0,23035	2.792-003
90,00	2,25	0,35238	2.754-003
95,00	2,96	0,47110	2.716-003
100,00	3.86	0,58663	2.680-003
105,00	5,00	0,69911	2.644-003
110,00	6,44	0,80866	2.610-003
115,00	8,23	0,91538	2.576-003
120,00	10.46	1,01938	2.544-003
125,00	13,21	1,12078	2.512-003
130,00	16,58	1,21966	2.480-003

8. TeF_2 Gas

a. Thermochemical Data. The standard enthalpy of formation of $TeF_2(g)$ was estimated by analogy. For both $SF_2(g)$ and $SeF_2(g)$, the enthalpy of atomization is related[69] to the average bond energy of the corresponding hexafluoride by

$$\Delta Ha°(MF_2,g) = 2.2\bar{D}(M\text{-}F)_{MF_6}.$$

$\bar{D}(Te\text{-}F)_{TeF_6}$ can be calculated as follows:

$$\bar{D}(Te\text{-}F)_{TeF_6} = (1/6)[\Delta Hf°(Te,g) + 6\Delta Hf°(F,g) - \Delta Hf°(TeF_6,g)]$$

$$= (1/6)[50.5 + 113.4 + 327.2]$$

$$= 81.85 \text{ kcal mol}^{-1}.$$

Thus,

$$\Delta Ha°(TeF_2,g) = 180.2 \text{ kcal mol}^{-1}.$$

Substitution of the appropriate values in the equation

$$\Delta Ha°(TeF_2,g) = \Delta Hf°(Te,g) + 2\Delta Hf°(F,g) - \Delta Hf°(TeF_2,g)$$

gives

$$\Delta Hf°(TeF_2,g) = -92.0 \pm 3.5 \text{ kcal mol}^{-1}$$

for the reaction

$$Te(c) + F_2(g) \rightarrow TeF_2(g).$$

For the reaction

$$\tfrac{1}{2}Te_2(g) + F_2(g) \rightarrow TeF_2(g),$$

$$\Delta Hf = -112.1 \pm 3.6 \text{ kcal mol}^{-1}.$$

Additional thermodynamic functions for $TeF_2(g)$ are given in Table XXXIII.

TABLE XXXIII. Thermodynamic Properties of Tellurium Difluoride

T (DEG.K.)	$-(G^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	47.622	7.9796	55.601	8.1433
200.00	53.254	8.3905	61.644	9.5840
273.15	55.937	8.8624	64.800	10.6815
298.15	56.721	9.0283	65.749	10.9950
300.00	56.777	9.0405	65.817	11.0169
400.00	59.464	9.6611	69.126	11.9545
500.00	61.678	10.1823	71.860	12.5335
600.00	63.573	10.6069	74.180	12.9002
700.00	65.235	10.9529	76.188	13.1422
800.00	66.717	11.2376	77.955	13.3087
900.00	68.055	11.4747	79.530	13.4273
1000.00	69.274	11.6745	80.949	13.5145
1100.00	70.395	11.8449	82.240	13.5804
1200.00	71.432	11.9918	83.424	13.6313
1300.00	72.397	12.1195	84.517	13.6713
1400.00	73.300	12.2315	85.531	13.7034
1500.00	74.147	12.3305	86.478	13.7294
1600.00	74.946	12.4186	87.364	13.7509
1700.00	75.701	12.4976	88.199	13.7688
1800.00	76.417	12.5686	88.986	13.7838
1900.00	77.099	12.6329	89.732	13.7966
2000.00	77.748	12.6914	90.440	13.8075

T (DEG.K.)	$(H^\circ-H^\circ_{298})$ (KCAL/MOL)	$-\Delta Hf$ (KCAL/MOL)	$-\Delta Gf$ (KCAL/MOL)	LOG Kf
0.00	-2.6918	111.49	111.49	INF
100.00	-1.8938	111.78	110.53	241.55
200.00	-1.0137	111.99	109.15	119.27
273.15	-0.2710	112.09	108.12	86.51
298.15	0.0000	112.10	107.70	78.95
300.00	0.0204	112.10	107.67	78.44
400.00	1.1727	112.16	106.19	58.02
500.00	2.3994	112.18	104.69	45.76
600.00	3.6724	112.18	103.20	37.59
700.00	4.9753	112.18	101.70	31.75
800.00	6.2983	112.16	100.20	27.37
900.00	7.6354	112.15	98.71	23.97
1000.00	8.9827	112.13	97.22	21.25
1100.00	10.3376	112.11	95.73	19.02
1200.00	11.6983	112.10	94.24	17.16
1300.00	13.0635	112.08	92.75	15.59
1400.00	14.4323	112.07	91.26	14.25
1500.00	15.8040	112.05	89.78	13.08
1600.00	17.1780	112.04	88.30	12.06
1700.00	18.5541	112.03	86.81	11.16
1800.00	19.9317	112.02	85.33	10.36
1900.00	21.3107	112.01	83.85	9.64
2000.00	22.6910	112.01	82.36	9.00

b. Data Used in the Statistical Calculations

M = 165.5968.

r(Te-F) = 1.87 Å; $\widehat{FTeF}$ = 100° (estimated values).

Symmetry = C_{2v}; σ = 2 ($TeCl_2$ structure[44] assumed).

$I_A I_B I_C$ = 1817.4 x 10^{-117} g^3 cm^6.

ω = 800, 630, and 420 cm^{-1} (estimated).

9. TeF Gas

a. Thermochemical Data. The standard enthalpy of formation of TeF(g) was estimated [as were $\Delta Hf°(SF,g)$ and $\Delta Hf°(SeF,g)$] by assuming that the enthalpies of the following decomposition reactions are the same:

$TeF_2(g) \rightarrow TeF(g) + F(g)$;

$TeF(g) \rightarrow Te(g) + F(g)$.

For the reactions

(1) $Te(c) + \frac{1}{2}F_2(g) \rightarrow TeF(g)$:

$\Delta Hf°$ = -20.8 ± 7.0 kcal mol^{-1}.

(2) $\frac{1}{2}Te_2(g) + \frac{1}{2}F_2(g) \rightarrow TeF(g)$:

ΔHf = -40.9 ± 7.1 kcal mol^{-1}.

Additional thermodynamic functions for TeF(g) are given in Table XXXIV.

b. Data Used in the Statistical Calculations

M = 146.5984.

r(Te-F) = 1.86 Å (estimated).

I = 9.4992 x 10^{-39} g cm^2.

ω = 623 cm^{-1}.[34]

TABLE XXXIV. Thermodynamic Properties of Tellurium Monofluoride

T (DEG.K.)	$-(G^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	42.699	6.9545	49.654	6.9755
200.00	47.541	7.0556	54.597	7.4170
273.15	49.762	7.2086	56.971	7.8230
298.15	50.396	7.2651	57.661	7.9385
300.00	50.441	7.2692	57.710	7.9465
400.00	52.562	7.4844	60.046	8.2841
500.00	54.252	7.6662	61.919	8.4858
600.00	55.664	7.8140	63.478	8.6105
700.00	56.877	7.9339	64.811	8.6916
800.00	57.944	8.0323	65.976	8.7468
900.00	58.894	8.1140	67.008	8.7858
1000.00	59.753	8.1827	67.936	8.8144
1100.00	60.536	8.2411	68.777	8.8358
1200.00	61.255	8.2914	69.546	8.8524
1300.00	61.920	8.3351	70.255	8.8654
1400.00	62.540	8.3733	70.913	8.8757
1500.00	63.118	8.4071	71.526	8.8842
1600.00	63.662	8.4371	72.099	8.8911
1700.00	64.174	8.4640	72.638	8.8968
1800.00	64.659	8.4882	73.147	8.9017
1900.00	65.118	8.5101	73.628	8.9058
2000.00	65.555	8.5300	74.085	8.9093

T (DEG.K.)	$(H^\circ - H^\circ_{298})$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG K_f
0.00	-2.1661	40.82	40.82	INF
100.00	-1.4706	40.86	41.05	89.71
200.00	-0.7550	40.89	41.19	45.01
273.15	-0.1970	40.90	41.32	33.06
298.15	0.0000	40.90	41.31	30.28
300.00	0.0147	40.90	41.32	30.10
400.00	0.8277	40.91	41.45	22.65
500.00	1.6670	40.92	41.59	18.18
600.00	2.5223	40.92	41.72	15.20
700.00	3.3877	40.93	41.85	13.07
800.00	4.2598	40.93	41.99	11.47
900.00	5.1365	40.94	42.12	10.23
1000.00	6.0166	40.95	42.25	9.23
1100.00	6.8991	40.96	42.38	8.42
1200.00	7.7836	40.97	42.51	7.74
1300.00	8.6695	40.98	42.63	7.17
1400.00	9.5566	40.99	42.76	6.68
1500.00	10.4446	41.01	42.88	6.25
1600.00	11.3334	41.02	43.01	5.88
1700.00	12.2228	41.04	43.13	5.54
1800.00	13.1127	41.06	43.26	5.25
1900.00	14.0031	41.07	43.38	4.99
2000.00	14.8938	41.09	43.50	4.75

10. Te_2F_{10} Gas

a. Thermochemical Data. The strength of the Te-Te bond in $Te_2F_{10}(g)$, i.e., the enthalpy of the reaction

$$Te_2F_{10}(g) \rightarrow 2TeF_5(g),$$

was estimated to be 34 ± 10 kcal mol^{-1} by the methods outlined in Section III.A.12.a.(2). (The stretching-force constant for the Te-Te bond was calculated from spectral data[70] to be 6.06 x 10^4 dyn cm^{-1}.) Substitution of this bond energy and the value $\Delta Hf°(TeF_5,g)$ = -277.2 ± 5.0 kcal mol^{-1} into the expression

$$\Delta Hf°(Te_2F_{10},g) = 2\Delta Hf°(TeF_5,g) - D(Te\text{-}Te)_{Te_2F_{10}}$$

yields

$$\Delta Hf°(Te_2F_{10},g) = -588 \pm 12 \text{ kcal mol}^{-1}.$$

For the reaction

$$Te_2(g) + 5F_2(g) = Te_2F_{10}(g):$$

$$\Delta Hf = -628.2 \pm 12 \text{ kcal mol}^{-1}.$$

Additional thermodynamic functions for $Te_2F_{10}(g)$ are given in Table XXXV.

b. Data Used in the Statistical Calculations

M = 445.1840.

r(Te-Te) = 3.02 ± 0.1 Å; r(Te-F) = 1.84 Å; $\widehat{FTeF}$ = 90°.

Symmetry = D_{4d}; σ = 8 (S_2F_{10} structure assumed).

$I_AI_BI_C$ = 6,121,700 x 10^{-117} g^3 cm^6.

ω = 726, 682, 475, 168, 50,* 752, 734, 468, 714(2), 468(2), 360(2), 800(2),* 670(2), 259(4), 670(2), 319(4), and 138(2) cm^{-1}.[70]

*Estimated by analogy with S_2F_{10}.

TABLE XXXV. Thermodynamic Properties of Ditellurium Decafluoride

T (DEG.K.)	$-(G^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ - H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0,00	0,000	0,0000	0,000	0,0000
100,00	58,287	12,3259	70,613	19,6418
200,00	69,228	20,2279	89,456	35,9681
273,15	76,357	25,6900	102,047	44,7896
298,15	78,681	27,3929	106,074	47,1557
300,00	78,851	27,5152	106,366	47,3189
400,00	87,605	33,3934	120,999	54,1385
500,00	95,571	37,9829	133,554	58,2076
600,00	102,827	41,5804	144,408	60,7398
700,00	109,460	44,4436	153,903	62,3944
800,00	115,551	46,7623	162,313	63,5248
900,00	121,173	48,6718	169,844	64,3271
1000,00	126,386	50,2682	176,654	64,9152
1100,00	131,242	51,6208	182,863	65,3582
1200,00	135,784	52,7804	188,565	65,6996
1300,00	140,050	53,7849	193,835	65,9681
1400,00	144,068	54,6631	198,732	66,1830
1500,00	147,867	55,4371	203,304	66,3574
1600,00	151,467	56,1242	207,591	66,5009
1700,00	154,888	56,7382	211,626	66,6204
1800,00	158,147	57,2901	215,437	66,7209
1900,00	161,258	57,7888	219,047	66,8062
2000,00	164,234	58,2415	222,476	66,8793

T (DEG.K.)	$(H^\circ - H^\circ_{298})$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG K_f
0,00	-8,1672	623,44	623,44	INF
100,00	-6,9346	626,45	607,68	1328,09
200,00	-4,1216	627,93	588,16	642,71
273,15	-1,1500	628,23	573,70	459,02
298,15	0,0000	628,20	568,49	416,72
300,00	0,0874	628,20	568,12	413,88
400,00	5,1902	627,82	548,14	299,49
500,00	10,8243	627,11	528,30	230,92
600,00	16,7811	626,20	508,62	185,26
700,00	22,9433	625,18	489,10	152,70
800,00	29,2427	624,10	469,73	128,33
900,00	35,6374	622,98	450,50	109,40
1000,00	42,1010	621,83	431,40	94,28
1100,00	48,6157	620,67	412,41	81,94
1200,00	55,1693	619,49	393,54	71,67
1300,00	61,7532	618,31	374,75	63,00
1400,00	68,3611	617,13	356,06	55,58
1500,00	74,9884	615,96	337,44	49,17
1600,00	81,6316	614,78	318,93	43,56
1700,00	88,2878	613,61	300,45	38,63
1800,00	94,9550	612,44	282,10	34,25
1900,00	101,6315	611,28	263,76	30,34
2000,00	108,3156	610,13	245,49	26,83

11. Te_2F_{10} Liquid

a. Boiling Point. 53°C.[71]

b. Vapor Pressure. English and Dale[71] give the following equation for the vapor pressure of $Te_2F_{10}(l)$:

$$\log P\ (\text{Torr}) = 9.200 - 2063.0/T\ (-33 \text{ to } 54°C).$$

This equation was used to calculate the vapor pressures in Table XXXVI.

c. Thermodynamic Data. For the reactions

(1) $Te_2F_{10}(l) \rightarrow Te_2F_{10}(g)$:

$\Delta Hv^\circ_{326} = 9.44$ kcal mol^{-1};[71]

$\Delta Sv^\circ_{326} = 29$ cal deg^{-1} mol^{-1};[71]

ΔHv°_{298} is estimated to be 9.8 ± 0.2 kcal mol^{-1}.

(2) $2Te(c) + 5F_2(g) \rightarrow Te_2F_{10}(l)$:

$\Delta Hf^\circ = -598 \pm 12$ kcal mol^{-1}.

D. Oxygen Fluorides

1. OF Gas (Oxygen Monofluoride)

a. Thermochemical Data. The enthalpy of formation of OF(g) was estimated by assuming that the strengths of the two O-F bonds in $OF_2(g)$ are equal. Consequently,

$$D(OF) = \tfrac{1}{2}\Delta Ha^\circ(OF_2) = \tfrac{1}{2}[\Delta Hf^\circ(O,g) + 2\Delta Hf^\circ(F,g) - \Delta Hf^\circ(OF_2,g)]$$

$$= \tfrac{1}{2}[59.6 + 2(18.9) - 5.86]$$

$$= 45.8 \text{ kcal mol}^{-1}.$$

Thus for the reaction

$\frac{1}{2}O_2(g) + \frac{1}{2}F_2(g) \rightarrow OF(g)$:

$\Delta Hf^\circ = 33 \pm 5$ kcal mol^{-1}.

Additional thermodynamic functions for OF(g) are given in Table XXXVII.

TABLE XXXVI. Vapor Pressure of Liquid Ditellurium Decafluoride

T(C)	P(TORR)	LOGP(TORR)	1/T(K)
-33.00	4.07	0.60954	4.164-003
-29.00	5.63	0.75028	4.096-003
-25.00	7.70	0.88648	4.030-003
-21.00	10.43	1.01836	3.966-003
-17.00	14.00	1.14613	3.904-003
-13.00	18.62	1.26996	3.844-003
-9.00	24.55	1.39004	3.786-003
-5.00	32.10	1.50654	3.729-003
-1.00	41.65	1.61962	3.674-003
3.00	53.63	1.72942	3.621-003
7.00	68.56	1.83609	3.570-003
11.00	87.05	1.93975	3.519-003
15.00	109.78	2.04053	3.470-003
19.00	137.58	2.13856	3.423-003
23.00	171.37	2.23394	3.377-003
27.00	212.21	2.32677	3.332-003
31.00	261.31	2.41716	3.288-003
35.00	320.04	2.50521	3.245-003
39.00	389.94	2.59100	3.204-003
43.00	472.73	2.67462	3.163-003
47.00	570.36	2.75615	3.124-003
51.00	684.96	2.83566	3.085-003

TABLE XXXVII. Thermodynamic Properties of Oxygen Monofluoride

T (DEG,K,)	$-(G^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0,00	0,000	0,0000	0,000	0,0000
100,00	36,607	6,9480	43,555	6,9552
200,00	41,426	6,9606	48,386	7,0219
273,15	43,601	7,0006	50,601	7,2167
298,15	44,215	7,0223	51,237	7,3026
300,00	44,258	7,0240	51,282	7,3091
400,00	46,294	7,1400	53,434	7,6630
500,00	47,901	7,2756	55,177	7,9594
600,00	49,240	7,4090	56,649	8,1810
700,00	50,391	7,5314	57,923	8,3427
800,00	51,404	7,6406	59,045	8,4612
900,00	52,310	7,7369	60,047	8,5495
1000,00	53,129	7,8217	60,951	8,6164
1100,00	53,879	7,8964	61,775	8,6681
1200,00	54,568	7,9624	62,531	8,7087
1300,00	55,208	8,0211	63,229	8,7411
1400,00	55,805	8,0735	63,878	8,7673
1500,00	56,363	8,1205	64,484	8,7888
1600,00	56,889	8,1629	65,052	8,8066
1700,00	57,385	8,2012	65,586	8,8215
1800,00	57,854	8,2360	66,090	8,8341
1900,00	58,301	8,2678	66,568	8,8449
2000,00	58,725	8,2969	67,022	8,8541

T (DEG,K,)	$(H^\circ-H^\circ_{298})$ (KCAL/MOL)	$-\Delta Hf$ (KCAL/MOL)	$-\Delta Gf$ (KCAL/MOL)	LOG Kf
0,00	-2,0937	-33,00	-33,00	INF
100,00	-1,3989	-33,00	-32,75	-71,57
200,00	-0,7016	-33,00	-32,50	-35,51
273,15	-0,1815	-33,00	-32,28	-25,83
298,15	0,0000	-33,00	-32,25	-23,64
300,00	0,0135	-33,00	-32,25	-23,49
400,00	0,7623	-33,01	-31,99	-17,48
500,00	1,5441	-33,02	-31,74	-13,87
600,00	2,3517	-33,04	-31,48	-11,47
700,00	3,1783	-33,05	-31,22	-9,75
800,00	4,0188	-33,06	-30,96	-8,46
900,00	4,8695	-33,06	-30,70	-7,45
1000,00	5,7280	-33,06	-30,44	-6,65
1100,00	6,5923	-33,06	-30,17	-5,99
1200,00	7,4612	-33,06	-29,91	-5,45
1300,00	8,3338	-33,05	-29,65	-4,98
1400,00	9,2092	-33,04	-29,39	-4,59
1500,00	10,0871	-33,03	-29,13	-4,24
1600,00	10,9669	-33,01	-28,87	-3,94
1700,00	11,8483	-32,99	-28,61	-3,68
1800,00	12,7311	-32,97	-28,35	-3,44
1900,00	13,6151	-32,95	-28,09	-3,23
2000,00	14,5000	-32,92	-27,84	-3,04

b. Data Used in the Statistical Calculations

M = 34.9978.

r(O-F) = 1.621 Å (calculated by Guggenheimer's rule[34]).

$I = 3.7894 \times 10^{-39}$ g cm^2.

$\omega = 1028$ cm^{-1}.[72]

2. OF_2 Gas

a. Critical Temperature. -58.0 ± 0.1°C.[73]

b. Critical Pressure. 48.9 atm.[73]

c. Critical Density. 0.553 g cm^{-3}.[73]

d. Critical Volume. 97.6 cm^3 mol^{-1}.[73]

e. Thermochemical Data. For the reaction

$\frac{1}{2}O_2(g) + F_2(g) \rightarrow OF_2(g)$:

$\Delta Hf° = 5.86 \pm 0.30$ kcal mol^{-1}.[74]

Additional thermodynamic functions for $OF_2(g)$ are given in Table XXXVIII.

f. Data Used in the Statistical Calculations. OF_2 has a non-linear structure.[75]

M = 53.9962.

r(O-F) = 1.4124 Å; $\widehat{FOF}$ = 103.3°.

Symmetry = C_{2v}; $\sigma = 2$.

$I_A I_B I_C = 101.98 \times 10^{-117}$ g^3 cm^6.

ω = 929, 826, and 461 cm^{-1}.[76]

3. OF_2 Liquid

a. Freezing Point. -223.8°C.[77]

b. Boiling Point. -145.3°C.[73]

TABLE XXXVIII. Thermodynamic Properties of Oxygen Difluoride

T (DEG,K,)	$-(G^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0,00	0,000	0,0000	0,000	0,0000
100,00	41,417	7,9662	49,384	8,0665
200,00	47,005	8,2445	55,250	9,0991
273,15	49,626	8,6018	58,228	10,0515
298,15	50,385	8,7362	59,121	10,3556
300,00	50,439	8,7462	59,186	10,3774
400,00	53,030	9,2865	62,316	11,3793
500,00	55,156	9,7782	64,934	12,0659
600,00	56,977	10,2005	67,178	12,5279
700,00	58,577	10,5570	69,134	12,8444
800,00	60,007	10,8576	70,865	13,0675
900,00	61,301	11,1126	72,414	13,2292
1000,00	62,484	11,3306	73,814	13,3495
1100,00	63,573	11,5184	75,091	13,4411
1200,00	64,582	11,6817	76,264	13,5123
1300,00	65,523	11,8248	77,348	13,5686
1400,00	66,404	11,9510	78,355	13,6140
1500,00	67,232	12,0632	79,295	13,6509
1600,00	68,014	12,1634	80,177	13,6814
1700,00	68,754	12,2535	81,008	13,7069
1800,00	69,457	12,3348	81,792	13,7283
1900,00	70,126	12,4087	82,534	13,7466
2000,00	70,764	12,4759	83,240	13,7623

T (DEG,K,)	$(H^\circ-H^\circ_{298})$ (KCAL/MOL)	$-\Delta H_f$ (KCAL/MOL)	$-\Delta G_f$ (KCAL/MOL)	LOG K_f
0,00	-2,6047	-6,40	-6,40	INF
100,00	-1,8081	-6,16	-7,36	-16,08
200,00	-0,9558	-5,96	-8,64	-9,44
273,15	-0,2551	-5,87	-9,59	-7,68
298,15	0,0000	-5,86	-9,98	-7,32
300,00	0,0192	-5,86	-10,01	-7,29
400,00	1,1099	-5,82	-11,40	-6,23
500,00	2,2844	-5,83	-12,79	-5,59
600,00	3,5156	-5,85	-14,18	-5,17
700,00	4,7852	-5,88	-15,57	-4,86
800,00	6,0814	-5,91	-16,95	-4,63
900,00	7,3966	-5,94	-18,33	-4,45
1000,00	8,7259	-5,97	-19,71	-4,31
1100,00	10,0656	-6,00	-21,08	-4,19
1200,00	11,4134	-6,03	-22,45	-4,09
1300,00	12,7675	-6,05	-23,82	-4,00
1400,00	14,1268	-6,07	-25,18	-3,93
1500,00	15,4901	-6,09	-26,55	-3,87
1600,00	16,8567	-6,10	-27,91	-3,81
1700,00	18,2262	-6,11	-29,27	-3,76
1800,00	19,5980	-6,11	-30,63	-3,72
1900,00	20,9717	-6,12	-32,00	-3,68
2000,00	22,3472	-6,12	-33,36	-3,65

c. Vapor Pressure

$$\log P\ (\text{Torr}) = 7.224 - 555.42/T;^{78} \quad (14)$$

$$\log P\ (\text{Torr}) = 7.3892 - 578.64/T.^{79} \quad (15)$$

Equation 14 was used to generate the vapor pressures given in Table XXXIX.

d. Thermochemical Data. For the reactions

(1) $OF_2(l) \rightarrow OF_2(g)$:

$\Delta Hv^\circ_{128} = 2.65 \pm 0.1$ kcal mol^{-1};[79]

$\Delta Sv^\circ_{128} = 20.65$ cal deg^{-1} mol^{-1}.[79]

(2) $\frac{1}{2}O_2(g) + F_2(g) \rightarrow OF_2(l)$:

$\Delta Hf^\circ \simeq 3$ kcal mol^{-1}.

4. O_2F_2 Gas

a. Thermochemical Data. For the reaction

$O_2(g) + F_2(g) \rightarrow O_2F_2(g)$:

$\Delta Hf^\circ = 4.3 \pm 0.3$ kcal mol^{-1}.[3,80]

Additional thermodynamic functions can be found in Table XL.

b. Data Used in the Statistical Calculations. O_2F_2 has a non-planar FOOF structure[81] and was assumed to have a trans configuration.

$M = 69.9956$.

$r(O\text{-}F) = 1.575 \pm 0.003$ Å; $r(O\text{-}O) = 1.217 \pm 0.003$ Å.

$\widehat{FOO} = 109.5°$; dihedral angle $= 87.5 \pm 0.5°$.

Symmetry $= C_{2v}$; $\sigma = 2$.

$I_A I_B I_C = 897.86 \times 10^{-117}$ g^3 cm^6.

$\omega = 1024(2), 628(2), 463$, and 180 cm^{-1}.[82]

TABLE XXXIX. Vapor Pressure of Liquid Oxygen Difluoride

T(C)	P(TORR)	LOGP(TORR)	1/T(K)
-195,00	1.31	0,11710	1.280-002
-192,00	2,40	0,37984	1.232-002
-189,00	4,21	0,62384	1.188-002
-186,00	7,10	0,85105	1.147-002
-183,00	11,56	1,06314	1.109-002
-180,00	18.26	1,26156	1.074-002
-177,00	28,03	1,44760	1.040-002
-174,00	41,92	1,62238	1.009-002
-171,00	61,22	1,78690	9.790-003
-168,00	87,50	1,94203	9.510-003
-165,00	122,62	2,08856	9.246-003
-162,00	168.72	2,22717	8.997-003
-159,00	228,30	2,35850	8.760-003
-156,00	304,16	2,48310	8.536-003
-153,00	399,46	2,60148	8.323-003
-150,00	517,71	2,71409	8.120-003
-147,00	662,74	2,82135	7.927-003

TABLE XL. Thermodynamic Properties of Dioxygen Difluoride

T (DEG.K.)	$-(G^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0,00	0.000	0,0000	0,000	0,0000
100,00	44.508	8,3874	52,895	9,2696
200,00	50.614	9,3816	59,995	11,5694
273,15	53.658	10,2010	63,859	13,2763
298,15	54.564	10,4810	65,045	13,7969
300,00	54.629	10,5015	65,130	13,8339
400,00	57.797	11,5581	69,356	15,5209
500,00	60.478	12,4737	72,952	16,6771
600,00	62.822	13,2439	76,066	17,4624
700,00	64.914	13,8876	78,801	18,0054
800,00	66.804	14,4277	81,232	18,3909
900,00	68.531	14,8845	83,415	18,6719
1000,00	70.120	15,2742	85,394	18,8819
1100,00	71.592	15,6098	87,201	19,0423
1200,00	72.963	15,9013	88,864	19,1674
1300,00	74.246	16,1565	90,402	19,2666
1400,00	75.451	16,3816	91,833	19,3465
1500,00	76.589	16,5815	93,170	19,4117
1600,00	77.664	16,7601	94,425	19,4656
1700,00	78.685	16,9206	95,606	19,5107
1800,00	79.657	17,0656	96,722	19,5487
1900,00	80.583	17,1971	97,780	19,5810
2000,00	81.468	17,3171	98,785	19,6088

T (DEG.K.)	$(H^\circ-H^\circ_{298})$ (KCAL/MOL)	$-\Delta Hf$ (KCAL/MOL)	$-\Delta Gf$ (KCAL/MOL)	LOG Kf
0,00	-3,1249	-5,36	-5,36	INF
100,00	-2,2862	-4,81	-7,73	-16,89
200,00	-1,2486	-4,45	-10,80	-11,81
273,15	-0,3385	-4,32	-13,09	-10,48
298,15	0,0000	-4,30	-13,96	-10,23
300,00	0,0256	-4,30	-14,02	-10,21
400,00	1,4983	-4,29	-17,27	-9,43
500,00	3,1120	-4,37	-20,50	-8,96
600,00	4,8214	-4,49	-23,72	-8,64
700,00	6,5964	-4,63	-26,92	-8,40
800,00	8,4173	-4,79	-30,09	-8,22
900,00	10,2711	-4,96	-33,24	-8,07
1000,00	12,1493	-5,12	-36,37	-7,95
1100,00	14,0459	-5,29	-39,49	-7,85
1200,00	15,9566	-5,45	-42,59	-7,76
1300,00	17,8785	-5,61	-45,68	-7,68
1400,00	19,8093	-5,77	-48,76	-7,61
1500,00	21,7473	-5,93	-51,82	-7,55
1600,00	23,6913	-6,08	-54,87	-7,50
1700,00	25,6401	-6,23	-57,92	-7,45
1800,00	27,5932	-6,37	-60,96	-7,40
1900,00	29,5497	-6,51	-63,99	-7,36
2000,00	31,5092	-6,64	-67,01	-7,32

5. O_2F_2 Liquid

a. Freezing Point. 109.7°K.[83]

b. Boiling Point. 216°K (dec).[83]

c. Vapor Pressure. The vapor pressures in Table XLI have been calculated from the following equation of Ruff and Menzel:[83]

$$\log P\ (\text{Torr}) = 7.515 - 100/T\ (110 \text{ to } 173°K).$$

d. Thermochemical Data. For the reactions

(1) $O_2F_2(l) \rightarrow O_2F_2(g)$:

$\Delta Hv^{\circ}_{216} = 4.586$ kcal mol^{-1};[82]

$\Delta Sv^{\circ}_{216} = 21.22$ cal deg^{-1} mol^{-1}.

(2) $O_2(g) + F_2(g) \rightarrow O_2F_2(l)$:

$\Delta Hf^{\circ}_{216} \simeq -0.2$ kcal mol^{-1}.

6. O_3F_2 Gas

a. Thermochemical Data. For the reaction

$\frac{3}{2} O_2(g) + F_2(g) \rightarrow O_3F_2(g)$:

$\Delta Hf^{\circ} = 3.8 \pm 0.75$ kcal mol^{-1}.[3,80]

Additional thermodynamic functions for $O_3F_2(g)$ are given in Table XLII.*

b. Data Used in the Statistical Calculations. O_3F_2 was assumed to have a rigid, planar, zig-zag structure.**

M = 85.9950.

r(O-F) = 1.5 Å; r(O-O) = 1.2 Å (estimated values).

$\widehat{FOO} = 104°$; $\widehat{OOO} = 104°$ (estimated values).

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*Because of the many assumptions made regarding the structure of O_3F_2, the moment of inertia and the calculated thermodynamic functions are probably somewhat inaccurate.

**From epr spectral studies of a solidified O_3F_2-$CClF_3$ mixture,[84] it appears that O_3F_2 may have the structure of an asymmetric top.

TABLE XLI. Vapor Pressure of Liquid Dioxygen Difluoride

T(C)	P(TORR)	LOGP(TORR)	1/T(K)
-163,00	4047129,23	6,60715	9.079-003
-160,00	4277769,80	6,63122	8.838-003
-157,00	4508627,33	6,65404	8.610-003
-154,00	4739382,70	6,67572	8.393-003
-151,00	4969748,66	6,69633	8.187-003
-148,00	5199467,28	6,71596	7.990-003
-145,00	5428307,68	6,73466	7.803-003
-142,00	5656063,76	6,75251	7.625-003
-139,00	5882552,13	6,76957	7.454-003
-136,00	6107610,16	6,78587	7.291-003
-133,00	6331094,16	6,80148	7.135-003
-130,00	6552877,73	6,81643	6.986-003
-127,00	6772850,16	6,83077	6.842-003
-124,00	6990915,07	6,84453	6.705-003
-121,00	7206989,04	6,85775	6.572-003
-118,00	7421000,41	6,87046	6.445-003
-115,00	7632888,23	6,88269	6.323-003
-112,00	7842601,18	6,89446	6.205-003
-109,00	8050096,69	6,90580	6.092-003
-106,00	8255340,08	6,91673	5.983-003
-103,00	8458303,79	6,92728	5.877-003
-100,00	8658966,71	6,93747	5.775-003

TABLE XLII. Thermodynamic Properties of Trioxygen Difluoride

T (DEG.K.)	$-(G^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0.00	0.000	0.0000	0.000	0.0000
100.00	48.865	8.6796	57.545	10.3712
200.00	55.463	10.6506	66.113	14.8704
273.15	59.009	12.1677	71.176	17.6364
298.15	60.096	12.6593	72.755	18.4092
300.00	60.174	12.6949	72.869	18.4630
400.00	64.075	14.4492	78.524	20.7806
500.00	67.457	15.8720	83.329	22.2356
600.00	70.456	17.0161	87.472	23.1724
700.00	73.151	17.9432	91.094	23.7986
800.00	75.598	18.7038	94.302	24.2332
900.00	77.839	19.3364	97.175	24.5450
1000.00	79.905	19.8694	99.774	24.7754
1100.00	81.820	20.3237	102.144	24.9500
1200.00	83.606	20.7151	104.321	25.0853
1300.00	85.278	21.0555	106.333	25.1920
1400.00	86.849	21.3541	108.203	25.2776
1500.00	88.332	21.6181	109.950	25.3473
1600.00	89.735	21.8530	111.588	25.4047
1700.00	91.066	22.0634	113.129	25.4526
1800.00	92.332	22.2528	114.585	25.4930
1900.00	93.540	22.4243	115.964	25.5272
2000.00	94.694	22.5802	117.275	25.5566

T (DEG.K.)	$(H^\circ-H^\circ_{298})$ (KCAL/MOL)	$-\Delta Hf$ (KCAL/MOL)	$-\Delta Gf$ (KCAL/MOL)	LOG Kf
0.00	-3.7744	-5.25	-5.25	INF
100.00	-2.9064	-4.38	-8.90	-19.46
200.00	-1.6442	-3.90	-13.65	-14.92
273.15	-0.4507	-3.79	-17.16	-13.73
298.15	0.0000	-3.80	-18.47	-13.54
300.00	0.0341	-3.80	-18.56	-13.52
400.00	2.0053	-3.94	-23.46	-12.82
500.00	4.1616	-4.19	-28.32	-12.38
600.00	6.4353	-4.50	-33.12	-12.06
700.00	8.7859	-4.83	-37.86	-11.82
800.00	11.1887	-5.17	-42.55	-11.62
900.00	13.6284	-5.51	-47.21	-11.46
1000.00	16.0950	-5.85	-51.82	-11.33
1100.00	18.5817	-6.19	-56.40	-11.21
1200.00	21.0837	-6.52	-60.95	-11.10
1300.00	23.5978	-6.85	-65.47	-11.01
1400.00	26.1214	-7.17	-69.97	-10.92
1500.00	28.6528	-7.48	-74.45	-10.85
1600.00	31.1904	-7.79	-78.90	-10.78
1700.00	33.7334	-8.09	-83.34	-10.71
1800.00	36.2807	-8.38	-87.75	-10.65
1900.00	38.8318	-8.67	-92.15	-10.60
2000.00	41.3860	-8.95	-96.54	-10.55

$\sigma = 2.$

$I_A I_B I_C = 3990.2 \times 10^{-117}\ g^3\ cm^6.$

$\omega = 930(2), 463(2), 628(2), 200(2)$, and $500\ cm^{-1}$ (est).

7. O_3F_2 Liquid

a. Freezing Point. 83-84°K.[82]

b. Boiling Point. 213°K.[82]

c. Vapor Pressure. The following equation was used to generate the vapor-pressure data given in Table XLIII:[82]

$$\log P\ (\text{Torr}) = 6.1343 - 675.57/T\ (79 \text{ to } 114°K).$$

TABLE XLIII. Vapor Pressure of Liquid Trioxygen Difluoride

T(C)	P(TORR)	LOGP(TORR)	1/T(K)
-194,00	0,00	-2,40101	1.263-002
-192,00	0,01	-2,19065	1.232-002
-190,00	0,01	-1,99041	1.203-002
-188,00	0,02	-1,79958	1.174-002
-186,00	0,02	-1,61751	1.147-002
-184,00	0,04	-1,44360	1.122-002
-182,00	0,05	-1,27733	1.097-002
-180,00	0,08	-1,11820	1.074-002
-178,00	0,11	-0,96575	1.051-002
-176,00	0,15	-0,81959	1.029-002
-174,00	0,21	-0,67932	1.009-002
-172,00	0,29	-0,54459	9.886-003
-170,00	0,38	-0,41509	9.695-003
-168,00	0,51	-0,29052	9.510-003
-166,00	0,68	-0,17060	9.333-003
-164,00	0,88	-0,05507	9.162-003
-162,00	1,14	0,05630	8.997-003
-160,00	1,46	0,16373	8.838-003

d. Thermochemical Data. For the reactions

(1) $O_3F_2(l) \rightarrow O_3F_2(g)$:

$\Delta Hv^\circ_{213} = 4.581 \pm 0.2$ kcal mol^{-1};[82]

$\Delta Sv^\circ_{213} = 21.51$ cal deg^{-1} mol^{-1}.

(2) $\frac{3}{2}O_2(g) + F_2(g) \rightarrow O_3F_2(l)$:

$\Delta Hf^\circ_{213} = -0.71 \pm 0.81$ kcal mol^{-1}.[80]

8. O_2F Gas

a. Thermochemical Data. For the reaction

$O_2(g) + \frac{1}{2}F_2(g) \rightarrow O_2F(g)$:

$\Delta Hf^\circ = 3.5 \pm 5$ kcal mol^{-1}.[85-87]

Additional thermodynamic functions for $O_2F(g)$ are given in Table XLIV.

b. Data Used in the Statistical Calculations

$M = 50.9972$.

$r(F\text{-}O) = 1.412$ Å;[88,89] $r(O\text{-}O) = 1.22$ Å.[88,89]

$\widehat{FOO} = 100°$.[88,89]

$\sigma = 1$.

$I_A I_B I_C = 54.821 \times 10^{-117}$ g^3 cm^6.

$\omega = 1495$, 585, and 376 cm^{-1}.[90-92]

TABLE XLIV. Thermodynamic Properties of Dioxygen Monofluoride

T (DEG,K,)	$-(G^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	$(H^\circ-H^\circ_0)/T$ (CAL/DEG/MOL)	S° (CAL/DEG/MOL)	C°_p (CAL/DEG/MOL)
0,00	0,000	0,0000	0,000	0,0000
100,00	43,392	8,0007	51,392	8,2422
200,00	49,059	8,4606	57,520	9,6095
273,15	51,759	8,8792	60,638	10,3944
298,15	52,542	9,0154	61,558	10,6099
300,00	52,598	9,0253	61,623	10,6250
400,00	55,264	9,5164	64,780	11,3183
500,00	57,433	9,9314	67,365	11,8422
600,00	59,276	10,2851	69,561	12,2469
700,00	60,885	10,5886	71,473	12,5588
800,00	62,316	10,8505	73,167	12,7994
900,00	63,606	11,0779	74,686	12,9860
1000,00	64,785	11,2763	76,062	13,1322
1100,00	65,868	11,4505	77,319	13,2481
1200,00	66,871	11,6043	78,476	13,3410
1300,00	67,806	11,7409	79,547	13,4163
1400,00	68,680	11,8628	80,543	13,4781
1500,00	69,503	11,9723	81,475	13,5293
1600,00	70,279	12,0710	82,350	13,5721
1700,00	71,013	12,1603	83,173	13,6082
1800,00	71,711	12,2417	83,952	13,6390
1900,00	72,374	12,3159	84,690	13,6653
2000,00	73,008	12,3840	85,392	13,6881

T (DEG,K,)	$(H^\circ-H^\circ_{298})$ (KCAL/MOL)	$-\Delta Hf$ (KCAL/MOL)	$-\Delta Gf$ (KCAL/MOL)	LOG KF
0,00	-2,6880	-3,94	-3,94	INF
100,00	-1,8879	-3,70	-4,74	-10,35
200,00	-0,9956	-3,55	-5,84	-6,38
273,15	-0,2626	-3,50	-6,64	-5,32
298,15	0,0000	-3,50	-6,98	-5,12
300,00	0,0196	-3,50	-7,00	-5,10
400,00	1,1186	-3,50	-8,17	-4,46
500,00	2,2778	-3,53	-9,33	-4,08
600,00	3,4831	-3,56	-10,49	-3,82
700,00	4,7241	-3,60	-11,64	-3,63
800,00	5,9925	-3,64	-12,79	-3,49
900,00	7,2821	-3,67	-13,93	-3,38
1000,00	8,5883	-3,71	-15,07	-3,29
1100,00	9,9076	-3,75	-16,20	-3,22
1200,00	11,2372	-3,78	-17,33	-3,16
1300,00	12,5752	-3,81	-18,46	-3,10
1400,00	13,9200	-3,84	-19,59	-3,06
1500,00	15,2704	-3,86	-20,71	-3,02
1600,00	16,6256	-3,88	-21,83	-2,98
1700,00	17,9846	-3,90	-22,96	-2,95
1800,00	19,3470	-3,91	-24,08	-2,92
1900,00	20,7123	-3,92	-25,20	-2,90
2000,00	22,0800	-3,92	-26,32	-2,88

APPENDIX

Computer Program for Calculation of Ideal Gas Thermodynamic Functions

1. Title

Calculation of Thermodynamic Functions of Gases.

2. Program Number

43E7152.

3. Description of the Problem

The program will produce a table of functions which represent certain thermodynamic properties of an ideal gas. For a detailed description of these functions, see Section 9 of this appendix.

4. Machine

3600-FORTRAN SCOPE.

5. Running Time

<5 sec per case.

6. Input Information Required

Card Type	No. of Cards	Format	Contents of Card
1	1	16	NEL = the number of elements in basic H°, S° table dictionary.
2	23	F12.2, 2F12.3	T_i, $H^\circ_{i,n}$, $S^\circ_{i,n}$, $(i = 1, 2, \ldots, 23)$. There are NEL blocks of cards of Type 2, each block corresponding to a different element, which is denoted by a subscript n $(n = 1, 2, \ldots, NEL)$. For each block, the program will check to be sure that $T_1 = 0$, $T_2 = 100$, $T_3 = 200$, $T_4 = 273.15$, $T_5 = 298.15$, and $T_k = (k-3) \cdot 100$ for $k = 6, 7, \ldots, 23$.
3	1	9A8	A 72-character label, with 1 in column 1, which identifies the gas under consideration.
4	1	2I6	NOA = the number of elements in the gas; Z = a value used in $-(G^\circ - H^\circ_0)/T$ and S° to allow for electron-spin degeneracy.

Card Type	No. of Cards	Format	Contents of Card
5	$\left[\frac{NOA+11}{12}\right]$	12I6	NOA values of K_n, where K_n is a subscript designating which element is in the gas. These values should appear six to a card, or less on the last card.
6	1	16	NFV = the number of vibrational frequencies.
7	$\left[\frac{NFV+5}{6}\right]$	6F12.4	FV_i (i = 1, NFV), six values to a card, or less on the last card.
8	$\left[\frac{NOA+4}{4}\right]$	4E20.9	σ, M_i (i = 1, 2, NOA), four values to a card, or less on last card.
9	1	16	NC = the number of atoms in the gas ($NC \geq 2$).
10	NC	4F12.4	X_i, Y_i, Z_i, W_i (i = 1, 2, ..., NC).
11	1	F12.4	ΔHf.

Input card Types 1 and 2 are input into the computer at the start of the run. Card Types 3 through 11 define a particular gas. As many gases as desired can be processed during the run as long as all the elements involved have been defined by the information of card Type 2 at the start of the run.

7. Possible Output

a. A listing of information which is input on card Type 2.

b. A listing of T_i, H_i°, and S_i° for each element defined by input Type 5.

c. A listing of the information defined by card Types 7, 8, 10, and 11.

d. A printout of the title given by input card Type 3.

e. A five-column labeled listing of T, $-(G^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, S°, and C_p°.

f. A five-column labeled listing of T, $(H^\circ - H_{298}^\circ)$, $-\Delta Hf$, $-\Delta Gf$, and LOG Kf.

g. Molecular weight of gas = M_w.

h. Symmetry number = σ.

i. Product of moments of inertia.

j. The results of four least-squares fits.

8. Special Features, Restrictions, or Program Limitations

a. Only 23 fixed temperatures can be processed.

b. The program will not handle more than 50 elements correctly.

9. Equations Used

a. Product of Moments of Inertia

This value is given in the output (Item 9) and is denoted in the code by EYE.

The equations use Avogadro's number, $A = 6.02252 \cdot 10^{23}$, and

$$M_w = \sum_{i=1}^{NC} W_i,$$

where NC and W_i are given by input (card Types 9 and 10).

If NC = 2,

$$EYE = \left(\frac{W_1 W_2}{M_w}\right)\left(\frac{X_2^2}{10^{16}A}\right).$$

If NC > 2,

$$EYE = \frac{\begin{vmatrix} I_{xx} & -I_{xy} & -I_{xz} \\ -I_{xy} & I_{yy} & -I_{yz} \\ -I_{xz} & -I_{yz} & I_{zz} \end{vmatrix}}{(10^{16}A)^3},$$

where

$$I_{xx} = \sum_{i=1}^{NC} (Y_i^2 + Z_i^2)\, W_i - \frac{\left(\sum_1^{NC} W_i Y_i\right)^2 + \left(\sum_1^{NC} W_i Z_i\right)^2}{M_w},$$

$$I_{yy} = \sum_{i=1}^{NC} (X_i^2 + Z_i^2)\, W_i - \frac{\left(\sum_1^{NC} W_i X_i\right)^2 + \left(\sum_1^{NC} W_i Z_i\right)^2}{M_w},$$

$$I_{zz} = \sum_{i=1}^{NC} (X_i^2 + Y_i^2)\, W_i - \frac{\left(\sum_1^{NC} W_i X_i\right)^2 + \left(\sum_1^{NC} W_i Y_i\right)^2}{M_w},$$

$$I_{xy} = \sum_1^{NC} W_i X_i Y_i - \frac{\sum_{i=1}^{NC} W_i X_i \sum_{i=1}^{NC} W_i Y_i}{M_w},$$

$$I_{yz} = \sum_{i=1}^{NC} W_i Y_i Z_i - \frac{\sum_{i=1}^{NC} W_i Y_i \sum_{i=1}^{NC} W_i Z_i}{M_w},$$

and

$$I_{xz} = \sum_{i=1}^{NC} W_i X_i Z_i - \frac{\sum_{i=1}^{NC} W_i X_i \sum_{i=1}^{NC} W_i Z_i}{M_w}.$$

b. <u>-(Gibbs Energy Function)</u>

This is labeled $-(G^\circ - H_0^\circ)/T$ in the output.

If NC = 2,

$$-(G^\circ - H_0^\circ)/T = 6.863426 \log M_w - 8.005804 + 11.439043 \log T$$
$$-4.575617 \log (\beta_T \sigma) + 0.0457074\beta_T^2 + 0.953038\beta_T$$
$$+ 1.98717 \sum_{j=1}^{NFV} \{-\ln [1 - \exp(-1.43879 FV_j/T)]\}$$
$$+ 1.98717 \ln Z$$

where $\beta_T = 2.799076 \cdot 10^{-39}/(T \cdot EYE)$, and FV_j are given by input data Type 7.

If NC > 2,

$$-(G^\circ - H_0^\circ)/T = 18.302469 \log T + 2.287809 \log (EYE \cdot 10^{117} M_w^3/\sigma^2)$$
$$-10.297926 + 1.98717 \sum_{j=1}^{NFV} \{-\ln [1 - \exp(-1.43879 FV_j/T)]\}$$
$$+ 1.98717 \ln Z.$$

c. Enthalpy Function

This is labeled $(H^\circ - H_0^\circ)/T$ in the output.

If NC > 2,

$$(H^\circ - H_0^\circ)/T = 7.948662 + 1.98717 \sum_{j=1}^{NFV} \frac{-1.43879FV_j}{T[\exp(-1.43879FV_j/T) - 1]}.$$

If NC = 2,

$$(H^\circ - H_0^\circ)/T = 6.955079 - 0.0914148\beta_T^2 - 0.953038\beta_T$$

$$+ 1.98717 \sum_{j=1}^{NFV} \frac{-1.43879FV_j}{T[\exp(-1.43879FV_j/T) - 1]}.$$

d. Entropy

This is labeled S° in the output.

S° = -(Gibbs Energy Function) + Enthalpy Function.

e. Heat Capacity

This is labeled C_p° in the output.

If NC = 2,

$$C_p^\circ = 6.955079 + 0.0914148\beta_T^2$$

$$+ 1.98717 \sum_{j=1}^{NFV} \left\{ \frac{-1.43879FV_j}{T[\exp(-1.43879FV_j/T) - 1]} \right\}^2 \exp(FV_j/T).$$

If NC > 2,

$$C_p^\circ = 7.948662 + 1.98717 \sum_{j=1}^{NFV} \left\{ \frac{-1.43879FV_j}{T[\exp(-1.43879FV_j/T) - 1]} \right\}^2 \exp(FV_j/T).$$

f. Enthalpy

This is labeled $H^\circ - H_{298}^\circ$ in the output and is equal to (T/1000)(Enthalpy Function at T) - 0.29815 (Enthalpy Function at 298.15°K).

g. -(Enthalpy of Formation)

This is labeled $-\Delta Hf$ in the output.

$$-\Delta Hf = -\left(\text{Enthalpy} - \sum_{j=1}^{NOA} M_j H^\circ_{knj} + \Delta H\right)_i + \left(\text{Enthalpy} - \sum_{j=1}^{NOA} M_j H^\circ_{knj}\right)_5 .$$

The subscripts i and 5 refer to the ith and 5th temperature values. The M_j values are taken from input (Type 8) and the values of H°_{knj} are defined from input Types 2 and 5.

h. -(Gibbs Energy of Formation)

This is labeled $-\Delta Gf$ in the output.

$$-\Delta Gf = -(\text{Enthalpy of Formation}) + \left(\text{Entropy} - \sum_{j=1}^{NOA} M_j S^\circ_{knj}\right) \frac{T}{1000} .$$

The S°_{knj} values are defined from input Types 2 and 5.

i. Log (Equilibrium Constant of Formation)

This is labeled LOG Kf in the output.

LOG Kf = -1000(Gibbs Energy of Formation)/(4.575617T).

j. Least-squares Fitting Procedure

The values $H^\circ_T - H^\circ_{298}$, defined above, are fitted by minimizing

$$g_i = \sum_{k=s}^{23} \left[f_i(T_k) - 1000(H^\circ - H^\circ_{298})_k\right]^2 \qquad (i = 1, 2, 3, 4),$$

subject to the conditions that

$$f_i(T) = 0$$

and

$$\frac{\partial f_i(T)}{\partial T} = C^\circ_p = \text{heat capacity at } T = 298.15.$$

We use four methods:

$$f_1(T) = aT + bT^2 + c/T + d;$$

$$f_2(T) = aT + bT^2 + c/T + d + eT^3;$$

$$f_3(T) = aT + bT^2 + c/T + d + eT^{5/2};$$

and

$$f_4(T) = aT + bT^{5/2} + c/T + d.$$

In each case, we determine c and d by using the above conditions and obtain

$$f_1(T) = \alpha(T) \cdot a + \beta(T) \cdot b + \partial(T),$$

$$f_2(T) = \alpha(T) \cdot a + \beta(T) \cdot b + \Delta(T) \cdot e + \partial(T),$$

$$f_3(T) = \alpha(T) \cdot a + \beta(T) \cdot b + \pi(T) \cdot e + \partial(T),$$

and

$$f_4(T) = \alpha(T) \cdot a + \pi(T) \cdot b + \partial(T),$$

where

$$\alpha(T) = T + (298.15)^2/T - 2(298.15),$$

$$\beta(T) = T^2 + 2(298.15)^3/T - 3(298.15)^2,$$

$$\partial(T) = C_p^\circ \cdot 298.15(1 - 298.15/T),$$

$$\Delta(T) = T^3 + 3(298.15)^4/T - 4(298.15)^3,$$

and

$$\pi(T) = T^{5/2} + (298.15)^{5/2} [2.5(298.15/T) - 3.5].$$

In Methods 1 and 4, a and b are determined from the linear system of equations

$$\frac{\partial g_m}{\partial a} = \frac{\partial g_m}{\partial b} = 0 \qquad (m = 1, 4).$$

In Methods 2 and 3, a, b, and c are obtained from the linear system of equations

$$\frac{\partial g_m}{\partial a} = \frac{\partial g_m}{\partial b} = \frac{\partial g_m}{\partial e} = 0 \qquad (m = 2, 3).$$

Finally, we have

$$c = (298.15)^2[a + 2b(298.15) - C_p^\circ]$$

and

$$d = 298.15[-2a - 3b(298.15) + C_p^\circ] \text{ for Method 1;}$$

$$c = (298.15)^2[a + 2b(298.15) - C_p^\circ + 3e(298.15)^2]$$

and

$$d = 298.15[-2a - 3b(298.15) - C_p^\circ - 4e(298.15)^2] \text{ for Method 2;}$$

$$c = (298.15)^2[a + 2b(298.15) - C_p^\circ + 2.5e(298.15)^{3/2}$$

and

$$d = 298.15[-2a - 3b(298.15) + C_p^\circ - 3.5e(298.15)^{3/2}] \text{ for Method 3;}$$

$$c = (298.15)^2[a + 2.5b(298.15)^{3/2} - C_p^\circ]$$

and

$$d = 298.15[-2a - 3.5b(298.15)^{3/2} + C_p^\circ] \text{ for Method 4.}$$

For each method, the program will print the values a, b, c, d, and e when applicable, followed by an unlabeled six-column printout containing

T_k,

observed $1000(H^\circ - H_{298}^\circ)_k$,

calculated $1000(H^\circ - H_{298}^\circ)_k$,

observed - calculated $1000(H^\circ - H_{298}^\circ)_k$,

square of preceding difference,

and

present error in calculated $1000(H^\circ - H_{298}^\circ)_k$.

In addition, the program will also output labeled values of the standard deviation and average percentage error.

```
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      PROGRAM E7152
      COMMON JUMP
      DIMENSION T(23),HZMHZZ(23,50),SZ(23,50),X(50),Y(50),Z(50),W(50)
     X,COL(23,9),FV(50),DELST(23),XMY(23),EM(50),CEMP(23),TAY(23),ARA(23
     X),LAB(9),KN(50)
 4000 FORMAT (F12.2,2F12.3)
 4001 FORMAT (12I6)
 4002 FORMAT(*1INPUT,Z=*I1)
 4003 FORMAT(*0COORDINATE POSITIONS*)
 4004 FORMAT(6F12.4)
 4005 FORMAT (4E20.9)
 4006 FORMAT (* TEMPERATURE INPUT IS OFF*)
 4007 FORMAT (F14.2,F14.4,F14.2,F14.2,2A8)
 4008 FORMAT (F14.2,F14.3,F14.4,F14.3,F14.4)
 4009 FORMAT (F14.2,F14.4,F14.2,F14.2,F14.2)
 4010 FORMAT (*1MOLECULAR WEIGHT IS *F14.4)
 4011 FORMAT(*0SYMMETRY NUMBER IS *F5.0)
 4012 FORMAT (*0PRODUCT OF MOMENTS OF INERTIA IS *E20.9)
 6001 FORMAT(70H0          T       -(G -H    )/T    (H -H   )/T        S
     X        C      )
 6002 FORMAT (70H       (DEG.K.) (CAL/DEG/MOL) (CAL/DEG/MOL) (CAL/DEG/MOL
     X) (CAL/DEG/MOL))
 6004 FORMAT (70H0          T        (H -H    )          - H            - G
     X          LOG K)
 6005 FORMAT (70H       (DEG.K.)     (KCAL/MOL)     (KCAL/MOL)     (KCAL/MOL
     X)                )
 6007 FORMAT (9A8)
 6008 FORMAT (*0*)
      JUMP=0
      LYP=6060606060606060B
      LZP=6060603145266060B
      COL(1,1)=CEMP(1)=0.
      CEMP(2)=100.
      CEMP(3)=200.
      CEMP(4)=273.15
      CEMP(5)=298.15
      DO 15 K=6,23
   15 CEMP(K)=(K-3)*100
      TEN8=10000**2 $ WOW=TEN8**3
      VM=1.43879
      ARE=1.98717
      AVOG=.602252*WOW
      TEN16=TEN8**2
      AWE=AVOG*TEN16    $ AW3=AWE**3
      TEN40=WOW*TEN16
      CL=LOGF(10.)
      WOW5=WOW**5
      WOW5=WOW5*.001
      READ 4001,NEL
      DO 3 I3=1,NEL
      DO 3 I=1,23
      READ 4000, T(I),HZMHZZ(I,I3),SZ(I,I3)
      IF ((T(I)-CEMP(I))**2-1.) 3,13,13
   13 PRINT 4006 $ CALL EXIT
    3 PRINT4000, T(I),HZMHZZ(I,I3),SZ(I,I3)
   14 READ 6007,(LAB(K),K=1,9)
```

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```
      IF (EOF,60)7830,7831
 7830 CALL EXIT
 7831 READ4001,NOA,IZ$ZEE=IZ  $RLOGZ=1.98717*LOGF(ZEE )
      PRINT 4002,IZ
      READ 4001,(KN(J),J=1,NOA)
      DO 7820 J=1,NOA $ MAR=KN(J) $ DO 7820 KM=1,23
 7820 PRINT 4000,T(KM),HZMHZZ(KM,MAR),SZ(KM,MAR)
      READ 4001,NFV
      READ 4004,(FV(KV),KV=1,NFV)
      PRINT4004,(FV(KV),KV=1,NFV)
      DO 4 NFX=1,NFV
    4 FV(NFX)=FV(NFX)*VM
      READ 4005,GAM,(EM(K),K=1,NOA)
      PRINT4005,GAM,(EM(K),K=1,NOA)
      READ 4001,NC $ PRINT 4003
      WTMOL=0.
      DO 1 K=1,NC
      READ 4004, X(K),Y(K),Z(K),W(K)
      WTMOL=WTMOL+W(K)
    1 PRINT4004, X(K),Y(K),Z(K),W(K)
      IF (NC-3) 57,56,56
   57 CG=6.863426*LOGF(WTMOL)/CL-8.005804
      EYE=W(1)/(W(1)+W(2))*W(2)*X(2)*X(2)/AWE
      BETA=27.99076/TEN40/EYE
      GO TO 58
   56 CCG=18.302469/CL
      SXX=SYY=SZZ=XYI=XZI=YZI=SM=SX=SY=SZ=0.
      DO2 L=1,NC
      U=W(L)        $ WX=U*X(L) $WY=U*Y(L) $ WZ=U*Z(L) $ SM=SM+U $SX=SX+WX
      SY=SY+WY $ SZ=SZ+WZ $ XYI=XYI+X(L)*WY $ XZI=XZI+X(L)*WZ $ YZI=YZI+
     XY(L)*WZ $ WX=WX*X(L) $ WY=WY*Y(L) $ WZ=WZ*Z(L) $ SXX=SXX+WX $ SYY=
     XSYY+WY
    2 SZZ=SZZ+WZ
      XXI=SZZ+SYY-(SZ**2+SY**2)/SM $ YYI=SZZ+SXX-(SZ**2+SX**2)/SM
      ZZI=SYY+SXX-(SY**2+SX**2)/SM $ YZI=YZI-SY/SM*SZ $ XZI=XZI-SX/SM*SZ
      XYI=XYI-SX/SM*SY
      EYE=XXI*(YYI*ZZI-YZI**2)+XYI*(-XYI*ZZI-YZI*XZI)-XZI*(XYI*YZI+YYI*
     XXZI)
      EYE=EYE/AW3
      CG=2.287809/CL+LOGF(EYE*WOW5*WTMOL**3/GAM**2)-10.297926
   58 COL(1,2)=COL(1,3)=COL(1,4)=COL(1,5)=COL(1,6)=0. $ COL(1,9)=WOW
      DO 8 J=2,23 $ COL(J,1)=AT=T(J) $  GEE=ACH=CEE=0.
      BOT=BETA/AT
      COPY=.0914148*BOT**2 $ CORY=.953038*BOT
      IF (NC-3) 60,59,59
   59 COL(J,2)=CCG+LOGF(AT)+CG $ COL(J,3)=7.948662
      COL(J,5)=7.948662
      GO TO 61
   60 COL(J,2)=CG+(11.439043*LOGF(AT)-4.575617*LOGF(BOT*GAM))/CL+.5*COPY
     X+CORY
      COL(J,5)=6.955079+COPY
      COL(J,3)=6.955079-COPY-CORY
   61 DO 7 MA=1,NFV $ EXS=FV(MA)/AT $ U=EXPF(EXS) $ UM=U-1. $ R=EXS/UM
      CEE=CEE+R*U*R $ ACH=ACH+R
    7 GEE=-LOGF(1.+1./U)+GEE
      COL(J,2)=COL(J,2)+ARE*GEE*RLOGZ $ COL(J,3)=COL(J,3)+ARE*ACH
```

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```
    8 COL(J,5)=COL(J,5)+ARE*CEE
      READ 4004,DELH
      PRINT4004,DELH
      DO 9 JN=1,23 $ COL(JN,4)=COL(JN,2)+COL(JN,3)
      COL(JN,6)=COL(JN,3)*.001*T(JN)
      SUM1=SUM2=0. $ DO 10 LUM=1,NOA
      LAM=KN(LUM)
      SUM1=SUM1+EM(LUM)*SZ(JN,LAM)
   10 SUM2=SUM2+EM(LUM)*WZMHZZ(JN,LAM)
      DELST(JN)=(COL(JN,4)-SUM1)*T(JN)*.001
      XMY(JN)=COL(JN,6)-SUM2
    9 COL(JN,7)= XMY(JN)+DELH
      XOY=XMY(5)
      DO 12  JM=1,23
      COL(JM,7)=-COL(JM,7)+XOY $ COL(JM,8)=DELST(JM)+COL(JM,7)
      COL(JM,9)=COL(JM,8)/4.575617/T(JM)*1000.
      IF (T(JM)) 11,11,12
   11 COL(JM,9)=WOW
   12 CONTINUE
      PRINT6007,(LAB(K),K=1,9)
      PRINT 6001$PRINT6002$PRINT6008
      CUMO=COL(5,6)
      DO 20 JJ=1,23
      COL(JJ,6)=COL(JJ,6)-CUMO
   20 PRINT 4008,COL(JJ,1),COL(JJ,2),COL(JJ,3),COL(JJ,4),COL(JJ,5)
      PRINT6008$PRINT6008$PRINT6004$PRINT6005$PRINT6008
      PRINT 4007,COL(1,1),COL(1,6),COL(1,7),COL(1,8),LYP,LZP
      DO 21 KK=2,23
   21 PRINT 4009,COL(KK,1),COL(KK,6),COL(KK,7),COL(KK,8),COL(KK,9)
      PRINT 4010,WTMOL
      PRINT 4011,GAM
      PRINT 4012,EYE
 1400 DO 1401 KI=5,23 $ I=KI-4 $ TAY(I)=T(KI)
 1401 ARA(I)=COL(KI,6)*1000.
      V1=COL(5,5)
      CALLPLOTHEAT(TAY,ARA,V1)
      GOTO14
      END
```

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```
      SUBROUTINE PLOTHEAT(T,EV,CP)
      DIMENSION T(19),EV(19),AL(19),BET(19),GC(19),DEL(19)
     X,PI(19),T3H(19)
      COMMON JUMP
4000  FORMAT (*0IN METHOD*,I4,*    A,B,ETC ARE*,5E20.6)
4002  FORMAT (6F20.1)
4003  FORMAT (*0 STD.DEV.=*,F20.1,*       AVG PERCENT ERROR=*,F10.2)
      PA=PB=PP=DELAL=ALAL=ALBET=BETBET=DELBET=DELDEL=0.
      DO1K=1,19
      T3H(K)=SQRTF(T(K))*T(K)
      AL(K)=T(K)+T(1)**2/T(K)-2.*T(1)
      BET(K)=T(K)**2+T(1)**2*(2.*T(1)/T(K)-3.)
      DEL(K)=T(K)**3+T(1)**3*(3.*T(1)/T(K)-4.)
      GC(K)=T(1)*CP*(T(1)/T(K)-1.)
      PI(K)=T3H(K)*T(K)+T3H(1)*T(1)*(2.5*T(1)/T(K)-3.5)
      PA=PA+AL(K)*PI(K)
      PB=PB+BET(K)*PI(K)
      PP=PI(K)**2+PP
      DELAL=DELAL+AL(K)*DEL(K)
      DELBET=DELBET+BET(K)*DEL(K)
      DELDEL=DELDEL+DEL(K)**2
      ALAL=ALAL+AL(K)**2
      ALBET=ALBET+AL(K)*BET(K)
    1 BETBET=BET(K)**2+BETBET
      A12=ALBET/ALAL
      A13=DELAL/ALAL
      A14=PA/ALAL
      DEN=ALAL*BETBET-ALBET**2
      JUMP=1
    2 S1=S2=S3=S4=0.
      M1=1
      DO 3 K=1,19
      AD=EV(K)+GC(K)
      S1=S1+AL(K)*AD
      S3=S3+AD*DEL(K)
      S4=S4+AD*PI(K)
    3 S2=S2+BET(K)*AD
      A=(S1*BETBET-S2*ALBET)/DEN
      B=(S2*ALAL-S1*ALBET)/DEN
      C=(A+B*2.*T(1)-CP)*T(1)**2
      D=T(1)*(CP-3.*T(1)*B-A-A)
      PRINT4000,M1,A,B,C,D
    7 SD=SPER=0.
      DO4 K=1,19
      GOTO(5,9,11,13),M1
    5 S=(A+B*T(K))*T(K)+C/T(K)+D
      GOTO6
    9 S=(A+T(K)*(B+E*T(K)))*T(K)+C/T(K)+D
      GOTO6
   11 S=T(K)*(A+B*T(K)+E*T3H(K))+C/T(K)+D
      GOTO6
   13 S=A*T(K)+C/T(K)+D+B*T(K)*T3H(K)
    6 ER=S-EV(K)
      PER=ABSF(ER)/EV(K)*100.
      SPER=SPER+PER
      SQ=ER**2
```

FORTRAN 5,301

```
      PRINT4002,T(K),EV(K),S,ER,SQ,PER
    4 SD=SD+SQ
       SD=SQRTF(SD/19.)
      SPER=SPER/19.
      PRINT4003,SD,SPER
      GOTO(8,10,12,15),M1
    8 M1=2
      T1=S1/ALAL
      A22=BETBET/ALBET-A12
      A23=DELBET/ALBET-A13
      A32=DELBET/DELAL-A12
      A33=DELDEL/DELAL-A13
      T2=S2/ALBET-T1
      T3=S3/DELAL-T1
      A23=A23/A22
      T2=T2/A22
      A33=A33/A32-A23
      T3=T3/A32-T2
      E=T3/A33
      B=T2-E*A23
      A=T1-A13*E-A12*B
      D=T(1)*(CP-3.*B*T(1)-A-A-4.*E*T(1)**2)
      C=T(1)**2*(A+2.*B*T(1)-CP+3.*T(1)**2*E)
      PRINT4000,M1,A,B,C,D,E
      GOTO7
   10 M1=3
      A24=PB/ALBET-A14
      A32=PB/PA-A12
      A34=PP/PA-A14
      T4=S4/PA-T1
      A24=A24/A22
      A34=A34/A32-A24
      T4=T4/A32-T2
      E=T4/A34
      B=T2-E*A24
      A=T1-A14*E-A12*B
      C=T(1)**2*(A+2.*B*T(1)-CP+2.5*T3H(1)*E)
      D=T(1)*(-2.*A-3.*B*T(1)+CP-3.5*T3H(1)*E)
      PRINT4000,M1,A,B,C,D,E
      GOTO7
   12 M1=4
      DOM=ALAL*PP-PA**2
      A=(S1*PP-S4*PA)/DOM
      B=(ALAL*S4-PA*S1)/DOM
      C=T(1)**2*(A-CP+2.5*B*T3H(1))
      D=T(1)*(-2.*A+CP-3.5*T3H(1)*B)
      PRINT4000,M1,A,B,C,D
      GOTO7
   15 RETURN
      END
```

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