IP(F, g) = 140524.5 ± 0.4 cm$^{-1}$
$S°$(298.15 K) = 158.750 ± 0.003 J K$^{-1}$·mol$^{-1}$

$\Delta_f H°$(0 K) = 77.28 ± 0.30 kJ·mol$^{-1}$
$\Delta_f H°$(298.15 K) = 79.39 ± 0.30 kJ·mol$^{-1}$

Electronic Levels and Quantum Weights

| State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|
| $^2P°_{3/2}$ | 0.0 | 4 |
| $^2P°_{1/2}$ | 404.1 | 2 |

## Enthalpy of Formation

The adopted value for the enthalpy of formation of F(g) is the value proposed by CODATA;[1] $\Delta_f H°$(F, g, 298.15 K) = 79.38 ± 0.30 kJ·mol$^{-1}$. This value is calculated from the dissociation energy of $F_2(g)$, $D_0° = 12920 \pm 50$ cm$^{-1}$ (154.56 ± 0.60 kJ·mol$^{-1}$), obtained from the extensive spectroscopic measurements of Colbourn *et al.*[2] This value is in satisfactory agreement with the results of the equilibrium measurements of Doescher[3] and the photoionization measurements of Berkowitz *et al.*[4] It is also in good agreement with the value calculated from the enthalpies of formation[5] and vaporization[6] of HF(l) and the spectroscopic data for the dissociation energy of HF(g).[4 7 8] This same value is recommended by Brewer and Winn,[9] Huber and Herzberg[10] and Gurvich *et al.*,[13] whereas Wagman *et al.*[21] adopted a dissociation energy which is approximately 0.76 kJ·mol$^{-1}$ smaller.

Additional discussions on the enthalpy of formation may be found in the earlier reviews by the JANAF[11] and NBS[12] groups and a recent review by Gurvich *et al.*[13] Coxon[14] has summarized the spectroscopic information on the lower electronic states of the halogens as of 1973. The more recent spectroscopic studies are discussed by Colbourn *et al.*[2]

## Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Moore.[15 16] Only two levels are included in the calculation. All other levels (observed and predicted) lie above 100000 cm$^{-1}$. Our calculations indicate that any reasonable method of filling in the missing levels and cutting off the summation in the partition function[17] has no effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels. Therefore, we list only the ground state and the first excited state. Extension to higher temperatures may require consideration of the higher excited states and utilization of different fill and cutoff procedures.

The thermodynamic functions at 298.15 K are in agreement with recent CODATA recommendations[1] except for two minor differences. First, the entropy differs by 0.1094 J K$^{-1}$·mol$^{-1}$ because this table uses a standard–state pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, entropy differences of the order of 0.001–0.004 J K$^{-1}$·mol$^{-1}$ for the monatomic halogens arise due to the use of slightly different values for the relative atomic mass and for $R$; this table uses $R$ = 8.31441 J K$^{-1}$·mol$^{-1}$. Considering these minor changes, this table agrees within the estimated uncertainty with those by Hultgren *et al.*,[18] Gurvich *et al.*[13] and Wagman *et al.*[21] The estimated uncertainty is due to uncertainties in the relative atomic mass and fundamental constants which are based on the 1981 scale[19] and the 1973 values,[20] respectively.

## References

[1] J. D Cox, chairman, ICSU–CODATA Task Group on Key Values for Thermodynamics, J. Chem. Thermodyn. 10, 903 (1978).
[2] E. A. Colbourn, M. Dagenais, A. E. Douglas and J. W. Raymonda, Can. J. Phys. 54, 1343 (1976).
[3] R. N. Doescher, J. Chem. Phys. 20, 330 (1952).
[4] J. Berkowitz, W. A. Chupka, P. M. Guyon, J. H. Holloway and R. Spohr, J. Chem. Phys. 54, 5165 (1971).
[5] G. K. Johnson, P. N. Smith and W. N. Hubbard, J. Chem. Thermodyn. 5, 793, (1973).
[6] C. E. Vanderzee and W. M. Rodenburg, J. Chem. Thermodyn. 3, 267 (1971).
[7] G. DiLonardo and A. E. Douglas, Can. J. Phys. 51, 434 (1973).
[8] J. W. C. Johns and R. F. Barrow, Proc. Roy. Soc. A251, 504 (1959).
[9] L. Brewer and J. S. Winn, Faraday Symp. Chem. Soc. (GB), No. 14, 126 (1980).
[10] K. P. Huber and G. Herzberg, "Constants of Diatomic Molecules," Van Nostrand Reinhold Company, New York, (1979).
[11] H. Prophet and D. R. Stull, ed., "JANAF Thermochemical Tables," 2nd ed., NSRDS–NBS 37, (1971).
[12] S Abramowitz *et al.*, U. S. Nat. Bur. Stand., Rept. 10904, 239, (July 1972).
[13] L. V. Gurvich, I. V. Veits *et al.*, "Thermodynamic Properties of Individual Substances," 3rd ed., Vol. 1, Nauka, Moscow, (1978).
[14] J. A. Coxon in "Molecular Spectroscopy," Vol. 1, R. F. Barrow, D. A Long and D. J. Miller, Senior Reporters, The Chemical Society, London, Chapter 4, (1973).
[15] C. E. Moore, U. S. Nat. Bur. Stand., NSRDS–NBS–35, Volume I, 1970 [Reprint of NBS Circular 467, Volume I, 1949].
[16] C. E. Moore, U. S. Nat. Bur. Stand., NSRDS–NBS–34, (1970).
[17] J. R. Downey, Jr. The Dow Chemical Company, AFOSR–TR–78–0960, Contract No. F44620–75–1–0048, (1978).
[18] R. Hultgren, P. D. Desai *et al.*, "Selected Values of the Thermodynamic Properties of the Elements," American Society for Metals, Metals Park, Ohio, (1973).
[19] N. E. Holden and R. L. Martin, Pure Appl. Chem. 55, 1101 (1983).
[20] E. R. Cohen and B. N. Taylor, J. Phys. Chem. Ref. Data 2, 663 (1973).
[21] D. D. Wagman, W. H. Evans *et al.*, J. Phys. Chem. Ref. Data 11, Supp. 2 (1982).

Enthalpy Reference Temperature = $T_r$ = 298.15 K  Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −6.518 | 77.284 | 77.284 | INFINITE |
| 100 | 21.205 | 134.479 | 178.805 | −4.433 | 77.916 | 72.987 | −38.124 |
| 200 | 22.605 | 149.670 | 160.833 | −2.233 | 78.652 | 67.783 | −17.703 |
| 250 | 22.783 | 154.738 | 159.125 | −1.097 | 79.037 | 65.021 | −13.585 |
| 298.15 | 22.746 | 158.750 | 158.750 | 0. | 79.390 | 62.289 | −10.913 |
| 300 | 22.742 | 158.891 | 158.751 | 0.042 | 79.403 | 62.183 | −10.827 |
| 350 | 22.603 | 162.387 | 159.027 | 1.176 | 79.743 | 59.286 | −8.848 |
| 400 | 22.431 | 165.394 | 159.639 | 2.302 | 80.053 | 56.342 | −7.358 |
| 450 | 22.259 | 168.026 | 160.428 | 3.419 | 80.337 | 53.361 | −6.194 |
| 500 | 22.100 | 170.363 | 161.307 | 4.528 | 80.597 | 50.350 | −5.260 |
| 600 | 21.832 | 174.368 | 163.161 | 6.724 | 81.056 | 44.256 | −3.853 |
| 700 | 21.628 | 177.717 | 165.008 | 8.897 | 81.453 | 38.090 | −2.842 |
| 800 | 21.474 | 180.594 | 166.780 | 11.051 | 81.803 | 31.871 | −2.081 |
| 900 | 21.357 | 183.117 | 168.458 | 13.193 | 82.117 | 25.611 | −1.486 |
| 1000 | 21.266 | 185.362 | 170.038 | 15.324 | 82.403 | 19.317 | −1.009 |
| 1100 | 21.194 | 187.385 | 171.525 | 17.446 | 82.666 | 12.995 | −0.617 |
| 1200 | 21.137 | 189.227 | 172.924 | 19.563 | 82.909 | 6.651 | −0.290 |
| 1300 | 21.091 | 190.917 | 174.244 | 21.674 | 83.136 | 0.287 | −0.012 |
| 1400 | 21.053 | 192.478 | 175.492 | 23.781 | 83.348 | −6.095 | 0.227 |
| 1500 | 21.022 | 193.930 | 176.673 | 25.885 | 83.546 | −12.490 | 0.435 |
| 1600 | 20.996 | 195.286 | 177.795 | 27.986 | 83.733 | −18.899 | 0.617 |
| 1700 | 20.974 | 196.558 | 178.861 | 30.085 | 83.909 | −25.319 | 0.778 |
| 1800 | 20.955 | 197.756 | 179.878 | 32.181 | 84.075 | −31.749 | 0.921 |
| 1900 | 20.939 | 198.889 | 180.849 | 34.276 | 84.234 | −38.188 | 1.050 |
| 2000 | 20.925 | 199.963 | 181.778 | 36.369 | 84.387 | −44.635 | 1.166 |
| 2100 | 20.913 | 200.983 | 182.669 | 38.461 | 84.535 | −51.090 | 1.271 |
| 2200 | 20.902 | 201.956 | 183.523 | 40.551 | 84.681 | −57.551 | 1.366 |
| 2300 | 20.893 | 202.885 | 184.345 | 42.641 | 84.827 | −64.020 | 1.454 |
| 2400 | 20.885 | 203.774 | 185.136 | 44.730 | 84.974 | −70.494 | 1.534 |
| 2500 | 20.877 | 204.626 | 185.899 | 46.818 | 85.125 | −76.975 | 1.608 |
| 2600 | 20.871 | 205.445 | 186.635 | 48.906 | 85.281 | −83.462 | 1.677 |
| 2700 | 20.865 | 206.232 | 187.346 | 50.992 | 85.444 | −89.956 | 1.740 |
| 2800 | 20.860 | 206.991 | 188.034 | 53.079 | 85.617 | −96.455 | 1.799 |
| 2900 | 20.855 | 207.723 | 188.701 | 55.164 | 85.800 | −102.961 | 1.855 |
| 3000 | 20.851 | 208.430 | 189.347 | 57.250 | 85.994 | −109.473 | 1.906 |
| 3100 | 20.847 | 209.114 | 189.973 | 59.334 | 86.202 | −115.992 | 1.954 |
| 3200 | 20.843 | 209.775 | 190.582 | 61.419 | 86.423 | −122.518 | 2.000 |
| 3300 | 20.840 | 210.417 | 191.173 | 63.503 | 86.660 | −129.051 | 2.043 |
| 3400 | 20.837 | 211.039 | 191.748 | 65.587 | 86.911 | −135.592 | 2.083 |
| 3500 | 20.834 | 211.643 | 192.308 | 67.670 | 87.179 | −142.140 | 2.121 |
| 3600 | 20.831 | 212.230 | 192.854 | 69.754 | 87.463 | −148.695 | 2.158 |
| 3700 | 20.829 | 212.800 | 193.385 | 71.837 | 87.764 | −155.259 | 2.192 |
| 3800 | 20.827 | 213.356 | 193.903 | 73.920 | 88.081 | −161.832 | 2.225 |
| 3900 | 20.825 | 213.897 | 194.409 | 76.002 | 88.416 | −168.413 | 2.256 |
| 4000 | 20.823 | 214.424 | 194.903 | 78.084 | 88.767 | −175.003 | 2.285 |
| 4100 | 20.821 | 214.938 | 195.385 | 80.167 | 89.135 | −181.602 | 2.314 |
| 4200 | 20.820 | 215.440 | 195.857 | 82.249 | 89.520 | −188.209 | 2.341 |
| 4300 | 20.818 | 215.930 | 196.318 | 84.331 | 89.921 | −194.827 | 2.367 |
| 4400 | 20.817 | 216.408 | 196.769 | 86.412 | 90.338 | −201.454 | 2.392 |
| 4500 | 20.815 | 216.876 | 197.211 | 88.494 | 90.771 | −208.090 | 2.415 |
| 4600 | 20.814 | 217.334 | 197.643 | 90.575 | 91.220 | −214.736 | 2.438 |
| 4700 | 20.813 | 217.781 | 198.067 | 92.657 | 91.685 | −221.392 | 2.461 |
| 4800 | 20.812 | 218.219 | 198.482 | 94.738 | 92.164 | −228.059 | 2.482 |
| 4900 | 20.811 | 218.648 | 198.889 | 96.819 | 92.658 | −234.735 | 2.502 |
| 5000 | 20.810 | 219.069 | 199.289 | 98.900 | 93.166 | −241.422 | 2.522 |
| 5100 | 20.809 | 219.481 | 199.681 | 100.981 | 93.687 | −248.119 | 2.541 |
| 5200 | 20.808 | 219.885 | 200.065 | 103.062 | 94.223 | −254.826 | 2.560 |
| 5300 | 20.807 | 220.281 | 200.443 | 105.143 | 94.771 | −261.544 | 2.578 |
| 5400 | 20.807 | 220.670 | 200.814 | 107.224 | 95.332 | −268.272 | 2.595 |
| 5500 | 20.806 | 221.052 | 201.179 | 109.304 | 95.905 | −275.011 | 2.612 |
| 5600 | 20.805 | 221.427 | 201.537 | 111.385 | 96.491 | −281.760 | 2.628 |
| 5700 | 20.805 | 221.795 | 201.889 | 113.465 | 97.088 | −288.520 | 2.644 |
| 5800 | 20.804 | 222.157 | 202.235 | 115.546 | 97.696 | −295.290 | 2.659 |
| 5900 | 20.803 | 222.513 | 202.576 | 117.626 | 98.315 | −302.071 | 2.674 |
| 6000 | 20.803 | 222.862 | 202.911 | 119.706 | 98.944 | −308.862 | 2.689 |

PREVIOUS September 1965 (1 atm)  CURRENT June 1982 (1 bar)

**Fluorine, Ion ($F^+$)** **IDEAL GAS** $M_r = 18.997854$ **Fluorine, Ion ($F^+$)** $F_1^+(g)$

IP($F^+$, g) = 282058.6 ± 1.5 cm$^{-1}$
$S°$(298.15 K) = 161.728 ± 0.005 J K$^{-1}$·mol$^{-1}$

$\Delta_f H°$(0 K) = 1758.33 ± 0.3 kJ·mol$^{-1}$
$\Delta_f H°$(298.15 K) = [1766.826] kJ·mol$^{-1}$

Electronic Levels and Quantum Weights

| State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|
| $^3P_2$ | 0.0 | 5 |
| $^3P_1$ | 341.0 | 3 |
| $^3P_0$ | 489.9 | 1 |
| $^1D_2$ | 20873.4 | 5 |
| $^1S_0$ | 44918.1 | 1 |

## Enthalpy of Formation

$\Delta_f H°$($F^+$, g, 0 K) is calculated from $\Delta_f H°$(F, g, 0 K)[1] using the spectroscopic value of IP(F) = 140524.5 ± 0.4 cm$^{-1}$(1681.047 ± 0.005 kJ·mol$^{-1}$) from Moore.[2] The ionization limit is converted from cm$^{-1}$ to kJ·mol$^{-1}$ using the factor, 1 cm$^{-1}$ = 0.01196266 kJ·mol$^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization potential and appearance potential data.

$\Delta_f H°$($F^+$, g, 298.15 K) is calculated from $\Delta_f H°$(F, g, 0 K) by using IP(F) with JANAF[1] enthalpies, $H°$(0 K)– $H°$(298.15 K), for F(g), $F^+$(g), and $e^-$(ref). $\Delta_f H°$($F \rightarrow F^+ + e^-$, 298.15 K) differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 kJ·mol$^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

## Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the lowest four excited states; the next lowest level is approximately 164797 cm$^{-1}$ above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and four excited states, with the energy of these states taken from recent study by Moore.[2] The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass, the fundamental constants, and the position of the four lowest excited states. Extension of these calculations above 6000 K may require consideration of the higher excited states and use of different fill and cutoff procedures.[7]

## References

[1] JANAF Thermochemical Tables: F(g), 3–31–82; $e^-$(ref), 3–31–82.
[2] C. E. Moore, U. S. Nat. Bur. Stand., NSRDS-NBS-34, (1970).
[3] E. R. Cohen and B. N. Taylor, J. Phys. Chem. Ref. Data 2, 663 (1973).
[4] H. M. Rosenstock, K. Draxl *et al.*, J. Phys. Chem. Ref. Data 6, Supp. 1 (1977).
[5] R. D. Levin and S. G. Lias, U. S. Nat. Bur. Stand., NSRDS-NBS-71, (1982).
[6] C. E. Moore, U. S. Nat. Bur. Stand., NSRDS-NBS-35, Volume I, (1970) [reprint of NBS Circular 467, Volume I, 1949].
[7] J. R. Downey, Jr., The Dow Chemical Company, AFOSR-TR-78-0960, Contract No. F44620-75-1-0048, (1978).

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −6.711 | 1758.331 | | |
| 100 | 21.738 | 136.478 | 182.608 | −4.613 | | | |
| 200 | 23.642 | 152.281 | 163.889 | −2.322 | | | |
| 250 | 23.694 | 157.569 | 162.116 | −1.137 | | | |
| 298.15 | 23.497 | 161.728 | 161.728 | 0. | 1766.826 | 1742.583 | −305.293 |
| 300 | 23.487 | 161.873 | 161.728 | 0.043 | 1766.879 | 1742.433 | −303.385 |
| 350 | 23.197 | 165.472 | 162.013 | 1.211 | 1768.291 | 1738.246 | −259.419 |
| 400 | 22.904 | 168.550 | 162.643 | 2.363 | 1769.668 | 1733.860 | −226.419 |
| 450 | 22.636 | 171.232 | 163.451 | 3.502 | 1771.012 | 1729.303 | −200.732 |
| 500 | 22.404 | 173.605 | 164.350 | 4.627 | 1772.328 | 1724.597 | −180.167 |
| 600 | 22.035 | 177.655 | 166.241 | 6.848 | 1774.891 | 1714.809 | −149.287 |
| 700 | 21.770 | 181.031 | 168.120 | 9.038 | 1777.383 | 1704.598 | −127.199 |
| 800 | 21.577 | 183.925 | 169.919 | 11.205 | 1779.824 | 1694.033 | −110.609 |
| 900 | 21.433 | 186.457 | 171.619 | 13.355 | 1782.225 | 1683.164 | −97.688 |
| 1000 | 21.324 | 188.710 | 173.217 | 15.492 | 1784.597 | 1672.030 | −87.338 |
| 1100 | 21.240 | 190.738 | 174.719 | 17.621 | 1786.943 | 1660.659 | −78.858 |
| 1200 | 21.174 | 192.583 | 176.132 | 19.741 | 1789.270 | 1649.076 | −71.782 |
| 1300 | 21.121 | 194.276 | 177.464 | 21.856 | 1791.578 | 1637.300 | −65.788 |
| 1400 | 21.078 | 195.840 | 178.721 | 23.966 | 1793.872 | 1625.346 | −60.642 |
| 1500 | 21.043 | 197.293 | 179.911 | 26.072 | 1796.151 | 1613.229 | −56.178 |
| 1600 | 21.014 | 198.650 | 181.041 | 28.174 | 1798.418 | 1600.960 | −52.266 |
| 1700 | 20.989 | 199.923 | 182.114 | 30.275 | 1800.674 | 1588.550 | −48.810 |
| 1800 | 20.968 | 201.122 | 183.137 | 32.372 | 1802.920 | 1576.007 | −45.735 |
| 1900 | 20.951 | 202.255 | 184.114 | 34.468 | 1805.159 | 1563.340 | −42.979 |
| 2000 | 20.935 | 203.329 | 185.048 | 36.563 | 1807.391 | 1550.555 | −40.496 |
| 2100 | 20.922 | 204.350 | 185.943 | 38.656 | 1809.619 | 1537.658 | −38.247 |
| 2200 | 20.911 | 205.324 | 186.802 | 40.747 | 1811.845 | 1524.655 | −36.200 |
| 2300 | 20.902 | 206.253 | 187.628 | 42.838 | 1814.070 | 1511.551 | −34.328 |
| 2400 | 20.894 | 207.142 | 188.422 | 44.928 | 1816.297 | 1498.351 | −32.611 |
| 2500 | 20.887 | 207.995 | 189.188 | 47.017 | 1818.527 | 1485.057 | −31.029 |
| 2600 | 20.882 | 208.814 | 189.928 | 49.105 | 1820.763 | 1471.674 | −29.566 |
| 2700 | 20.879 | 209.602 | 190.642 | 51.193 | 1823.006 | 1458.205 | −28.211 |
| 2800 | 20.876 | 210.361 | 191.333 | 53.281 | 1825.259 | 1444.653 | −26.950 |
| 2900 | 20.876 | 211.094 | 192.001 | 55.368 | 1827.522 | 1431.020 | −25.775 |
| 3000 | 20.876 | 211.802 | 192.650 | 57.456 | 1829.798 | 1417.309 | −24.678 |
| 3100 | 20.878 | 212.486 | 193.279 | 59.544 | 1832.087 | 1403.521 | −23.649 |
| 3200 | 20.882 | 213.149 | 193.889 | 61.632 | 1834.391 | 1389.660 | −22.684 |
| 3300 | 20.888 | 213.792 | 194.483 | 63.720 | 1836.710 | 1375.726 | −21.776 |
| 3400 | 20.895 | 214.416 | 195.060 | 65.809 | 1839.045 | 1361.722 | −20.920 |
| 3500 | 20.904 | 215.021 | 195.622 | 67.899 | 1841.398 | 1347.649 | −20.113 |
| 3600 | 20.914 | 215.610 | 196.169 | 69.990 | 1843.768 | 1333.508 | −19.349 |
| 3700 | 20.926 | 216.184 | 196.702 | 72.082 | 1846.156 | 1319.302 | −18.625 |
| 3800 | 20.940 | 216.742 | 197.222 | 74.175 | 1848.563 | 1305.030 | −17.939 |
| 3900 | 20.956 | 217.286 | 197.729 | 76.270 | 1850.988 | 1290.695 | −17.287 |
| 4000 | 20.974 | 217.817 | 198.225 | 78.367 | 1853.432 | 1276.297 | −16.667 |
| 4100 | 20.993 | 218.335 | 198.709 | 80.465 | 1855.895 | 1261.839 | −16.076 |
| 4200 | 21.014 | 218.841 | 199.183 | 82.565 | 1858.377 | 1247.319 | −15.513 |
| 4300 | 21.037 | 219.336 | 199.645 | 84.668 | 1860.877 | 1232.741 | −14.975 |
| 4400 | 21.061 | 219.820 | 200.099 | 86.773 | 1863.396 | 1218.104 | −14.461 |
| 4500 | 21.086 | 220.293 | 200.542 | 88.880 | 1865.934 | 1203.410 | −13.969 |
| 4600 | 21.113 | 220.757 | 200.976 | 90.990 | 1868.490 | 1188.659 | −13.498 |
| 4700 | 21.141 | 221.211 | 201.402 | 93.103 | 1871.064 | 1173.852 | −13.046 |
| 4800 | 21.171 | 221.657 | 201.820 | 95.218 | 1873.656 | 1158.991 | −12.612 |
| 4900 | 21.202 | 222.094 | 202.229 | 97.337 | 1876.266 | 1144.075 | −12.196 |
| 5000 | 21.234 | 222.522 | 202.630 | 99.459 | 1878.893 | 1129.105 | −11.796 |
| 5100 | 21.267 | 222.943 | 203.025 | 101.584 | 1881.538 | 1114.083 | −11.411 |
| 5200 | 21.300 | 223.356 | 203.412 | 103.712 | 1884.199 | 1099.009 | −11.040 |
| 5300 | 21.335 | 223.762 | 203.792 | 105.844 | 1886.877 | 1083.884 | −10.682 |
| 5400 | 21.371 | 224.162 | 204.165 | 107.979 | 1889.571 | 1068.708 | −10.338 |
| 5500 | 21.407 | 224.554 | 204.532 | 110.118 | 1892.282 | 1053.482 | −10.005 |
| 5600 | 21.443 | 224.940 | 204.893 | 112.261 | 1895.007 | 1038.206 | −9 684 |
| 5700 | 21.480 | 225.320 | 205.248 | 114.407 | 1897.749 | 1022.882 | −9.374 |
| 5800 | 21.518 | 225.694 | 205.598 | 116.557 | 1900.505 | 1007.509 | −9.074 |
| 5900 | 21.556 | 226.062 | 205.942 | 118.710 | 1903.276 | 992.089 | −8.783 |
| 6000 | 21.594 | 226.425 | 206.280 | 120.868 | 1906.061 | 976.622 | −8.502 |

PREVIOUS:    CURRENT: June 1982 (1 bar)

# Fluorine, Ion ($F^-$) IDEAL GAS $M_r = 18.998952$ Fluorine, Ion ($F^-$) $F_1^-(g)$

EA(F, g) = 3.399 ± 0.003 eV
$S^\circ$(298.15 K) = 145.576 ± 0.005 J K$^{-1}$·mol$^{-1}$

$\Delta_f H^\circ$(0 K) = −250.67 ± 0.6 kJ·mol$^{-1}$
$\Delta_f H^\circ$(298.15 K) = [−265.085] kJ·mol$^{-1}$

| Electronic Level and Quantum Weight<br>State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|
| $^1S_0$ | 0.0 | 1 |

## Enthalpy of Formation

$\Delta_f H^\circ(F^-$, g, 0 K) is calculated from $\Delta_f H^\circ$(F, g, 0 K)[1] using the adopted electron affinity of EA (F) = 3.399 ± 0.003 eV (327.951 ± 0.289 kJ·mol$^{-1}$). This value, recommended by Hotop and Lineberger,[10] is based on plasma absorption and plasma emission studies.[5, 6] Additional information on $F^-$(g) may be obtained in the critical discussions of Hotop and Lineberger,[2, 10] Rosenstock *et al.*[3] and Massey.[4]

$\Delta_f H^\circ(F^-$, g, 298.15 K) is obtained from $\Delta_f H^\circ$(F, g, 0 K) by using EA(F) with JANAF[1] enthalpies, $H^\circ$(0 K) − $H^\circ$(298.15 K), for $F^-$(g), F(g), and $e^-$(ref). $\Delta_r H^\circ(F^- \rightarrow F + e^-$, 298.15 K) differs from a room–temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[3] $\Delta_f H^\circ$(298.15 K) should be changed by +6.197 kJ·mol$^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

## Heat Capacity and Entropy

The ground state configuration for $F^-$(g) is given by Hotop and Lineberger,[2, 10] Rosenstock *et al.*[3] and Massey.[4] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

entropy at all temperatures (0–6000 K) agrees within 0.001 J K$^{-1}$ mol$^{-1}$ with the values of Gurvich *et al*[8] except for one minor difference. The entropy differs by 0.1094 J K$^{-1}$·mol$^{-1}$ because this table uses a standard–state pressure of 1 bar, whereas the tabulation of Gurvich *et al.*[8] is based on 1 atm. The estimated uncertainty is due to uncertainties in the relative ionic mass and the fundamental constants which are based on the 1981 scale[9] and the 1973 values,[7] respectively.

## References

[1] JANAF Thermochemical Tables: F(g), 6–30–82; $e^-$(ref), 3–31–82.
[2] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data 4, 539 (1975).
[3] H. M. Rosenstock, K. Draxl *et al.*, J. Phys. Chem Ref Data 6, Supp. 1 (1977).
[4] H. S. W. Massey, "Negative Ions," 3rd ed., Cambridge University Press, Cambridge, (1976).
[5] R. Milstein and R. S. Berry, J. Chem. Phys. 55, 4146 (1971).
[6] H.-P. Popp, Z. Naturforsch. 22a, 254 (1967).
[7] E. R. Cohen and B. N. Taylor, J Phys. Chem. Ref. Data 2, 663 (1973).
[8] L. V. Gurvich, I. V Veits *et al.*, "Thermodynamic Properties of Individual Substances," 3rd ed., Vol. 1, Nauka, Moscow, (1978).
[9] N E. Holden and R. L. Martin, Pure Appl Chem. 55, 1101 (1983).
[10] H. Hotop and W C. Lineberger, J. Phys Chem. Ref Data, to be published, (1985).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p^\circ$ = 0.1 MPa

| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log $K_f$ |
|---|---|---|---|---|---|---|---|
|  | J·K$^{-1}$mol$^{-1}$ |  |  | kJ·mol$^{-1}$ |  |  |  |
| 0 | 0. | 0. | INFINITE | −6.197 | −250.667 |  |  |
| 100 | 20.786 | 122.869 | 164.056 | −4.119 |  |  |  |
| 200 | 20.786 | 137.276 | 147.477 | −2.040 |  |  |  |
| 250 | 20.786 | 141.915 | 145.918 | −1.001 |  |  |  |
| 298.15 | 20 786 | 145.576 | 145.576 | 0. | −255.079 | −261.997 | 45.901 |
| 300 | 20.786 | 145.704 | 145.576 | 0.038 | −255.108 | −262.040 | 45.625 |
| 350 | 20.786 | 148.909 | 145.829 | 1.078 | −255.903 | −263.133 | 39.270 |
| 400 | 20.786 | 151.684 | 146.392 | 2.117 | −256.718 | −264.110 | 34.489 |
| 450 | 20.786 | 154.132 | 147.118 | 3.156 | −257.552 | −264.984 | 30.759 |
| 500 | 20.786 | 156.322 | 147.931 | 4.196 | −258.401 | −265.765 | 27.764 |
| 600 | 20.786 | 160.112 | 149.655 | 6.274 | −260.138 | −267.075 | 23.251 |
| 700 | 20.786 | 163.316 | 151.384 | 8.353 | −261.913 | −268.092 | 20.005 |
| 800 | 20.786 | 166.092 | 153.053 | 10.431 | −263.718 | −268.852 | 17.554 |
| 900 | 20.786 | 168.540 | 154.640 | 12.510 | −265.545 | −269.384 | 15.635 |
| 1000 | 20.786 | 170.730 | 156.142 | 14.589 | −267.390 | −269.711 | 14.088 |
| 1100 | 20.786 | 172.711 | 157.559 | 16.667 | −269.250 | −269.854 | 12.814 |
| 1200 | 20.786 | 174.520 | 158.898 | 18.746 | −271.123 | −269.826 | 11.745 |
| 1300 | 20.786 | 176.184 | 160.165 | 20.824 | −273.008 | −269.641 | 10.834 |
| 1400 | 20.786 | 177.724 | 161.365 | 22.903 | −274.903 | −269.312 | 10.048 |
| 1500 | 20.786 | 179.158 | 162.504 | 24.982 | −276.808 | −268.846 | 9.362 |
| 1600 | 20 786 | 180.500 | 163.587 | 27.060 | −278.723 | −268.253 | 8.758 |
| 1700 | 20.786 | 181.760 | 164.619 | 29.139 | −280.645 | −267.539 | 8.220 |
| 1800 | 20 786 | 182.948 | 165.605 | 31.217 | −282.575 | −266.713 | 7.740 |
| 1900 | 20 786 | 184 072 | 166.548 | 33.296 | −284.511 | −265.779 | 7.307 |
| 2000 | 20 786 | 185 138 | 167.451 | 35.375 | −286.452 | −264.743 | 6.914 |
| 2100 | 20.786 | 186.152 | 168.317 | 37.453 | −288.395 | −263.609 | 6.557 |
| 2200 | 20.786 | 187 119 | 169.150 | 39.532 | −290.340 | −262.383 | 6.230 |
| 2300 | 20.786 | 188.043 | 169.952 | 41.610 | −292.284 | −261.069 | 5.929 |
| 2400 | 20.786 | 188.928 | 170.724 | 43.689 | −294.226 | −259.670 | 5.652 |
| 2500 | 20.786 | 189.776 | 171.469 | 45.768 | −296.163 | −258.191 | 5.395 |
| 2600 | 20.786 | 190.591 | 172.189 | 47.846 | −298.094 | −256.634 | 5.156 |
| 2700 | 20.786 | 191.376 | 172.885 | 49.925 | −300.017 | −255.002 | 4.933 |
| 2800 | 20 786 | 192.132 | 173.559 | 52.004 | −301.931 | −253.300 | 4.725 |
| 2900 | 20.786 | 192.861 | 174.212 | 54.082 | −303.834 | −251.530 | 4.531 |
| 3000 | 20.786 | 193.566 | 174.846 | 56.161 | −305.725 | −249.694 | 4.348 |
| 3100 | 20.786 | 194.248 | 175.461 | 58.239 | −307.602 | −247.795 | 4.175 |
| 3200 | 20.786 | 194.907 | 176.058 | 60.318 | −309.465 | −245.836 | 4.013 |
| 3300 | 20.786 | 195.547 | 176.639 | 62.397 | −311.313 | −243.819 | 3.859 |
| 3400 | 20.786 | 196.168 | 177.204 | 64.475 | −313.145 | −241.746 | 3.714 |
| 3500 | 20.786 | 196.770 | 177.755 | 66.554 | −314.961 | −239.620 | 3.576 |
| 3600 | 20.786 | 197.356 | 178.291 | 68.632 | −316.760 | −237.442 | 3.445 |
| 3700 | 20 786 | 197.925 | 178.814 | 70.711 | −318.542 | −235.214 | 3.321 |
| 3800 | 20.786 | 198 480 | 179.324 | 72.790 | −320.308 | −232.938 | 3.202 |
| 3900 | 20.786 | 199.019 | 179.823 | 74.868 | −322.056 | −230.616 | 3.089 |
| 4000 | 20.786 | 199.546 | 180.309 | 76.947 | −323.787 | −228.249 | 2.981 |
| 4100 | 20.786 | 200.059 | 180.785 | 79.025 | −325.501 | −225.840 | 2.877 |
| 4200 | 20.786 | 200.560 | 181.249 | 81.104 | −327.199 | −223.388 | 2.778 |
| 4300 | 20.786 | 201.049 | 181.704 | 83.183 | −328.879 | −220.897 | 2.683 |
| 4400 | 20.786 | 201.527 | 182.149 | 85.261 | −330.544 | −218.367 | 2.592 |
| 4500 | 20.786 | 201.994 | 182.585 | 87.340 | −332.192 | −215.798 | 2.505 |
| 4600 | 20.786 | 202.451 | 183.012 | 89.418 | −333.825 | −213.194 | 2.421 |
| 4700 | 20.786 | 202.898 | 183.430 | 91.497 | −335.442 | −210.554 | 2.340 |
| 4800 | 20.786 | 203.335 | 183.841 | 93.576 | −337.044 | −207.880 | 2.262 |
| 4900 | 20.786 | 203.764 | 184.243 | 95.654 | −338.631 | −205.172 | 2.187 |
| 5000 | 20.786 | 204.184 | 184.637 | 97.733 | −340.204 | −202.433 | 2.115 |
| 5100 | 20.786 | 204.596 | 185.025 | 99.811 | −341.763 | −199.662 | 2.045 |
| 5200 | 20.786 | 204.999 | 185.405 | 101.890 | −343.309 | −196.860 | 1.977 |
| 5300 | 20.786 | 205.395 | 185.778 | 103.969 | −344.841 | −194.029 | 1.912 |
| 5400 | 20.786 | 205.784 | 186.145 | 106.047 | −346.361 | −191.170 | 1.849 |
| 5500 | 20.786 | 206.165 | 186.506 | 108.126 | −347.868 | −188.282 | 1.788 |
| 5600 | 20.786 | 206.540 | 186.860 | 110.204 | −349.363 | −185.367 | 1.729 |
| 5700 | 20.786 | 206.908 | 187.209 | 112.283 | −350.847 | −182.425 | 1.672 |
| 5800 | 20.786 | 207.269 | 187.552 | 114.362 | −352.319 | −179.458 | 1.616 |
| 5900 | 20.786 | 207 624 | 187.889 | 116.440 | −353.781 | −176.465 | 1.562 |
| 6000 | 20.786 | 207.974 | 188.221 | 118.519 | −355.231 | −173.447 | 1.510 |

PREVIOUS December 1971 (1 atm) CURRENT: June 1982 (1 bar)

## Iron Fluoride (FeF) IDEAL GAS $M_r = 74.845403$ Iron Fluoride (FeF) $F_1Fe_1(g)$

$\Delta_f H°(0\ K) = [47.549 \pm 20.9]\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = [240.337]\ J\ K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [47.698 \pm 20.9]\ kJ \cdot mol^{-1}$

| Electronic Level and Quantum Weight<br>State | $\epsilon_i$, $cm^{-1}$ | $g_i$ |
|---|---|---|
| $[^6\Sigma]$ | 0 | [6] |

$\omega_e = [630.0]\ cm^{-1}$ $\omega_e x_e = [2.7]\ cm^{-1}$ $\sigma = 1$

$B_e = [0.3670]\ cm^{-1}$ $\alpha_e = [0.0017]\ cm^{-1}$ $r_e = [1.8]$ Å

### Enthalpy of Formation

The dissociation energy of FeF(g) was estimated as 4.64±0.22 eV or 107±5 kcal·mol$^{-1}$ by Margrave [1] From the value of $D_0°$(FeF), the enthalpy of formation, $\Delta_f H°$(298.15 K), for FeF(g) is derived to be 11.4±5.0 kcal·mol$^{-1}$.

### Heat Capacity and Entropy

The ground state configuration and bond distance ($r_e$) were estimated by comparison with those for FeCl(g) The value of $B_e$ was calculated using the relationship $B_e = (2.79889 \times 10^{-39})/I$ where $I$ = moment of inertia of FeF(g), and $\alpha_e$ was estimated by comparison with those for AlF(g), AlCl(g) and FeCl(g). The value of $\omega_e$ was derived from the bond distance, reduced mass and number of valence electrons according to the method given by Guggenheimer[2] and the $\omega_e x_e$ was estimated from those for AlF(g), AlCl(g) and FeCl(g).

### References

[1] J. L. Margrave, "Optical Spectra and Molecular Parameters of Light Element Molecules," William Marsh Rice University, Houston, Texas, Progress Report No. 8, (January 1st to March 31, 1965).

[2] K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946).

| Enthalpy Reference Temperature = $T_r$ = 298.15 K | | | | | | Standard State Pressure = $p°$ = 0.1 MPa | |
|---|---|---|---|---|---|---|---|
| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −9.067 | 47.549 | 47.549 | INFINITE |
| 100 | 29.193 | 206.817 | 268.389 | −6.157 | 48.583 | 37 027 | −19.341 |
| 200 | 31.049 | 227.505 | 243.314 | −3.162 | 48.345 | 25.499 | −6.660 |
| 250 | 32.266 | 234.566 | 240.880 | −1.578 | 48.040 | 19.822 | −4.142 |
| 298.15 | 33.264 | 240.337 | 240.337 | 0. | 47.698 | 14.418 | −2.526 |
| 300 | 33.298 | 240.543 | 240.338 | 0.062 | 47.684 | 14.211 | −2.474 |
| 350 | 34.117 | 245.740 | 240.747 | 1.748 | 47.289 | 8.663 | −1.293 |
| 400 | 34.754 | 250.339 | 241.664 | 3.470 | 46.855 | 3.174 | −0.414 |
| 450 | 35.249 | 254.463 | 242.861 | 5.221 | 46.374 | −2.258 | 0.262 |
| 500 | 35.639 | 258.197 | 244.211 | 6.993 | 45.842 | −7.633 | 0.797 |
| 600 | 36.201 | 264.749 | 247.103 | 10.587 | 44.614 | −18.217 | 1.586 |
| 700 | 36.578 | 270.359 | 250.034 | 14.228 | 43.152 | −28.576 | 2.132 |
| 800 | 36.846 | 275.262 | 252.888 | 17.899 | 41.405 | −38.708 | 2.527 |
| 900 | 37.045 | 279.614 | 255.620 | 21.594 | 39.244 | −48.598 | 2.821 |
| 1000 | 37.200 | 283.525 | 258.218 | 25.307 | 36.364 | −58.213 | 3.041 |
| 1100 | 37.324 | 287.077 | 260.683 | 29.033 | 32.588 | −67.474 | 3.204 |
| 1200 | 37.428 | 290.329 | 263.020 | 32.771 | 29.363 | −76.447 | 3.328 |
| 1300 | 37.516 | 293.328 | 265.237 | 36.518 | 27.782 | −85.201 | 3.423 |
| 1400 | 37.594 | 296.111 | 267.344 | 40.274 | 26.115 | −93.830 | 3.501 |
| 1500 | 37.663 | 298.708 | 269.350 | 44.037 | 24.362 | −102.337 | 3.564 |
| 1600 | 37.725 | 301.140 | 271.261 | 47.806 | 22.523 | −110.724 | 3.615 |
| 1700 | 37.783 | 303.429 | 273.087 | 51.582 | 19.647 | −118.975 | 3.656 |
| 1800 | 37.837 | 305.590 | 274.833 | 55.363 | 17.302 | −127.062 | 3.687 |
| 1900 | 37.887 | 307.637 | 276.506 | 59.149 | 0.774 | −134.314 | 3.693 |
| 2000 | 37.935 | 309.582 | 278.112 | 62.940 | −1.978 | −141.353 | 3.692 |
| 2100 | 37.981 | 311.434 | 279.655 | 66.736 | −4.728 | −148.254 | 3.688 |
| 2200 | 38.026 | 313.202 | 281.140 | 70.536 | −7.474 | −155.024 | 3.681 |
| 2300 | 38.068 | 314.893 | 282.571 | 74.341 | −10.216 | −161.670 | 3.672 |
| 2400 | 38.110 | 316.514 | 283.952 | 78.150 | −12.951 | −168.196 | 3.661 |
| 2500 | 38.151 | 318.071 | 285.285 | 81.963 | −15.678 | −174.609 | 3.648 |
| 2600 | 38.191 | 319.568 | 286.575 | 85.780 | −18.394 | −180.912 | 3.635 |
| 2700 | 38.230 | 321.010 | 287.824 | 89.601 | −21.099 | −187.111 | 3.620 |
| 2800 | 38.268 | 322.401 | 289.034 | 93.426 | −23.790 | −193.211 | 3.604 |
| 2900 | 38.306 | 323.744 | 290.208 | 97.255 | −26.467 | −199.214 | 3.588 |
| 3000 | 38.344 | 325.044 | 291.348 | 101.087 | −29.127 | −205.126 | 3.572 |
| 3100 | 38.381 | 326.302 | 292.455 | 104.923 | −31.771 | −210.949 | 3.554 |
| 3200 | 38.417 | 327.521 | 293.532 | 108.763 | −382.696 | −209.263 | 3.416 |
| 3300 | 38.454 | 328.703 | 294.580 | 112.607 | −383.402 | −203.832 | 3.226 |
| 3400 | 38.490 | 329.852 | 295.601 | 116.454 | −384.122 | −198.380 | 3.048 |
| 3500 | 38.525 | 330.968 | 296.595 | 120.305 | −384.855 | −192.906 | 2.879 |
| 3600 | 38.561 | 332.054 | 297.565 | 124.159 | −385.602 | −187.411 | 2.719 |
| 3700 | 38.596 | 333.111 | 298.512 | 128.017 | −386.363 | −181.895 | 2.568 |
| 3800 | 38.632 | 334.141 | 299.436 | 131.878 | −387.139 | −176.359 | 2.424 |
| 3900 | 38.667 | 335.145 | 300.339 | 135.743 | −387.931 | −170.802 | 2.288 |
| 4000 | 38.702 | 336.124 | 301.221 | 139.612 | −388.740 | −165.224 | 2.158 |
| 4100 | 38.736 | 337.080 | 302.084 | 143.484 | −389.567 | −159.626 | 2.034 |
| 4200 | 38.771 | 338.014 | 302.928 | 147.359 | −390.414 | −154.007 | 1.915 |
| 4300 | 38.806 | 338.927 | 303.755 | 151.238 | −391.280 | −148.369 | 1.802 |
| 4400 | 38.840 | 339.819 | 304.565 | 155.120 | −392.168 | −142.709 | 1.694 |
| 4500 | 38.874 | 340.692 | 305.358 | 159.006 | −393.079 | −137.030 | 1.591 |
| 4600 | 38.909 | 341.547 | 306.135 | 162.895 | −394.014 | −131.329 | 1.491 |
| 4700 | 38.943 | 342.384 | 306.898 | 166.788 | −394.976 | −125.608 | 1.396 |
| 4800 | 38.977 | 343.205 | 307.645 | 170.684 | −395.964 | −119.867 | 1.304 |
| 4900 | 39.011 | 344.009 | 308.379 | 174.583 | −396.982 | −114.104 | 1.216 |
| 5000 | 39.045 | 344.797 | 309.100 | 178.486 | −398.030 | −108.321 | 1.132 |
| 5100 | 39.079 | 345.571 | 309.807 | 182.392 | −399.110 | −102.516 | 1.050 |
| 5200 | 39.113 | 346.330 | 310.503 | 186.301 | −400.224 | −96.689 | 0.971 |
| 5300 | 39.147 | 347.075 | 311.186 | 190.214 | −401.374 | −90.841 | 0.895 |
| 5400 | 39.180 | 347.807 | 311.857 | 194.131 | −402.561 | −84.971 | 0.822 |
| 5500 | 39.214 | 348.526 | 312.517 | 198.050 | −403.789 | −79.079 | 0.751 |
| 5600 | 39.248 | 349.233 | 313.167 | 201.974 | −405.059 | −73.163 | 0.682 |
| 5700 | 39.281 | 349.928 | 313.805 | 205.900 | −406.374 | −67.225 | 0.616 |
| 5800 | 39.315 | 350.612 | 314.434 | 209.830 | −407.736 | −61.264 | 0.552 |
| 5900 | 39.349 | 351.284 | 315.053 | 213.763 | −409.148 | −55.278 | 0.489 |
| 6000 | 39.382 | 351.946 | 315.662 | 217.700 | −410.613 | −49.268 | 0.429 |

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

**Hydrogen Fluoride (HF)** **IDEAL GAS** $M_r = 20.006343$ **Hydrogen Fluoride (HF)** $F_1H_1(g)$

$S°(298.15\ K) = 173.780 \pm 0.033\ J\ K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -272.499 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -272.546 \pm 0.8\ kJ \cdot mol^{-1}$

Electronic States and Molecular Constants ($\sigma = 1$)

| State | $T_o$, cm$^{-1}$ | $g_i$ | $\omega_e$, cm$^{-1}$ | $\omega_e x_e$, cm$^{-1}$ | $B_e$, cm$^{-1}$ | $\alpha_e$, cm$^{-1}$ | $r_e$, Å |
|---|---|---|---|---|---|---|---|
| $X^1\Sigma^+$ | 0 | 1 | 4138.73 | 90.05 | 20.9555 | 0.7958 | 0.9168 |
| $B^1\Sigma^+$ | 83275 | 1 | 1158.46 | 17.718 | 4.0263 | 0.0173 | 2.091 |

## Enthalpy of Formation

The enthalpy of formation was adopted from the 1968 JANAF Thermochemical Table.[1] This value was obtained by simultaneous selection[2] of $\Delta_f H°$(298.15 K) for HF(g), $BF_3$(g), $NF_3$(g), $CF_4$(g), NaF(cr), and $C_2F_4$(polymer). Subsequent data have led CODATA[3] to recommend the more negative value of $-65.32 \pm 0.17$ kcal·mol$^{-1}$ for HF(g).

## Heat Capacity and Entropy

The vibrational and rotational constants of the respective electronic levels were taken from Rosen.[4] These constants do not differ appreciably from those given in the 1968 JANAF Tables.[1] The values of $\Delta_f H°$, $\Delta_f G°$, and log *Kp* are appreciably different because of the new thermal functions for the reference state $F_2$.[5]

The National Bureau of Standards prepared this table[6] from data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[6] we recalculate the table in terms of 1973 fundamental constants,[7] 1975 atomic weights,[8] and current JANAF reference states for the elements.[5] A more complete analysis of electronic states and molecular constants is now available.[9]

## References

[1] JANAF Thermochemical Tables, 2nd ed., NSRDS–NBS 37, 1971, HF(g), 6–31–68.
[2] H. Prophet and A. N Syverud, The Dow Chemical Co., AD–867952, 76 pp (1970).
[3] ICSU–CODATA Task Group on Key Values for Thermodynamics, J. Chem Thermodyn 8, 603 (1976).
[4] B. Rosen, "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, (1970).
[5] JANAF Thermochemical Tables: $F_2$(ref), 6–30–77, $H_2$(ref), 3–31–77.
[6] S. Abramowitz *et al*., U. S. Nat. Bur. Stand. Rept. 10904, 239, (July 1972).
[7] CODATA Task Group on Fundamental Constants, CODATA Bulletin **11**, (December 1973).
[8] IUPAC Commission on Atomic Weights, Pure Appl. Chem. **47**, 75 (1976).
[9] G. Di Lonardo and A. E. Douglas, Can. J. Phys. **51**, 434 (1973).

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

|  | J·K$^{-1}$mol$^{-1}$ |  |  | kJ·mol$^{-1}$ |  |  |  |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −8.599 | −272.499 | −272.499 | INFINITE |
| 100 | 29.128 | 141.959 | 199.679 | −5.772 | −272.625 | −273.266 | 142.739 |
| 200 | 29.128 | 162.148 | 176.445 | −2.859 | −272.524 | −273.947 | 71.548 |
| 250 | 29.133 | 168.648 | 174.260 | −1.403 | −272.516 | −274.304 | 57.313 |
| 298.15 | 29.138 | 173.780 | 173.780 | 0. | −272.546 | −274.646 | 48.117 |
| 300 | 29.138 | 173.960 | 173.780 | 0.054 | −272.548 | −274.659 | 47.822 |
| 350 | 29.143 | 178.452 | 174.135 | 1.511 | −272.609 | −275.007 | 41.043 |
| 400 | 29.150 | 182.344 | 174.923 | 2.968 | −272.696 | −275.344 | 35.956 |
| 450 | 29.159 | 185.778 | 175.943 | 4.426 | −272.802 | −275.669 | 31.999 |
| 500 | 29.173 | 188.851 | 177.082 | 5.884 | −272.924 | −275.981 | 28.831 |
| 600 | 29.230 | 194.174 | 179.501 | 8.804 | −273.205 | −276.566 | 24.077 |
| 700 | 29.351 | 198.688 | 181.927 | 11.732 | −273.522 | −277.102 | 20.678 |
| 800 | 29.550 | 202.619 | 184.273 | 14.677 | −273.858 | −277.590 | 18.125 |
| 900 | 29.827 | 206.115 | 186.510 | 17.645 | −274.205 | −278.036 | 16.137 |
| 1000 | 30.169 | 209.275 | 188.631 | 20.644 | −274.552 | −278.443 | 14.544 |
| 1100 | 30.556 | 212.168 | 190.641 | 23.680 | −274.896 | −278.816 | 13.240 |
| 1200 | 30.971 | 214.845 | 192.547 | 26.757 | −275.231 | −279.157 | 12.151 |
| 1300 | 31.397 | 217.340 | 194.360 | 29.875 | −275.558 | −279.471 | 11.229 |
| 1400 | 31.822 | 219.683 | 196.086 | 33.036 | −275.874 | −279.760 | 10.438 |
| 1500 | 32.237 | 221.893 | 197.733 | 36.239 | −276.181 | −280.027 | 9.751 |
| 1600 | 32.636 | 223.986 | 199.309 | 39.483 | −276.477 | −280.273 | 9.150 |
| 1700 | 33.017 | 225.976 | 200.820 | 42.766 | −276.763 | −280.502 | 8.619 |
| 1800 | 33.376 | 227.873 | 202.270 | 46.085 | −277.040 | −280.714 | 8.146 |
| 1900 | 33.713 | 229.687 | 203.666 | 49.440 | −277.308 | −280.911 | 7.723 |
| 2000 | 34.029 | 231.424 | 205.011 | 52.827 | −277.566 | −281.093 | 7.341 |
| 2100 | 34.325 | 233.092 | 206.309 | 56.245 | −277.815 | −281.264 | 6.996 |
| 2200 | 34.601 | 234.695 | 207.563 | 59.692 | −278.053 | −281.422 | 6.682 |
| 2300 | 34.858 | 236.239 | 208.776 | 63.165 | −278.279 | −281.570 | 6.395 |
| 2400 | 35.099 | 237.728 | 209.952 | 66.663 | −278.493 | −281.709 | 6.131 |
| 2500 | 35.323 | 239.165 | 211.092 | 70.184 | −278.694 | −281.838 | 5.889 |
| 2600 | 35.533 | 240.555 | 212.198 | 73.727 | −278.882 | −281.961 | 5.665 |
| 2700 | 35.730 | 241.899 | 213.273 | 77.290 | −279.054 | −282.076 | 5.457 |
| 2800 | 35.914 | 243.202 | 214.319 | 80.872 | −279.210 | −282.185 | 5.264 |
| 2900 | 36.088 | 244.466 | 215.337 | 84.473 | −279.349 | −282.288 | 5.085 |
| 3000 | 36.251 | 245.692 | 216.329 | 88.090 | −279.472 | −282.388 | 4.917 |
| 3100 | 36.405 | 246.883 | 217.295 | 91.723 | −279.576 | −282.483 | 4.760 |
| 3200 | 36.550 | 248.041 | 218.238 | 95.370 | −279.662 | −282.575 | 4.613 |
| 3300 | 36.687 | 249.168 | 219.158 | 99.032 | −279.730 | −282.665 | 4.474 |
| 3400 | 36.818 | 250.265 | 220.057 | 102.708 | −279.779 | −282.754 | 4.344 |
| 3500 | 36.941 | 251.334 | 220.935 | 106.395 | −279.809 | −282.841 | 4.221 |
| 3600 | 37.059 | 252.376 | 221.794 | 110.096 | −279.821 | −282.927 | 4.105 |
| 3700 | 37.171 | 253.393 | 222.635 | 113.807 | −279.814 | −283.013 | 3.995 |
| 3800 | 37.279 | 254.386 | 223.457 | 117.530 | −279.789 | −283.100 | 3.891 |
| 3900 | 37.381 | 255.356 | 224.263 | 121.263 | −279.746 | −283.188 | 3.793 |
| 4000 | 37.480 | 256.303 | 225.052 | 125.006 | −279.685 | −283.277 | 3.699 |
| 4100 | 37.574 | 257.230 | 225.826 | 128.759 | −279.607 | −283.367 | 3.610 |
| 4200 | 37.665 | 258.137 | 226.584 | 132.521 | −279.512 | −283.460 | 3.525 |
| 4300 | 37.753 | 259.024 | 227.328 | 136.292 | −279.400 | −283.556 | 3.445 |
| 4400 | 37.837 | 259.893 | 228.059 | 140.071 | −279.273 | −283.654 | 3.367 |
| 4500 | 37.919 | 260.744 | 228.775 | 143.859 | −279.130 | −283.755 | 3.294 |
| 4600 | 37.998 | 261.578 | 229.479 | 147.655 | −278.971 | −283.859 | 3.223 |
| 4700 | 38.074 | 262.396 | 230.171 | 151.458 | −278.798 | −283.967 | 3.156 |
| 4800 | 38.149 | 263.199 | 230.851 | 155.270 | −278.611 | −284.079 | 3.091 |
| 4900 | 38.221 | 263.986 | 231.519 | 159.088 | −278.410 | −284.195 | 3.030 |
| 5000 | 38.291 | 264.759 | 232.176 | 162.914 | −278.195 | −284.315 | 2.970 |
| 5100 | 38.359 | 265.518 | 232.823 | 166.746 | −277.967 | −284.440 | 2.913 |
| 5200 | 38.426 | 266.263 | 233.459 | 170.585 | −277.725 | −284.569 | 2.859 |
| 5300 | 38.491 | 266.996 | 234.084 | 174.431 | −277.471 | −284.703 | 2.806 |
| 5400 | 38.555 | 267.716 | 234.701 | 178.284 | −277.204 | −284.842 | 2.755 |
| 5500 | 38.617 | 268.424 | 235.307 | 182.142 | −276.925 | −284.987 | 2.707 |
| 5600 | 38.678 | 269.120 | 235.905 | 186.007 | −276.633 | −285.135 | 2.660 |
| 5700 | 38.737 | 269.806 | 236.494 | 189.878 | −276.329 | −285.290 | 2.614 |
| 5800 | 38.796 | 270.480 | 237.074 | 193.754 | −276.013 | −285.450 | 2.571 |
| 5900 | 38.853 | 271.143 | 237.646 | 197.637 | −275.684 | −285.616 | 2.529 |
| 6000 | 38.910 | 271.797 | 238.209 | 201.525 | −275.343 | −285.787 | 2.488 |

PREVIOUS: June 1977 (1 atm)    CURRENT June 1977 (1 bar)

## Hypofluorous Acid (HOF) IDEAL GAS $M_r = 56.005743$ Hypofluorous Acid (HOF) $F_1H_1O_1(g)$

$S°(298.15 \text{ K}) = 226.772 \pm 0.21 \text{ J K}^{-1}\cdot\text{mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = -95.423 \pm 4.2 \text{ kJ}\cdot\text{mol}^{-1}$
$\Delta_f H°(298.15 \text{ K}) = -98.324 \pm 4.2 \text{ kJ}\cdot\text{mol}^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, cm$^{-1}$ |
|---|
| 3578.5(1) |
| 1354.8(1) |
| 889.0(1) |

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: $C_s$
Bond Distances: H–O = 0.966 Å; O–F = 1.442 Å
Bond Angle: H–O–F = 96.78°
Product of the Moments of Inertia: $I_A I_B I_C = 1.4723 \times 10^{-117} \text{ g}^3\cdot\text{cm}^6$

### Enthalpy of Formation

$\Delta_f H°(0 \text{ K})$ is the value derived by Berkowitz *et al.*[1] from photoionization data which gave 14.34 eV as the threshold of $O^+$ formation, $HOF + h + O^+HF + e^-$. The threshold of $OH^+$ formation, 15.07 eV for $HOF + h \rightarrow + OH^+ + F + e^-$, yields $\Delta_f H°(0 \text{ K}) = -21.7 \text{ kcal mol}^{-1}$ assuming $\Delta_f H°(OH^+, 0 \text{ K}) = 307.5 \pm 0.5 \text{ kcal}\cdot\text{mol}^{-1}$ from Dibeler *et al.*[2] The latter authors found 18.05 eV for $H_2O + h \rightarrow OH^+ + H^+ + e.^-$ Our adopted value for HOF differs by only 2.5 kcal·mol$^{-1}$ from the mean $\Delta_f H°(0 \text{ K})$ of $H_2O$ and $F_2O$, namely −25.3 kcal·mol$^{-1}$.

### Heat Capacity and Entropy

Vibrational frequencies are from gas–phase infrared spectra of Appelman and Kim,[3] the values are confirmed by IR spectra of HOF isolated in a matrix of $N_2$.[4] Structural parameters are those derived by Pearson and Kim[5] from centrifugal distortion analysis of mm wave rotational spectra[5 6] of HOF and DOF. We use the atomic coordinates[5] to derive the principal moments of inertia are $I_A = 0.1431 \times 10^{-39}$, $I_B = 3.1363 \times 10^{-39}$, and $I_C = 3.2795 \times 10^{-39} \text{ g}\cdot\text{cm}^2$ and their product, the corresponding bond distances are 0.96648 and 1.44215 Å, i.e., slightly longer than the rounded values[5] listed above. The earlier study[6] gave 0.964 ± 0.01 and 1.442 ± 0.001 Å and a bond angle of 97.2 ± 0.6°.

### References

[1] J. Berkowitz, E. H. Appelman and W. A. Chupka, J. Chem. Phys., in press.
[2] V. H. Dibeler, J. A. Walker and H. M. Rosenstock, J Res. Nat. Bur. Stand. 70A, 459 (1966).
[3] E. H. Appelman and H. Kim, J Chem. Phys. 57, 3272 (1972).
[4] J. A. Goleb, H. H. Claasen, M. H Studier and E. H. Appelman, Spectrochim. Acta 28A, 65 (1972).
[5] E. F. Pearson and H. Kim, J. Chem. Phys. 57, 4230 (1972).
[6] H. Kim, E. F. Pearson and E. H. Appelman, J. Chem Phys. 56, 1 (1972).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −10.087 | −95.423 | −95.423 | INFINITE |
| 100 | 33.261 | 189.739 | 257.352 | −6.761 | −96.503 | −93.257 | 48.712 |
| 200 | 33.873 | 212.899 | 229.983 | −3.417 | −97.425 | −89.650 | 23.414 |
| 250 | 34.787 | 220.549 | 227.357 | −1.702 | −97.889 | −87.653 | 18.314 |
| 298.15 | 35.929 | 226.772 | 226.772 | 0. | −98.324 | −85.642 | 15.004 |
| 300 | 35.976 | 226.994 | 226.772 | 0.067 | −98.340 | −85.563 | 14.898 |
| 350 | 37.277 | 232.637 | 227.215 | 1.898 | −98.766 | −83.399 | 12.447 |
| 400 | 38.571 | 237.700 | 228.215 | 3.794 | −99.161 | −81.177 | 10.601 |
| 450 | 39.790 | 242.314 | 229.528 | 5.753 | −99.524 | −78.907 | 9.159 |
| 500 | 40.907 | 246.565 | 231.022 | 7.771 | −99.857 | −76.598 | 8.002 |
| 600 | 42.830 | 254.199 | 234.263 | 11.962 | −100.448 | −71.889 | 6.258 |
| 700 | 44.409 | 260.924 | 237.601 | 16.326 | −100.956 | −67.088 | 5.006 |
| 800 | 45.744 | 266.943 | 240.899 | 20.835 | −101.396 | −62.219 | 4.062 |
| 900 | 46.906 | 272.400 | 244.101 | 25.469 | −101.779 | −57.298 | 3.325 |
| 1000 | 47.936 | 277.396 | 247.184 | 30.212 | −102.114 | −52.337 | 2.734 |
| 1100 | 48.858 | 282.009 | 250.143 | 35.053 | −102.408 | −47.345 | 2.248 |
| 1200 | 49.687 | 286.296 | 252.979 | 39.981 | −102.666 | −42.328 | 1.842 |
| 1300 | 50.432 | 290.303 | 255.698 | 44.987 | −102.896 | −37.290 | 1.498 |
| 1400 | 51.102 | 294.066 | 258.305 | 50.065 | −103.103 | −32.235 | 1.203 |
| 1500 | 51.703 | 297.612 | 260.809 | 55.205 | −103.292 | −27.167 | 0.946 |
| 1600 | 52.242 | 300.967 | 263.215 | 60.403 | −103.468 | −22.086 | 0.721 |
| 1700 | 52.726 | 304.148 | 265.530 | 65.652 | −103.634 | −16.995 | 0.522 |
| 1800 | 53.160 | 307.175 | 267.760 | 70.946 | −103.794 | −11.894 | 0.345 |
| 1900 | 53.550 | 310.060 | 269.911 | 76.282 | −103.951 | −6.784 | 0.186 |
| 2000 | 53.901 | 312.815 | 271.988 | 81.655 | −104.105 | −1.666 | 0.043 |
| 2100 | 54.217 | 315.453 | 273.995 | 87.061 | −104.257 | 3.460 | −0.086 |
| 2200 | 54.503 | 317.982 | 275.938 | 92.498 | −104.409 | 8.593 | −0.204 |
| 2300 | 54.761 | 320.410 | 277.819 | 97.961 | −104.561 | 13.733 | −0.312 |
| 2400 | 54.994 | 322.746 | 279.642 | 103.449 | −104.712 | 18.879 | −0.411 |
| 2500 | 55.206 | 324.995 | 281.412 | 108.959 | −104.861 | 24.032 | −0.502 |
| 2600 | 55.399 | 327.164 | 283.130 | 114 489 | −105.009 | 29.191 | −0.586 |
| 2700 | 55.575 | 329.259 | 284.800 | 120.038 | −105.154 | 34.355 | −0.665 |
| 2800 | 55.736 | 331.283 | 286.424 | 125.604 | −105.296 | 39.525 | −0.737 |
| 2900 | 55.883 | 333.241 | 288.005 | 131.185 | −105.433 | 44.699 | −0.805 |
| 3000 | 56.018 | 335.138 | 289.545 | 136.780 | −105.566 | 49.879 | −0.868 |
| 3100 | 56.141 | 336.977 | 291.045 | 142.388 | −105.693 | 55.062 | −0.928 |
| 3200 | 56.255 | 338.761 | 292.508 | 148.008 | −105.814 | 60.250 | −0.983 |
| 3300 | 56.360 | 340.494 | 293.936 | 153.639 | −105.928 | 65 441 | −1.036 |
| 3400 | 56.457 | 342.178 | 295.331 | 159.280 | −106.035 | 70.636 | −1.085 |
| 3500 | 56.547 | 343.816 | 296.693 | 164.930 | −106.135 | 75.833 | −1.132 |
| 3600 | 56.630 | 345.410 | 298.024 | 170.589 | −106.228 | 81.034 | −1 176 |
| 3700 | 56.708 | 346.962 | 299.326 | 176.256 | −106.313 | 86.236 | −1.217 |
| 3800 | 56.780 | 348.476 | 300.599 | 181.930 | −106.390 | 91.442 | −1.257 |
| 3900 | 56.847 | 349.951 | 301.846 | 187.612 | −106.459 | 96.649 | −1.294 |
| 4000 | 56.909 | 351.391 | 303.067 | 193.300 | −106.522 | 101.858 | −1.330 |
| 4100 | 56.967 | 352.797 | 304.262 | 198.994 | −106.577 | 107.068 | −1.364 |
| 4200 | 57.022 | 354.171 | 305.434 | 204.693 | −106.625 | 112.279 | −1.396 |
| 4300 | 57.073 | 355.513 | 306.583 | 210.398 | −106.666 | 117.492 | −1.427 |
| 4400 | 57.121 | 356.826 | 307.710 | 216.107 | −106.702 | 122.705 | −1.457 |
| 4500 | 57.166 | 358.110 | 308.816 | 221.822 | −106.731 | 127.919 | −1.485 |
| 4600 | 57.208 | 359.367 | 309.902 | 227.541 | −106.755 | 133.133 | −1.512 |
| 4700 | 57.248 | 360.598 | 310.967 | 233.263 | −106.774 | 138.349 | −1.538 |
| 4800 | 57.285 | 361.803 | 312.014 | 238.990 | −106.789 | 143.565 | −1.562 |
| 4900 | 57.320 | 362.985 | 313.042 | 244.720 | −106.800 | 148.781 | −1.586 |
| 5000 | 57.354 | 364.143 | 314.052 | 250.454 | −106.807 | 153.997 | −1.609 |
| 5100 | 57.385 | 365.279 | 315.046 | 256.191 | −106.812 | 159.213 | −1.631 |
| 5200 | 57.415 | 366.394 | 316.023 | 261.931 | −106.814 | 164.429 | −1.652 |
| 5300 | 57.443 | 367.488 | 316.983 | 267.674 | −106.814 | 169.645 | −1.672 |
| 5400 | 57.470 | 368.562 | 317.929 | 273.420 | −106.813 | 174.861 | −1.691 |
| 5500 | 57 496 | 369.617 | 318.859 | 279.168 | −106.811 | 180.077 | −1 710 |
| 5600 | 57.520 | 370.653 | 319.774 | 284.919 | −106.809 | 185.294 | −1.728 |
| 5700 | 57.543 | 371.671 | 320.676 | 290.672 | −106.807 | 190.509 | −1.746 |
| 5800 | 57.564 | 372.672 | 321.564 | 296.427 | −106.806 | 195.726 | −1.763 |
| 5900 | 57.585 | 373.656 | 322.438 | 302.185 | −106.805 | 200 941 | −1.779 |
| 6000 | 57.605 | 374.624 | 323.300 | 307.944 | −106.807 | 206.158 | −1.795 |

PREVIOUS: December 1972 (1 atm) CURRENT. December 1972 (1 bar)

# Fluorosulfuric Acid ($HSO_3F$) IDEAL GAS $M_r = 100.064543$ Fluorosulfuric Acid ($HSO_3F$) $F_1H_1O_3S_1(g)$

$\Delta_fH°(0\ K) = -742.051 \pm 8.4\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = 297.267 \pm 3.3\ J\ K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = -753.120 \pm 8.4\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|---|
| 3602(1) | 825(1) | 1486(1) |
| 1243(1) | 550(1) | 562(1) |
| 1150(1) | 410(1) | 390(1) |
| 896(1) | 390(1) | 265(1) |

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: [$C_s$]
Bond Distances: O–S = [1.405] Å; S–OH = S–F = [1.53] Å; O–H = [1.00] Å
Bond Angles: O–S–O = [124°]; F–S–OH = S–O–H = [100°]
Product of the Moments of Inertia: $I_AI_BI_C = [4.2743 \times 10^{-114}]\ g^3{\cdot}cm^6$

## Enthalpy of Formation

$\Delta_fH°(l, 298.15\ K)$ may be derived from calorimetric data of Richards and Woolf[1] which yield $\Delta_rH°(298.15\ K) = -14.94 \pm 0.2\ kcal{\cdot}mol^{-1}$ for $SO_3(l) + HF$ (real gas, 1 atm) $\rightarrow HSO_3F(l)$. Using $\Delta_fH°(SO_3, l, 0\ K) = -105.41$[2] and $\Delta_fH°$(HF, real gas, 0 K) = $-70.12$[3,4] $kcal{\cdot}mol^{-1}$, we derive $\Delta_fH° = -190.5\ kcal{\cdot}mol^{-1}$ for $HSO_3F(l)$ and $-180.3 \pm 1.5\ kcal{\cdot}mol^{-1}$ for the ideal gas. The latter value agrees well with $-179.2 \pm 3\ kcal{\cdot}mol^{-1}$ estimated for $HSO_3F(g)$ from the related molecules $SO_2F_2$ and $H_2SO_4$.[4] We adopt $\Delta_fH° = -180 \pm 2\ kcal{\cdot}mol^{-1}$ ($-753.120 \pm 8.4\ kJ{\cdot}mol^{-1}$).

Derivation of $\Delta_fH°(g)$ presumes that the heat of vaporization is $10.2 \pm 1.0\ kcal{\cdot}mol^{-1}$ at 25°C. Measurements of the heat of condensation[5] yield $12.8 \pm 0.8\ kcal\ mol^{-1}$ for the enthalpy difference between real gas at 164 4°C and the liquid at 25°C. Added to this value should be $\pm 0.2\ kcal{\cdot}mol^{-1}$ (estimated correction for gas imperfection) and $-2.8\ kcal{\cdot}mol^{-1}$ (calculated enthalpy difference for the ideal gas between 25°C and 164.4°C, the approximate normal boiling point).

Other calorimetric data bearing on $\Delta_fH°$ were reported by Lenskii *et al.*[5] and Woolf,[6] but these results are much more uncertain[1] due to experimental error and to inadequate definition of the states of the reactants and products.

## Heat Capacity and Entropy

Savoie and Giguere[7] reviewed possible molecular structures and preferred eclipsed (cis) forms, arbitrarily selecting one in which F–S–O–H is coplanar. We adopt this structure since the choice changes the thermodynamic functions very little. Possible structures all have $\sigma = 1$ ($C_s$ or $C_1$ symmetry) and similar values of the product of the moments of inertia. Bond lengths and angles are estimated by comparison with $SO_2ClF$,[8]

$SO_2Cl_2$ and $H_2SO_4$.[4] These parameters yield O = S–F and O = S–OH angles of 107.56° and principal moments of inertia are: $I_A = 15.9647 \times 10^{-39}$, $I_B = 16.1688 \times 10^{-39}$, and $I_C = 16.5588 \times 10^{-39}\ g{\cdot}cm^2$.

Vibrational fundamentals are from the assignment of Savoie and Giguere[7] as modified by Chackalackal and Stafford.[9] Data include Raman spectra of the liquid[1] and infrared spectra of all three phases[7] plus the superheated vapor.[9] Spectra of the superheated vapor helped to clarify the vibrational distinction between the monomer and associated molecules. Savoie and Giguere derived a barrier of about $1.3\ kcal{\cdot}mol^{-1}$ for hindered interal rotation of the OH group and used this to calculate $C_p° = 17.64$ and $S° = 71.38\ cal\ K^{-1}{\cdot}mol^{-1}$ at 298.15 K. We calculated $C_p° = 17.98$ and $S° = 71.02\ cal\ K^{-1}{\cdot}mol^{-1}$ using the OH–torsional frequency ($265\ cm^{-1}$) instead of hindered rotation.

## References

[1] G. W. Richards and A. A. Woolf, J. Chem. Soc. A1967, 1118 (1967).
[2] U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).
[3] C. E. Vanderzee and W. W. Rodenburg, J Chem. Thermodyn. 2, 461 (1970).
[4] JANAF Thermochemical Tables: HF(g), 12–31–68; $H_2SO_4(g)$, 12–31–66; $SO_2F_2(g)$ and $SO_2Cl_2(g)$, 6–30–71.
[5] A. S. Lenskii, A. D. Shaposhnikova and E. S. Sokolova, Russ. J. Inorg. Chem. 9, 626 (1964); 8, 1424 (1963).
[6] A. A. Woolf, J. Inorg. Nucl. Chem. 14, 21 (1960).
[7] R. Savoie and P. A. Giguere, Can. J. Chem. 42, 277 (1964).
[8] C. W. Holt and M. C. L. Gerry, Chem. Phys. Letters 9, 621 (1971).
[9] S. M. Chackalackal and F. E. Stafford, J. Amer. Chem. Soc. 88, 4815 (1966).
[10] R. J. Gillespie and E. A. Robinson, Can. J. Chem. 40, 644 (1962).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

|  | J·K$^{-1}$mol$^{-1}$ |  |  | kJ·mol$^{-1}$ |  |  |  |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −15.014 | −742.051 | −742.051 | INFINITE |
| 100 | 39.145 | 237.149 | 352.791 | −11.564 | −746.601 | −729.513 | 381.058 |
| 200 | 59.278 | 270.467 | 303.667 | −6.640 | −750.497 | −710.811 | 185.645 |
| 250 | 67.997 | 284.656 | 298.466 | −3.453 | −751.965 | −700.713 | 146.406 |
| 298.15 | 75.243 | 297.267 | 297.267 | 0. | −753.120 | −690.734 | 121.014 |
| 300 | 75.501 | 297.733 | 297.268 | 0.139 | −753.160 | −690.347 | 120.200 |
| 350 | 81.950 | 309.869 | 298.212 | 4.080 | −754.119 | −679.799 | 101.454 |
| 400 | 87.477 | 321.182 | 300.384 | 8.319 | −757.096 | −669.040 | 87.368 |
| 450 | 92.198 | 331.765 | 303.290 | 12.814 | −758.366 | −657.964 | 76.374 |
| 500 | 96.227 | 341.693 | 306.639 | 17.527 | −759.549 | −646.741 | 67.565 |
| 600 | 102.624 | 359.833 | 314.023 | 27.486 | −761.115 | −624.019 | 54.326 |
| 700 | 107.389 | 376.027 | 321.745 | 37.998 | −762.077 | −601.087 | 44.854 |
| 800 | 111.041 | 390.616 | 329.457 | 48.927 | −762.646 | −578.046 | 37.743 |
| 900 | 113.926 | 403.867 | 337.000 | 60.181 | −816.071 | −553.870 | 32.146 |
| 1000 | 116.264 | 415.996 | 344.302 | 71.694 | −814.954 | −524.795 | 27.412 |
| 1100 | 118.199 | 427.170 | 351.334 | 83.420 | −813.742 | −495.837 | 23.545 |
| 1200 | 119.826 | 437.527 | 358.090 | 95.324 | −812.461 | −466.992 | 20.328 |
| 1300 | 121.210 | 447.174 | 364.576 | 107.377 | −811.130 | −438.257 | 17.609 |
| 1400 | 122.397 | 456.201 | 370.802 | 119.559 | −809.764 | −409.626 | 15.283 |
| 1500 | 123.425 | 464.682 | 376.781 | 131.851 | −808.376 | −381.093 | 13.271 |
| 1600 | 124.318 | 472.676 | 382.527 | 144.239 | −806.977 | −352.653 | 11.513 |
| 1700 | 125.100 | 480.237 | 388.054 | 156.711 | −805.575 | −324.301 | 9.965 |
| 1800 | 125.786 | 487.407 | 393.376 | 169.256 | −804.177 | −296.031 | 8.591 |
| 1900 | 126.392 | 494.225 | 398.506 | 181.866 | −802.788 | −267.839 | 7.363 |
| 2000 | 126.929 | 500.722 | 403.456 | 194.532 | −801.412 | −239 719 | 6.261 |
| 2100 | 127 406 | 506.927 | 408.236 | 207.250 | −800.052 | −211.668 | 5.265 |
| 2200 | 127.832 | 512.864 | 412.858 | 220.012 | −798.708 | −183.680 | 4.361 |
| 2300 | 128.214 | 518.554 | 417.331 | 232.815 | −797.383 | −155.755 | 3.537 |
| 2400 | 128.556 | 524.019 | 421.663 | 245.653 | −796.077 | −127.887 | 2.783 |
| 2500 | 128.865 | 529.273 | 425.863 | 258.525 | −794 789 | −100.072 | 2.091 |
| 2600 | 129.144 | 534.333 | 429.938 | 271.425 | −793.518 | −72.308 | 1.453 |
| 2700 | 129.397 | 539.211 | 433.895 | 284.353 | −792.264 | −44.593 | 0.863 |
| 2800 | 129.626 | 543.921 | 437.741 | 297.304 | −791.026 | −16.924 | 0.316 |
| 2900 | 129.836 | 548.474 | 441.482 | 310.277 | −789.802 | 10.700 | −0.193 |
| 3000 | 130.027 | 552.879 | 445.122 | 323.271 | −788.593 | 38.284 | −0 667 |
| 3100 | 130.202 | 557.145 | 448.667 | 336.282 | −787.395 | 65.827 | −1.109 |
| 3200 | 130.362 | 561.281 | 452.122 | 349.310 | −786.209 | 93.330 | −1.523 |
| 3300 | 130.510 | 565.295 | 455.491 | 362.354 | −785.034 | 120.798 | −1.912 |
| 3400 | 130.645 | 569 193 | 458.778 | 375.412 | −783.868 | 148.230 | −2.277 |
| 3500 | 130.771 | 572.982 | 461.987 | 388.483 | −782.711 | 175.627 | −2.621 |
| 3600 | 130.887 | 576.668 | 465.122 | 401.566 | −781.564 | 202.993 | −2.945 |
| 3700 | 130.994 | 580.256 | 468.185 | 414.660 | −780.424 | 230.325 | −3.252 |
| 3800 | 131.094 | 583.750 | 471 181 | 427.764 | −779.292 | 257.629 | −3.541 |
| 3900 | 131.187 | 587.157 | 474.111 | 440.878 | −778.168 | 284.902 | −3.816 |
| 4000 | 131.273 | 590.479 | 476.979 | 454.001 | −777.053 | 312.145 | −4.076 |
| 4100 | 131.353 | 593.722 | 479.787 | 467.133 | −775.945 | 339.361 | −4.324 |
| 4200 | 131.429 | 596.888 | 482.537 | 480.272 | −774.846 | 366.551 | −4.559 |
| 4300 | 131.499 | 599.981 | 485.233 | 493.418 | −773.756 | 393.714 | −4.783 |
| 4400 | 131.565 | 603.005 | 487.875 | 506.572 | −772.675 | 420.852 | −4 996 |
| 4500 | 131.626 | 605.962 | 490.467 | 519.731 | −771.604 | 447.964 | −5.200 |
| 4600 | 131.684 | 608.856 | 493.009 | 532.897 | −770.545 | 475.054 | −5.394 |
| 4700 | 131.739 | 611.689 | 495.504 | 546.068 | −769.497 | 502.121 | −5.580 |
| 4800 | 131.790 | 614.463 | 497.954 | 559.244 | −768.462 | 529.166 | −5.759 |
| 4900 | 131.838 | 617.181 | 500.359 | 572.426 | −767.440 | 556.190 | −5.929 |
| 5000 | 131.884 | 619.845 | 502.722 | 585.612 | −766.434 | 583.193 | −6.093 |
| 5100 | 131.927 | 622.457 | 505.044 | 598.803 | −765.443 | 610.176 | −6.249 |
| 5200 | 131.968 | 625.019 | 507.327 | 611.997 | −764.470 | 637.138 | −6.400 |
| 5300 | 132.006 | 627.533 | 509.572 | 625.196 | −763.516 | 664.084 | −6.545 |
| 5400 | 132.043 | 630.001 | 511.779 | 638.399 | −762.582 | 691.011 | −6.684 |
| 5500 | 132.077 | 632.424 | 513.950 | 651.605 | −761.669 | 717.919 | −6.818 |
| 5600 | 132.110 | 634.804 | 516.087 | 664.814 | −760.780 | 744.815 | −6.947 |
| 5700 | 132.141 | 637.143 | 518.191 | 678.027 | −759.915 | 771.692 | −7.072 |
| 5800 | 132.171 | 639.441 | 520.261 | 691.242 | −759.075 | 798.556 | −7.192 |
| 5900 | 132.199 | 641.701 | 522.301 | 704.461 | −758.264 | 825.402 | −7.308 |
| 6000 | 132.226 | 643.923 | 524.309 | 717.682 | −757.482 | 852.239 | −7.419 |

PREVIOUS: June 1972 (1 atm) CURRENT: June 1972 (1 bar)

Fluorosulfuric Acid ($HSO_3F$) $F_1H_1O_3S_1(g)$

## Fluorosilane (SiH$_3$F) IDEAL GAS $M_r = 50.107723$ Fluorosilane (SiH$_3$F) F$_1$H$_3$Si$_1$(g)

$S°(298.15 \text{ K}) = 238.402 \pm 0.8 \text{ J K}^{-1}\cdot\text{mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = [-367.16 \pm 20.9] \text{ kJ}\cdot\text{mol}^{-1}$
$\Delta_f H°(298.15 \text{ K}) = [-376.560 \pm 20.9] \text{ kJ}\cdot\text{mol}^{-1}$

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|
| 2206(1) | 2209(2) |
| 991(1) | 961(2) |
| 875(1) | 729(2) |

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: $C_{3v}$
Bond Distances: Si–H = 1.468 Å, Si–F = 1.593 Å
Bond Angles: H–Si–H = 110.43°; H–Si–F = 108.50°
Product of the Moments of Inertia: $I_A I_B I_C = 3.42403 \times 10^{-116} \text{ g}^3\cdot\text{cm}^6$

### Enthalpy of Formation

There are no reported experimental studies leading to the heat of formation of SiH$_3$F(g). We estimate this value via a linear interpolation between the established $\Delta_f H°$(298.15 K) values of SiH$_4$(g) and SiF$_4$(g).[1] The reasonableness of this approach has been demonstrated by Lapidus *et al.*,[2] Hunt and Sirtl,[3] and Seiter and Sirtl.[4] Lapidus *et al.*[2] examined the trends in the thermodynamic properties of halogenated silanes and methanes Hunt and Sirtl[3] and Seiter and Sirtl[4] studied the chlorinated silanes and proposed a linear $\Delta_f H$ relationship within the sequence SiH$_4$(g) to SiCl$_4$(g).

### Heat Capacity and Entropy

The adopted vibrational frequencies are from the gas phase infrared spectra of SiH$_3$F and SiD$_3$F as documented by Robiette *et al.*[5] Except for $\nu_4$ and $\nu_5$ these values are within ±3 cm$^{-1}$ of those suggested in the compilation by Shimanouchi.[6] In particular, based on earlier work, Shimanouchi[6] suggested $\nu_4 = 2196$ cm$^{-1}$ and $\nu_5 = 956$ cm$^{-1}$. The work of Robiette *et al.*[5] is judged to yield more accurate frequencies than the earlier work.

The adopted bond angles and bond distances are obtained from the microwave spectra study on SiH$_3$F and various isotopic derivatives by Kewley *et al.*[7] This work is deemed more accurate than earlier studies.[8-11] The individual moments of inertia are calculated to be $I_A = 0.9972 \times 10^{-39} \text{ g}\cdot\text{cm}^2$ and $I_B = I_C = 5.8599 \times 10^{-39} \text{ g}\cdot\text{cm}^2$.

### References

[1] JANAF Thermochemical Tables: SiH$_4$(g) and SiF$_4$(g), 6–30–76.
[2] I. I. Lapidus, L. A. Nisel'son, and A. L. Seifer in "Thermophysical Properties of Gases and Liquids," No. 1, V. A Rabinovich, Ed., Israel Program for Scientific Translations, Jerusalem, (1970), pp. 102–135 [Translated from Russian].
[3] L. P. Hunt and E. Sirtl, J. Electrochem. Soc. **119**, 1741 (1972)
[4] H. Seiter and E. Sirtl, Z. Naturforsch. **21a**, 1956 (1966).
[5] A. G. Robiette, G. J. Cartwright, A. R. Hoy, and I M. Mills, Mol. Phys. **20**, 541 (1971).
[6] T. Shimanouchi, J. Phys. Chem. Ref. Data **1**, 189 (1972).
[7] R. Kewley, P. M. McKinney, and A. G. Robiette, J Mol. Spectrosc. **34**, 390 (1970).
[8] A. H. Sharbaugh, V. G. Thomas and B. S. Pritchard, Phys. Rev. **78**, 64 (1950).
[9] B Bak, J. Bruhn, and J. Rastrup–Andersen, J. Chem. Phys. **21**, 752 (1953).
[10] B. Bak, J. Bruhn, and J Rastrup–Andersen, Acta Chem. Scand. **8**, 459 (1954).
[11] C Newman, J. K. O'Loane, S. R. Polo, and M. K. Wilson, J Chem. Phys. **25**, 855 (1956).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log K$_f$ |
| 0 | 0. | 0. | INFINITE | −10.931 | −367.160 | −367.160 | INFINITE |
| 100 | 33.317 | 197.814 | 273.865 | −7.605 | −370.052 | −365.823 | 191.086 |
| 200 | 37.439 | 221.708 | 242.386 | −4.136 | −373.267 | −360.386 | 94.123 |
| 250 | 42.143 | 230.548 | 239.150 | −2.150 | −374.977 | −356.968 | 74.584 |
| 298.15 | 47.196 | 238.402 | 238.402 | 0. | −376.560 | −353.354 | 61.906 |
| 300 | 47.391 | 238.694 | 238.402 | 0.087 | −376.619 | −353.210 | 61.499 |
| 350 | 52.495 | 246.387 | 238.998 | 2.586 | −378.123 | −349.188 | 52.113 |
| 400 | 57.187 | 253.708 | 240.383 | 5.330 | −379.466 | −344.960 | 45.047 |
| 450 | 61.420 | 260.693 | 242.255 | 8.297 | −380.647 | −340.575 | 39.533 |
| 500 | 65.229 | 267.364 | 244.435 | 11.465 | −381.676 | −336.066 | 35 109 |
| 600 | 71.784 | 279.856 | 249.312 | 18.326 | −383.321 | −326.781 | 28.449 |
| 700 | 77.185 | 291.340 | 254.507 | 25.783 | −384 494 | −317.258 | 23.674 |
| 800 | 81.656 | 301.948 | 259.783 | 33.732 | −385.288 | −307.595 | 20.084 |
| 900 | 85.359 | 311.787 | 265.021 | 42.089 | −385.782 | −297.851 | 17.287 |
| 1000 | 88 429 | 320.944 | 270.161 | 50.783 | −386.050 | −288.065 | 15.047 |
| 1100 | 90.981 | 329.496 | 275.171 | 59.758 | −386.150 | −278.260 | 13.213 |
| 1200 | 93.109 | 337.506 | 280.035 | 68.965 | −386.131 | −268.452 | 11.685 |
| 1300 | 94.894 | 345.031 | 284.748 | 78.368 | −386.034 | −258.649 | 10.393 |
| 1400 | 96.398 | 352.120 | 289.310 | 87.935 | −385.892 | −248.856 | 9.285 |
| 1500 | 97.673 | 358.816 | 293.722 | 97.640 | −385.728 | −239.073 | 8.325 |
| 1600 | 98.761 | 365.155 | 297.991 | 107.463 | −385.562 | −229.301 | 7.486 |
| 1700 | 99.694 | 371.171 | 302.120 | 117.387 | −435.586 | −219.093 | 6.732 |
| 1800 | 100.500 | 376.893 | 306.116 | 127.398 | −435.226 | −206.369 | 5.989 |
| 1900 | 101.199 | 382.346 | 309.986 | 137.483 | −434.855 | −193.664 | 5.324 |
| 2000 | 101.808 | 387.552 | 313.735 | 147 634 | −434.479 | −180.980 | 4.727 |
| 2100 | 102.343 | 392.533 | 317.370 | 157.843 | −434.102 | −168.314 | 4.187 |
| 2200 | 102.814 | 397.305 | 320.895 | 168.101 | −433.726 | −155.667 | 3.696 |
| 2300 | 103.230 | 401.885 | 324.318 | 178 404 | −433.354 | −143.036 | 3.248 |
| 2400 | 103.601 | 406.286 | 327.642 | 188.745 | −432.985 | −130.421 | 2.839 |
| 2500 | 103.931 | 410.522 | 330.873 | 199.122 | −432.620 | −117.822 | 2.462 |
| 2600 | 104.227 | 414.604 | 334.016 | 209.530 | −432.259 | −105.237 | 2.114 |
| 2700 | 104.493 | 418.543 | 337.074 | 219.967 | −431.902 | −92.666 | 1.793 |
| 2800 | 104.732 | 422.347 | 340.052 | 230.428 | −431.548 | −80.108 | 1.494 |
| 2900 | 104.949 | 426.026 | 342.953 | 240.912 | −431.197 | −67.563 | 1.217 |
| 3000 | 105.146 | 429.588 | 345.782 | 251.417 | −430.848 | −55.030 | 0.958 |
| 3100 | 105.325 | 433.038 | 348.541 | 261.941 | −430.501 | −42.508 | 0.716 |
| 3200 | 105.489 | 436.385 | 351.234 | 272.482 | −430.156 | −29.998 | 0.490 |
| 3300 | 105.638 | 439.633 | 353.864 | 283.038 | −429.812 | −17.498 | 0.277 |
| 3400 | 105.776 | 442.789 | 356.433 | 293.609 | −429.470 | −5.009 | 0.077 |
| 3500 | 105.902 | 445.857 | 358.945 | 304.193 | −429.128 | 7.470 | −0.111 |
| 3600 | 106.018 | 448.842 | 361.401 | 314.789 | −812.940 | 30.400 | −0.441 |
| 3700 | 106.125 | 451.748 | 363.803 | 325.396 | −812.188 | 53.816 | −0.760 |
| 3800 | 106.224 | 454.580 | 366.155 | 336.014 | −811.439 | 77.212 | −1.061 |
| 3900 | 106.316 | 457.340 | 368.458 | 346 641 | −810.694 | 100.588 | −1.347 |
| 4000 | 106.401 | 460.033 | 370.714 | 357.277 | −809.953 | 123.944 | −1.619 |
| 4100 | 106.481 | 462.661 | 372.924 | 367.921 | −809.215 | 147.282 | −1.876 |
| 4200 | 106.554 | 465.228 | 375.092 | 378.573 | −808.480 | 170.603 | −2.122 |
| 4300 | 106.623 | 467.736 | 377.217 | 389.232 | −807.749 | 193.906 | −2.355 |
| 4400 | 106.688 | 470.188 | 379.302 | 399.897 | −807.022 | 217.192 | −2.578 |
| 4500 | 106 748 | 472.586 | 381.349 | 410.569 | −806.300 | 240.461 | −2.791 |
| 4600 | 106.805 | 474.933 | 383.358 | 421.247 | −805.581 | 263.714 | −2.995 |
| 4700 | 106.858 | 477.231 | 385.331 | 431.930 | −804.866 | 286.952 | −3.189 |
| 4800 | 106.908 | 479.481 | 387.269 | 442.618 | −804.156 | 310.175 | −3.375 |
| 4900 | 106.954 | 481.686 | 389.173 | 453.311 | −803.449 | 333.383 | −3.554 |
| 5000 | 106.999 | 483.847 | 391.045 | 464.009 | −802.747 | 356.577 | −3.725 |
| 5100 | 107.040 | 485.966 | 392.886 | 474 711 | −802.049 | 379.755 | −3.889 |
| 5200 | 107.079 | 488.045 | 394.696 | 485.417 | −801.354 | 402.922 | −4 047 |
| 5300 | 107.117 | 490.085 | 396.476 | 496.127 | −800.663 | 426.074 | −4.199 |
| 5400 | 107.152 | 492.088 | 398.229 | 506.840 | −799.975 | 449.214 | −4.345 |
| 5500 | 107.185 | 494 054 | 399.953 | 517.557 | −799.289 | 472.340 | −4.486 |
| 5600 | 107.217 | 495.986 | 401.651 | 528.277 | −798.607 | 495.455 | −4.621 |
| 5700 | 107.246 | 497.884 | 403.322 | 539.000 | −797.926 | 518.557 | −4.752 |
| 5800 | 107.275 | 499.749 | 404.969 | 549.726 | −797.246 | 541.648 | −4.878 |
| 5900 | 107.302 | 501.583 | 406.591 | 560 455 | −796.567 | 564.726 | −5.000 |
| 6000 | 107.328 | 503.387 | 408.189 | 571.187 | −795.888 | 587.792 | −5.117 |

PREVIOUS June 1976 (1 atm) CURRENT: June 1976 (1 bar)

## Mercury Fluoride (HgF) IDEAL GAS $M_r = 219.588403$ Mercury Fluoride (HgF) $F_1Hg_1(g)$

$\Delta_f H°(0\ K) = 7.370\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 248.373\ J\ K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = 2.929 \pm 50.2\ kJ \cdot mol^{-1}$

| Electronic Level and Quantum Weight<br>State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|
| $^2\Sigma$ | 0 | 2 |

$\omega_e = 490.8\ cm^{-1}$ $\omega_e x_e = 4.05\ cm^{-1}$ $\sigma = 1$

$B_e = [0.2732]\ cm^{-1}$ $\alpha_e = [0.0026]\ cm^{-1}$ $r_e = [1.89]$ Å

### Enthalpy of Formation

Gaydon[1] gives $32 \pm 12\ kcal \cdot mol^{-1}$ for the enthalpy of dissociation into gaseous atoms.

### Heat Capacity and Entropy

Vibrational constants are from Herzberg.[2] Rotational constants were estimated using relationships in Herzberg.[2] Bond length estimated by comparison of the mercurous halides with thalium and cesium halides.

### References

[1] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd ed., Chapman and Hall, London (1953).

[2] G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York, equation III, 123 p. 108, (1950).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −9.314 | 7.370 | 7.370 | INFINITE |
| 100 | 29.502 | 213.636 | 277.625 | −6.399 | 7.126 | −1.997 | 1.043 |
| 200 | 32.488 | 234.956 | 251.483 | −3.305 | 6.170 | −10.751 | 2.808 |
| 250 | 33.752 | 242.348 | 248.939 | −1.648 | 3.380 | −14.771 | 3.086 |
| 298.15 | 34.651 | 248.373 | 248.373 | 0. | 2.929 | −18.225 | 3.193 |
| 300 | 34.680 | 248.588 | 248.374 | 0.064 | 2.912 | −18.356 | 3.196 |
| 350 | 35.356 | 253.987 | 248.799 | 1.816 | 2.480 | −21.867 | 3.263 |
| 400 | 35.857 | 258.743 | 249.751 | 3.597 | 2.070 | −25.316 | 3.306 |
| 450 | 36.236 | 262.989 | 250.990 | 5.400 | 1.672 | −28.716 | 3.333 |
| 500 | 36.532 | 266.823 | 252.385 | 7.219 | 1.282 | −32.071 | 3.350 |
| 600 | 36.960 | 273.524 | 255.365 | 10.895 | 0.507 | −38.669 | 3.366 |
| 700 | 37.258 | 279.245 | 258.378 | 14.607 | −59.031 | −38.566 | 2.878 |
| 800 | 37.481 | 284.235 | 261.305 | 18.344 | −59.177 | −35.632 | 2.327 |
| 900 | 37.659 | 288.660 | 264.103 | 22.102 | −59.325 | −32.680 | 1.897 |
| 1000 | 37.809 | 292.636 | 266.761 | 25.875 | −59.475 | −29 711 | 1.552 |
| 1100 | 37.939 | 296.246 | 269.280 | 29.663 | −59.626 | −26.728 | 1.269 |
| 1200 | 38.055 | 299.552 | 271.667 | 33.462 | −59.778 | −23.730 | 1.033 |
| 1300 | 38.162 | 302.602 | 273.931 | 37.273 | −59.930 | −20.720 | 0.833 |
| 1400 | 38.263 | 305.434 | 276.081 | 41.095 | −60.083 | −17.698 | 0.660 |
| 1500 | 38.358 | 308.077 | 278.127 | 44.926 | −60.236 | −14.665 | 0.511 |
| 1600 | 38.449 | 310.556 | 280.077 | 48.766 | −60.389 | −11.622 | 0.379 |
| 1700 | 38.537 | 312.889 | 281.939 | 52.615 | −60.540 | −8.569 | 0.263 |
| 1800 | 38.623 | 315.095 | 283.720 | 56.473 | −60.691 | −5.508 | 0.160 |
| 1900 | 38.706 | 317.185 | 285.427 | 60.340 | −60.839 | −2.438 | 0.067 |
| 2000 | 38.788 | 319.173 | 287.065 | 64.215 | −60.983 | 0.639 | −0.017 |
| 2100 | 38.869 | 321.067 | 288.640 | 68.098 | −61.123 | 3.724 | −0.093 |
| 2200 | 38.949 | 322.877 | 290.155 | 71.988 | −61.255 | 6.815 | −0.162 |
| 2300 | 39.028 | 324.610 | 291.616 | 75.887 | −61.379 | 9.912 | −0.225 |
| 2400 | 39.106 | 326.273 | 293.025 | 79.794 | −61.492 | 13.014 | −0.283 |
| 2500 | 39.184 | 327.871 | 294.387 | 83.709 | −61.594 | 16.120 | −0.337 |
| 2600 | 39.261 | 329.409 | 295.705 | 87.631 | −61.681 | 19.231 | −0.386 |
| 2700 | 39.338 | 330.892 | 296.981 | 91.561 | −61.753 | 22.344 | −0.432 |
| 2800 | 39.414 | 332.324 | 298.218 | 95.498 | −61.808 | 25.460 | −0.475 |
| 2900 | 39.490 | 333.709 | 299.418 | 99.444 | −61.844 | 28.577 | −0.515 |
| 3000 | 39.566 | 335.049 | 300.583 | 103.396 | −61.861 | 31.696 | −0.552 |
| 3100 | 39.641 | 336.347 | 301.716 | 107.357 | −61.856 | 34.814 | −0.587 |
| 3200 | 39.716 | 337.607 | 302.818 | 111.325 | −61.830 | 37.932 | −0.619 |
| 3300 | 39.791 | 338.830 | 303.891 | 115.300 | −61.781 | 41.049 | −0.650 |
| 3400 | 39.866 | 340.019 | 304.936 | 119.283 | −61.709 | 44.164 | −0.678 |
| 3500 | 39.940 | 341.176 | 305.955 | 123.273 | −61.613 | 47.277 | −0.706 |
| 3600 | 40.015 | 342.302 | 306.949 | 127.271 | −61.494 | 50.386 | −0.731 |
| 3700 | 40.089 | 343.400 | 307.920 | 131.276 | −61.350 | 53.492 | −0.755 |
| 3800 | 40.164 | 344.470 | 308.867 | 135.289 | −61.181 | 56.594 | −0.778 |
| 3900 | 40.238 | 345.514 | 309.794 | 139.309 | −60.988 | 59.691 | −0.799 |
| 4000 | 40.312 | 346.534 | 310.700 | 143.336 | −60.771 | 62.782 | −0.820 |
| 4100 | 40.386 | 347.530 | 311.586 | 147.371 | −60.530 | 65.868 | −0.839 |
| 4200 | 40.460 | 348.504 | 312.453 | 151.413 | −60.265 | 68.948 | −0.857 |
| 4300 | 40.534 | 349.457 | 313.303 | 155.463 | −59.976 | 72.021 | −0.875 |
| 4400 | 40.607 | 350.390 | 314.135 | 159.520 | −59.663 | 75.087 | −0.891 |
| 4500 | 40.681 | 351.303 | 314.951 | 163.585 | −59.328 | 78.146 | −0.907 |
| 4600 | 40.755 | 352.198 | 315.751 | 167.656 | −58.971 | 81.197 | −0.922 |
| 4700 | 40.829 | 353.075 | 316.536 | 171.736 | −58.591 | 84.240 | −0.936 |
| 4800 | 40.902 | 353.936 | 317.306 | 175.822 | −58.190 | 87.275 | −0.950 |
| 4900 | 40.976 | 354.780 | 318.062 | 179.916 | −57.768 | 90.301 | −0.963 |
| 5000 | 41.049 | 355.608 | 318.805 | 184.017 | −57.326 | 93.318 | −0.975 |
| 5100 | 41.123 | 356.422 | 319.534 | 188.126 | −56.864 | 96.327 | −0.987 |
| 5200 | 41.196 | 357.221 | 320.252 | 192.242 | −56.382 | 99.326 | −0.998 |
| 5300 | 41.270 | 358.006 | 320.956 | 196.365 | −55.883 | 102.315 | −1.008 |
| 5400 | 41.343 | 358.779 | 321.650 | 200.496 | −55.365 | 105.295 | −1.019 |
| 5500 | 41.416 | 359.538 | 322.332 | 204.634 | −54.831 | 108.266 | −1.028 |
| 5600 | 41.490 | 360.285 | 323.003 | 208.779 | −54.280 | 111.226 | −1.037 |
| 5700 | 41.563 | 361.020 | 323.663 | 212.932 | −53.714 | 114.176 | −1.046 |
| 5800 | 41.637 | 361.743 | 324.314 | 217.092 | −53.133 | 117.117 | −1.055 |
| 5900 | 41.710 | 362.456 | 324.954 | 221.259 | −52.538 | 120.047 | −1.063 |
| 6000 | 41.783 | 363.157 | 325.585 | 225.434 | −51.929 | 122.967 | −1.071 |

PREVIOUS: December 1961 (1 atm) CURRENT: December 1961 (1 bar)

## Iodine Fluoride (IF) IDEAL GAS $M_r = 145.902903$ Iodine Fluoride (IF) $F_1I_1(g)$

$S°(298.15 K) = 236.296 J·K^{-1}·mol^{-1}$

$\Delta_f H°(0 K) = 92.854 \pm 3.8 kJ·mol^{-1}$
$\Delta_f H°(298.15 K) = 94.759 \pm 3.8 kJ·mol^{-1}$

Electronic Level and Quantum Weight

| State | $\epsilon_i$, $cm^{-1}$ | $g_i$ |
|---|---|---|
| $^2\Sigma$ | 0 | 2 |

$\omega_e = 612 cm^{-1}$ $\omega_e x_e = 4 cm^{-1}$ $\sigma = 1$
$B_e = 0.2799 cm$ $\alpha_e = 0.00763 cm^{-1}$ $r_e = 1.906$ Å

### Enthalpy of Formation

Durie and Gaydon[1] have obtained the dissociation limit (from the spectra) of IF as 23570 $cm.^{-1}$ The first excited states of F and I are 404 and 7598 $cm^{-1}$ above the ground state, respectively. There are two sets of dissociation products possible: $I(^2P_{1/2}) + F(^2P_{3/2})$ or $I(^2P_{3/2}) + F(^2P_{1/2})$. When corrected to the normal atoms, the observed limit gives $D_0^\circ$ (IF) 2 87 ± 0.04 eV or 66 18 ± 0.9 $kcal·mol^{-1}$ and 1.98 ± 0.04 eV or 45.66 ± 0.9 $kcal·mol^{-1}$ for dissociation energy, respectively. Durie and Gaydon[1] favored the lower value. However, Slutsky and Bauer[2] have pointed out a numerical error in their calculations which removes the chief support for the lower value and presented additional evidence favoring the higher value. More weight was given to the higher value which gives $\Delta_f H°(298.15 K) = 22.648 \pm 0.9$ $kcal·mol^{-1}$ for the reaction $1/2 I_2(cr) + 1/2 F_2(g) = IF(g)$.

### Heat Capacity and Entropy

All molecular constants were obtained from Evans *et al.*[3] except $r_e$ = 1 906 Å which was obtained from Cole and Elverun[4] and ground state configuration which was estimated by comparison with that for IBr and ICl from Herzberg.[5]

### References

[1] R. A. Durie and A. G. Gaydon, J. Phys. Chem. 56, 316 (1952).
[2] L. Slutsky and S. H. Bauer, J. Am. Chem. Soc. 76, 270 (1954).
[3] W. H. Evans, T. R. Munson and D. D. Wagman, J. Res. Nat. Bur. Stand. 55, 147 (1955).
[4] L. G. Cole and G. W. Elverun Jr., J. Chem. Phys. 20, 1543 (1952).
[5] G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc , New York, (1950).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | $J·K^{-1}mol^{-1}$ | | | $kJ·mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −9.106 | −92.854 | −92.854 | INFINITE |
| 100 | 29.216 | 202.594 | 264.549 | −6.196 | −92.922 | −101.613 | 53.077 |
| 200 | 31.268 | 223.358 | 239.297 | −3.188 | −93.845 | −109.955 | 28.717 |
| 250 | 32.537 | 230.474 | 236.843 | −1.592 | −94.314 | −113.929 | 23.804 |
| 298.15 | 33.561 | 236.296 | 236.296 | 0. | −94.759 | −117.666 | 20.615 |
| 300 | 33.596 | 236.503 | 236.296 | 0.062 | −94.776 | −117.808 | 20.512 |
| 350 | 34.429 | 241.748 | 236.709 | 1.764 | −95.275 | −121.609 | 18.149 |
| 400 | 35.076 | 246.389 | 237.634 | 3.502 | −103.765 | −125.062 | 16.331 |
| 450 | 35.583 | 250.551 | 238.842 | 5.269 | −104.849 | −127.659 | 14.818 |
| 500 | 35.986 | 254.321 | 240.204 | 7.058 | −125.990 | −128.236 | 13.397 |
| 600 | 36.577 | 260.938 | 243.124 | 10.689 | −125.974 | −128.687 | 11.203 |
| 700 | 36.991 | 266.609 | 246.084 | 14.368 | −125.954 | −129.141 | 9.637 |
| 800 | 37.298 | 271.570 | 248.966 | 18.083 | −125.933 | −129.597 | 8.462 |
| 900 | 37.541 | 275.977 | 251.727 | 21.826 | −125.913 | −130.057 | 7.548 |
| 1000 | 37.740 | 279.943 | 254.353 | 25.590 | −125.894 | −130.518 | 6.818 |
| 1100 | 37.911 | 283.549 | 256.846 | 29.373 | −125.879 | −130.981 | 6.220 |
| 1200 | 38.062 | 286.854 | 259.211 | 33.172 | −125.870 | −131.446 | 5.722 |
| 1300 | 38 199 | 289.906 | 261.456 | 36.985 | −125.869 | −131.910 | 5.300 |
| 1400 | 38.325 | 292.742 | 263.591 | 40.811 | −125.881 | −132.375 | 4.939 |
| 1500 | 38.443 | 295.390 | 265.623 | 44 649 | −125.912 | −132.838 | 4.626 |
| 1600 | 38.555 | 297.874 | 267.562 | 48.499 | −125.965 | −133.298 | 4.352 |
| 1700 | 38.663 | 300.215 | 269.415 | 52.360 | −126.045 | −133.754 | 4.110 |
| 1800 | 38.766 | 302.428 | 271.188 | 56.232 | −126.153 | −134.204 | 3.895 |
| 1900 | 38.867 | 304.527 | 272.888 | 60.113 | −126.293 | −134.648 | 3.702 |
| 2000 | 38.965 | 306.523 | 274.520 | 64.005 | −126.462 | −135.083 | 3.528 |
| 2100 | 39.062 | 308.426 | 276.090 | 67.906 | −126.658 | −135.510 | 3.371 |
| 2200 | 39.157 | 310.246 | 277.601 | 71.817 | −126.877 | −135.926 | 3.227 |
| 2300 | 39.250 | 311.988 | 279.059 | 75.738 | −127.114 | −136.332 | 3.096 |
| 2400 | 39.342 | 313.661 | 280.466 | 79.667 | −127.361 | −136.728 | 2.976 |
| 2500 | 39.434 | 315.269 | 281.826 | 83.606 | −127.611 | −137.113 | 2.865 |
| 2600 | 39.524 | 316.817 | 283.142 | 87.554 | −127.857 | −137.488 | 2.762 |
| 2700 | 39 614 | 318.310 | 284.417 | 91.511 | −128.092 | −137.854 | 2.667 |
| 2800 | 39.704 | 319.753 | 285.654 | 95.477 | −128.308 | −138.211 | 2.578 |
| 2900 | 39.792 | 321.147 | 286.854 | 99.452 | −128.498 | −138.562 | 2.496 |
| 3000 | 39.881 | 322.498 | 288.019 | 103.435 | −128.657 | −138.906 | 2.419 |
| 3100 | 39.969 | 323.807 | 289.153 | 107.428 | −128.778 | −139.245 | 2.346 |
| 3200 | 40.056 | 325.077 | 290.256 | 111.429 | −128.858 | −139.582 | 2.278 |
| 3300 | 40.144 | 326.311 | 291.330 | 115.439 | −128.893 | −139.916 | 2.215 |
| 3400 | 40.231 | 327.511 | 292.376 | 119.458 | −128.879 | −140.250 | 2.155 |
| 3500 | 40.317 | 328.678 | 293.397 | 123.485 | −128.813 | −140.585 | 2.098 |
| 3600 | 40.404 | 329.815 | 294.393 | 127.521 | −128.695 | −140.923 | 2.045 |
| 3700 | 40 490 | 330.924 | 295.365 | 131.566 | −128.523 | −141.265 | 1.994 |
| 3800 | 40.576 | 332.005 | 296.315 | 135.619 | −128.296 | −141.612 | 1.947 |
| 3900 | 40.662 | 333.060 | 297.244 | 139.681 | −128.013 | −141.966 | 1.901 |
| 4000 | 40 748 | 334.090 | 298.152 | 143.752 | −127.675 | −142.328 | 1.859 |
| 4100 | 40 834 | 335 097 | 299.041 | 147.831 | −127.282 | −142.700 | 1.818 |
| 4200 | 40.920 | 336.082 | 299.911 | 151.919 | −126.834 | −143.081 | 1.779 |
| 4300 | 41.005 | 337 046 | 300 764 | 156.015 | −126.333 | −143.474 | 1.743 |
| 4400 | 41.091 | 337 990 | 301.599 | 160.120 | −125.778 | −143.879 | 1.708 |
| 4500 | 41.176 | 338.914 | 302.418 | 164.233 | −125.171 | −144.296 | 1.675 |
| 4600 | 41.262 | 339.820 | 303.221 | 168.355 | −124.514 | −144.729 | 1.643 |
| 4700 | 41.347 | 340.709 | 304.010 | 172.485 | −123.806 | −145.176 | 1.613 |
| 4800 | 41.432 | 341.580 | 304.783 | 176.624 | −123.050 | −145.638 | 1.585 |
| 4900 | 41.517 | 342.435 | 305.543 | 180.772 | −122.247 | −146.117 | 1.558 |
| 5000 | 41.602 | 343.275 | 306.289 | 184.928 | −121.398 | −146.613 | 1.532 |
| 5100 | 41.687 | 344.099 | 307.023 | 189.092 | −120.504 | −147.126 | 1.507 |
| 5200 | 41.772 | 344.910 | 307.743 | 193.265 | −119.566 | −147.657 | 1.483 |
| 5300 | 41.857 | 345.706 | 308.452 | 197.447 | −118.586 | −148.206 | 1.461 |
| 5400 | 41.942 | 346.489 | 309.149 | 201.637 | −117.564 | −148.775 | 1.439 |
| 5500 | 42.027 | 347.260 | 309.835 | 205.835 | −116.503 | −149.363 | 1.419 |
| 5600 | 42.112 | 348.018 | 310.510 | 210.042 | −115.403 | −149.970 | 1.399 |
| 5700 | 42.196 | 348.764 | 311.175 | 214.257 | −114.265 | −150.597 | 1.380 |
| 5800 | 42.281 | 349.499 | 311.829 | 218.481 | −113.090 | −151.245 | 1.362 |
| 5900 | 42.366 | 350.222 | 312.474 | 222.714 | −111.880 | −151.913 | 1.345 |
| 6000 | 42.450 | 350.935 | 313.109 | 226.954 | −110.635 | −152.602 | 1.329 |

PREVIOUS· December 1965 (1 atm) CURRENT: December 1965 (1 bar)

Iodine Fluoride (IF) $F_1I_1(g)$

## Potassium Fluoride (KF) CRYSTAL $M_r = 58.096703$ Potassium Fluoride (KF) $F_1K_1(cr)$

$S°(298.15\ K) = 66.547 \pm 0.21\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 1131\ K$

$\Delta_fH°(0\ K) = -567.111 \pm 0.4\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -568.606 \pm 0.4\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 27.196\ kJ{\cdot}mol^{-1}$

### Enthalpy of Formation

The enthalpy of solution of KF(cr) in water has been measured by several investigators. Their results have been converted to $\Delta_{sol}H°$(aq, ∞) by Parker[5] and listed in the table below. Using $\Delta_{sol}H°(aq, \infty) = -4.24$, $\Delta_fH°(K^+, aq, \infty, 298.15\ K) = -60.32$,[6] and $\Delta_fH°(F^-, aq, \infty, 298.15\ K) = -79.82\ kcal{\cdot}mol^{-1}$,[7] we obtain $\Delta_fH°(298.15\ K) = -135.9 \pm 0.1\ kcal{\cdot}mol^{-1}$ ($-568.606 \pm 0.4\ kJ{\cdot}mol^{-1}$) which is adopted.

| Source | T/K | Concentration Molality | No. of Determinations | $\Delta_{sol}H°(aq,\infty)$ kcal·mol$^{-1}$ |
|---|---|---|---|---|
| Guntz (1884)[1] | 291 | 0.28 | 1 | −3.95 |
| Forcrand (1911)[2] | 288 | 0.50 | 1 | −4.54 |
| Lange and Eichler (1927)[3] | 298 | 3.16 − 0.21 | 8 | −4.24±0.4 |
| Lange and Martin (1937)[4] | 298 | 0.31 | 1 | −4.01 |

### Heat Capacity and Entropy

The low temperature heat capacities, 16–323 K, were measured by Westrum and Pitzer.[8] The high temperature enthalpies, 298.15–530 K and 291–1187 K, were determined by Westrum and Pitzer,[8] and Lyashenko,[9] respectively. However, the high temperature $C_p°$ values derived from both sets appear to be inconsistent with the low temperature $C_p°$ values. The heat capacities derived from the enthalpy data of Westrum and Pitzer are too high (3% at 530 K and less at lower temperatures) to be joined smoothly with their low temperature $C_p°$'s. The adopted enthalpy at 530 K is about 1.4% lower than the reported value. The heat capacity derived from the enthalpy data of Lyashenko is 2.5% lower than the adopted one at 900 K. The differences are smaller at lower temperatures. At 900 K, the adopted enthalpy is 1.3% higher than the reported value. The adopted heat capacities in the temperature range, 323–2000 K, are estimated by graphical comparison with other alkali fluorides and chlorides, and joined smoothly with the low temperature data at 298.15 K.

$S°(298.15\ K)$ is derived based on the adopted low temperature heat capacities.

### Fusion Data

Refer to the liquid table for details.

### Sublimation Data

The value of $\Delta_{sub}H°(298.15\ K) = 241.835\ kJ{\cdot}mol^{-1}$ for the process KF(cr) = KF(g) for the process KF(cr) = KF(g) is obtained as the difference between $\Delta_fH°(298.15\ K)$ for KF(cr) and KF(g).

### References

[1] A. Guntz, Ann. Chim. Phys. (6) 3, 5 (1884).
[2] R. de Forcrand, Compt. Rend. 152, 1073 (1911).
[3] E. Lange and A. Eichler, Z. Physik. Chem. 129, 285 (1927).
[4] E. Lange and W. Martin, Z. Physik. Chem. A180, 233 (1937).
[5] V. B. Parker, U. S. Nat. Bur. Stand. NSRDS-NBS 2, (1965).
[6] U. S. Nat. Bur. Stand. Tech. Note 270-3, (1968).
[7] JANAF Thermochemical Tables: HF(g), 12-31-68.
[8] E. F. Westrum, Jr. and K. S. Pitzer, J. Amer. Chem. Soc. 71, 1940 (1949).
[9] V. S. Lyashenko, Metallurg (USSR) 10, 85 (1935).

Enthalpy Reference Temperature = $T_r$ = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ (J·K$^{-1}$mol$^{-1}$) | $S°$ (J·K$^{-1}$mol$^{-1}$) | $-[G°-H°(T_r)]/T$ (J·K$^{-1}$mol$^{-1}$) | $H°-H°(T_r)$ (kJ·mol$^{-1}$) | $\Delta_fH°$ (kJ·mol$^{-1}$) | $\Delta_fG°$ (kJ·mol$^{-1}$) | log $K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0. | 0. | INFINITE | −10.000 | −567.111 | −567.111 | INFINITE |
| 100 | 31.606 | 20.497 | 107.023 | −8.653 | −568.949 | −558.920 | 291.950 |
| 200 | 45.187 | 47.660 | 70.944 | −4.657 | −569.013 | −548.781 | 143.327 |
| 298.15 | 48.982 | 66.547 | 66.547 | 0. | −568.606 | −538.934 | 94.419 |
| 300 | 49.022 | 66.850 | 66.547 | 0.091 | −568.599 | −538.750 | 93.805 |
| 400 | 51.045 | 81.245 | 68.496 | 5.099 | −570.678 | −528.399 | 69.002 |
| 500 | 52.718 | 92.820 | 72.240 | 10.290 | −570.278 | −517.872 | 54.102 |
| 600 | 54.266 | 102.571 | 76.504 | 15.640 | −569.704 | −507.442 | 44.177 |
| 700 | 55.856 | 111.056 | 80.846 | 21.147 | −568.969 | −497.121 | 37.096 |
| 800 | 57.404 | 118.614 | 85.103 | 26.808 | −568.089 | −486.915 | 31.792 |
| 900 | 59.078 | 125.468 | 89.213 | 32.630 | −567.077 | −476.828 | 27.674 |
| 1000 | 61.170 | 131.797 | 93.159 | 38.639 | −565.926 | −466.860 | 24.386 |
| 1100 | 63.848 | 137.748 | 96.944 | 44.884 | −643.560 | −452.406 | 21.483 |
| 1131.000 | 64.852 | 139.536 | 98.087 | 46.878 | --- CRYSTAL <--> LIQUID --- | | |
| 1200 | 66.777 | 143.436 | 100.583 | 51.423 | −640.972 | −435.140 | 18.941 |
| 1300 | 68.618 | 148.858 | 104.090 | 58.198 | −638.160 | −418.101 | 16.799 |
| 1400 | 69.789 | 153.989 | 107.472 | 65.123 | −635.210 | −401.283 | 14.972 |
| 1500 | 70.500 | 158.830 | 110.736 | 72.140 | −632.178 | −384.679 | 13.396 |
| 1600 | 70.919 | 163.394 | 113.886 | 79.212 | −629.101 | −368.280 | 12.023 |
| 1700 | 71.128 | 167.701 | 116.926 | 86.316 | −626.002 | −352.073 | 10.818 |
| 1800 | 71.128 | 171.766 | 119.861 | 93.429 | −622.904 | −336.049 | 9.752 |
| 1900 | 71.128 | 175.612 | 122.695 | 100.542 | −619.816 | −320.197 | 8.803 |
| 2000 | 71.128 | 179.260 | 125.433 | 107.655 | −616.738 | −304.507 | 7.953 |

PREVIOUS: December 1963 CURRENT: June 1969

## Potassium Fluoride (KF) LIQUID $M_r = 58.096703$

$S°(298.15\ K) = [67\ 634]\ J{\cdot}K^{-1}\ mol^{-1}$
$T_{fus} = 1131\ K$

$\Delta_f H°(298.15\ K) = [-554.467]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 27\ 196\ kJ{\cdot}mol^{-1}$

### Enthalpy of Formation

$\Delta_f H°$(KF,l, 298 15 K) is calculated from $\Delta_f H°$(KF, cr, 298.15 K) by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°$(1131 K)–$H°$(298.15 K), between the crystal and liquid.

### Heat Capacity and Entropy

The heat capacity is estimated by comparison with those of the alkali fluorides and chlorides, and is assumed to be constant in the temperature range, 298–3000 K. The $C_p°$ value, 16 cal $K^{-1}$ $mol^{-1}$, derived from the enthalpy data of Lyashenko[12] appears low and is not adopted.

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

### Fusion Data

$T_{fus}$ has been reported as 1119,[1,2] 1129,[3,4] 1131,[5,6] and 1153 K.[7] The value 1131 K is adopted. Kelley[8] evaluated the following freezing-point data of binary systems. KF-AlF$_3$,[9] KF-K$_2$SO$_4$,[10] KF-KCl,[11] KF-K$_2$CO$_3$,[13] and KF- K$_3$PO$_4$,[14] and derived the values of $\Delta_{fus}H°$ (in kcal·mol$^{-1}$) as 5.5, 5.55, 6.51, 7.1, and 7.1, respectively. The best value is recommended as 6.50 kcal mol$^{-1}$. Other reported $\Delta_{fus}H°$ values are 6.70[7] and 6.75±0.1 kcal·mol$^{-1}$.[12] The value of heat of melting is tentatively adopted as 6.50 kcal·mol$^{-1}$.

### Vaporization Data

The boiling point ($T_{vap}$=1790K) is calculated to be the temperature at which the partial pressures of KF(g) and $K_2F_2$(g) equal one atmosphere. The composition of the gaseous mixture in equilibrium with KF(l) at $T_{fus}$ is calculated as $K_2F_2$ 21.1% and KF 78.9%. The heat required to vaporize one mole of liquid at $T_{vap}$ is evaluated to be 33.9 kcal·mol$^{-1}$ (141.838 kJ·mol$^{-1}$).

The experimental values for the boiling point are 1778 K$^{-1}$ and 1771 K.[15]

### References

[1] H. von Wartenberg and H. Schulz, Z. Elektrochem. **27**, 568 (1921).
[2] B S. Zakharova, L. P. Reshetnikova, and A. V. Novoselova, Vestn. Mosk. Univ., Ser II **22**, 102 (1967).
[3] O. Schmitz-Dumont and E. Schmitz, Z. Anorg. Chem. **252**, 329 (1944).
[4] E. P. Dergunov and A G. Bergman, Zh. Fiz. Khim. **22**, 625 (1948).
[5] J. W Johnson and M. A. Bredig, J Phys. Chem. **62**, 604 (1958).
[6] B. Porter and E. A Brown, J. Amer. Ceram. Soc. **45**, 49 (1962).
[7] G Petit and A. Crémieu, Compt. Rend **243**, 360 (1956).
[8] K K. Kelley, U S Bur. Mines Bull. 393, (1936).
[9] N. A. Puschin and A. B. Baskow, J. Russ. Phys. Chem. Soc **45**, 82 (1913); Z Anorg Chem. **81**, 347 (1913).
[10] B. Karandeeff, Zentr. Min. Geol. 728, (1909).
[11] W. Plato, Z. Physik, Chem. **55**, 721 (1906).
[12] V. S Lyashenko, Metallurg (USSR) **10**, 85 (1935)
[13] M. Amadori, Atti Accad. Lincei, Ser 5, **22**, 366 (1913).
[14] M. Amadori, Atti Accad. Lincei, Ser. 5, **21**, 688 (1912).
[15] O. Ruff, G. Schmidt, and S. Mugdan, Z. Anorg Allg. Chem. **123**, 83 (1922).

## Potassium Fluoride (KF) $F_1K_1(l)$

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T/K$ | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 71.965 | 67.634 | 67.634 | 0. | −554.467 | −525 120 | 91.999 |
| 300 | 71.965 | 68.079 | 67.635 | 0 133 | −554.418 | −524 938 | 91.400 |
| 400 | 71.965 | 88.782 | 70.458 | 7.330 | −554.309 | −515 045 | 67.258 |
| 500 | 71.965 | 104.840 | 75.788 | 14.526 | −551.903 | −505.507 | 52.810 |
| 600 | 71.965 | 117 961 | 81 757 | 21.723 | −549.483 | −496.455 | 43.220 |
| 700 | 71 965 | 129.055 | 87.742 | 28.919 | −547.058 | −487.809 | 36.401 |
| 800 | 71 965 | 138 664 | 93.520 | 36.116 | −544.643 | −479.510 | 31 309 |
| 900 | 71.965 | 147 140 | 99.016 | 43.312 | −542.256 | −471.512 | 27.366 |
| 1000 | 71 965 | 154 723 | 104.214 | 50.508 | −539.918 | −463.777 | 24.225 |
| 1100 | 71.965 | 161.582 | 109.123 | 57.705 | −616.600 | −451.664 | 21 448 |
| 1131 000 | 71.965 | 163.582 | 110.588 | 59.936 | --- CRYSTAL <--> LIQUID --- | | |
| 1200 | 71.965 | 167.843 | 113.759 | 64.901 | −613.355 | −436.813 | 19 014 |
| 1300 | 71.965 | 173 604 | 118.144 | 72.098 | −610.122 | −422.232 | 16.965 |
| 1400 | 71.965 | 178.937 | 122.298 | 79.294 | −606.900 | −407.900 | 15.219 |
| 1500 | 71.965 | 183.902 | 126.241 | 86.491 | −603.688 | −393 798 | 13.713 |
| 1600 | 71.965 | 188.546 | 129.992 | 93.687 | −600 487 | −379.910 | 12.403 |
| 1700 | 71.965 | 192.909 | 133.566 | 100.884 | −597.296 | −366.221 | 11.253 |
| 1800 | 71.965 | 197.023 | 136.978 | 108.080 | −594 114 | −352 720 | 10.236 |
| 1900 | 71.965 | 200.914 | 140.242 | 115.277 | −590.942 | −339.396 | 9.331 |
| 2000 | 71.965 | 204.605 | 143.368 | 122.473 | −587.781 | −326.239 | 8.520 |
| 2100 | 71 965 | 208 116 | 146.368 | 129.670 | −584 629 | −313.239 | 7.791 |
| 2200 | 71 965 | 211.464 | 149.252 | 136.866 | −581.488 | −300.390 | 7.132 |
| 2300 | 71 965 | 214.663 | 152.027 | 144.063 | −578.357 | −287.683 | 6.533 |
| 2400 | 71 965 | 217.726 | 154.701 | 151.259 | −575.238 | −275 111 | 5.988 |
| 2500 | 71 965 | 220.663 | 157.281 | 158.456 | −572.130 | −262 670 | 5.488 |
| 2600 | 71.965 | 223 486 | 159.773 | 165.652 | −569.035 | −250.353 | 5.030 |
| 2700 | 71 965 | 226.202 | 162.184 | 172.849 | −565.954 | −238 154 | 4.607 |
| 2800 | 71 965 | 228.819 | 164.517 | 180.045 | −562.889 | −226 070 | 4.217 |
| 2900 | 71 965 | 231.344 | 166.778 | 187.242 | −559.841 | −214 094 | 3.856 |
| 3000 | 71.965 | 233.784 | 168.971 | 194.438 | −556.811 | −202.224 | 3.521 |

PREVIOUS December 1963 CURRENT· June 1969

Potassium Fluoride (KF) $F_1K_1(l)$

**Potassium Fluoride (KF)** **CRYSTAL-LIQUID**

| | | | |
|---|---|---|---|
| 0 | to 1131 | K | crystal |
| above | 1131 | K | liquid |

Refer to the individual tables for details.

**$M_r = 58.096703$ Potassium Fluoride (KF)** **$F_1K_1(cr,l)$**

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −10.000 | −567.111 | −567.111 | INFINITE |
| 100 | 31.606 | 20.497 | 107.023 | −8.653 | −568.949 | −558.920 | 291.950 |
| 200 | 45.187 | 47.660 | 70.944 | −4.657 | −569.013 | −548.781 | 143.327 |
| 298.15 | 48.982 | 66.547 | 66.547 | 0. | −568.606 | −538.934 | 94.419 |
| 300 | 49.022 | 66.850 | 66.547 | 0.091 | −568.599 | −538.750 | 93.805 |
| 400 | 51.045 | 81.245 | 68.496 | 5.099 | −570.678 | −528.399 | 69.002 |
| 500 | 52.718 | 92.820 | 72.240 | 10.290 | −570.278 | −517.872 | 54.102 |
| 600 | 54.266 | 102.571 | 76.504 | 15.640 | −569.704 | −507.442 | 44.177 |
| 700 | 55.856 | 111.056 | 80.846 | 21.147 | −568.969 | −497.121 | 37.096 |
| 800 | 57.404 | 118.614 | 85.103 | 26.808 | −568.089 | −486.915 | 31.792 |
| 900 | 59.078 | 125.468 | 89.213 | 32.630 | −567.077 | −476.828 | 27 674 |
| 1000 | 61.170 | 131.797 | 93.159 | 38.639 | −565.926 | −466.860 | 24.386 |
| 1100 | 63.848 | 137.748 | 96.944 | 44.884 | −643.560 | −452.406 | 21.483 |
| 1131.000 | 64.852 | 139.536 | 98.087 | 46.878 | CRYSTAL <--> LIQUID TRANSITION | | |
| 1131.000 | 71.965 | 163.582 | 98.087 | 74.074 | | | |
| 1200 | 71.965 | 167.843 | 101.977 | 79.040 | −613.355 | −436.813 | 19.014 |
| 1300 | 71.965 | 173.604 | 107.268 | 86.236 | −610.122 | −422.232 | 16.965 |
| 1400 | 71.965 | 178.937 | 112.199 | 93.433 | −606.900 | −407.900 | 15.219 |
| 1500 | 71.965 | 183.902 | 116.816 | 100.629 | −603.688 | −393.798 | 13.713 |
| 1600 | 71.965 | 188.546 | 121.155 | 107.826 | −600.487 | −379.910 | 12.403 |
| 1700 | 71.965 | 192.909 | 125.249 | 115.022 | −597.296 | −366.221 | 11.253 |
| 1800 | 71.965 | 197.023 | 129.123 | 122.219 | −594.114 | −352.720 | 10.236 |
| 1900 | 71.965 | 200.914 | 132.800 | 129.415 | −590.942 | −339.396 | 9.331 |
| 2000 | 71.965 | 204.605 | 136.299 | 136.612 | −587.781 | −326.239 | 8.520 |
| 2100 | 71 965 | 208.116 | 139.636 | 143.808 | −584.629 | −313.239 | 7.791 |
| 2200 | 71.965 | 211.464 | 142.825 | 151.005 | −581.488 | −300.390 | 7.132 |
| 2300 | 71.965 | 214.663 | 145.880 | 158.201 | −578.357 | −287.683 | 6.533 |
| 2400 | 71.965 | 217.726 | 148.810 | 165.398 | −575.238 | −275.111 | 5.988 |
| 2500 | 71.965 | 220.663 | 151.626 | 172.594 | −572.130 | −262.670 | 5.488 |
| 2600 | 71.965 | 223.486 | 154.336 | 179.791 | −569.035 | −250.353 | 5.030 |
| 2700 | 71.965 | 226.202 | 156.947 | 186.987 | −565.954 | −238.154 | 4.607 |
| 2800 | 71.965 | 228.819 | 159.468 | 194.184 | −562.889 | −226.070 | 4.217 |
| 2900 | 71 965 | 231.344 | 161.903 | 201.380 | −559.841 | −214.094 | 3.856 |
| 3000 | 71.965 | 233 784 | 164.258 | 208.577 | −556.811 | −202.224 | 3.521 |

PREVIOUS· CURRENT. June 1969

**Potassium Fluoride (KF)** **$F_1K_1(cr,l)$**

**Potassium Fluoride (KF)** IDEAL GAS $M_r$ = 58.096703 **Potassium Fluoride (KF)** $F_1K_1(g)$

$S°(298.15 \text{ K}) = 226.612 \pm 0.04 \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = -324.729 \pm 2.1 \text{ kJ·mol}^{-1}$
$\Delta_f H°(298.15 \text{ K}) = -326.770 \pm 2.1 \text{ kJ·mol}^{-1}$

| Electronic Level and Quantum Weight | | |
|---|---|---|
| State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
| $^1\Sigma$ | 0 | 1 |

$\omega_e = 426.04 \text{ cm}^{-1}$ $\omega_e x_e = 2.43 \text{ cm}^{-1}$ $\sigma = 1$
$B_e = 0.27994 \text{ cm}^{-1}$ $\alpha_e = 0.002335 \text{ cm}^{-1}$ $r_e = 2.17155$ Å

## Enthalpy of Formation

The total vapor pressures of KF(g) and $K_2F_2(g)$ over KF(cr, l) have been determined by many investigators using the boiling point,[1 2,5] Knudsen–effusion,[3] transpiration,[4] and torsion–effusion 6 methods. A method of trial and error is employed to select the appropriate values for $\Delta_{sub}H°$(KF, cr, 298.15 K) and $\Delta_{vap}H°$(KF, l, 298.15 K) such that by use of these two values and $\Delta_r H°(298.15 \text{ K}) = 50 \text{ kcal·mol}^{-1}$ for the reaction $K_2F_2(g) = 2\ KF(g)$ and the Gibbs energy functions for KF(cr), KF(l), KF(g), and $K_2F_2(g)$, the calculated total pressures of KF(g) and $K_2F_2(g)$ are consistent with the measured ones. Adopting $\Delta_{sub}H°(298.15 \text{ K}) = 57.8$ and $\Delta_{vap}H°(298.15 \text{ K}) = 54\ 42 \text{ kcal·mol}^{-1}$, we evaluate the partial pressures of KF(g) and $K_2F_2(g)$ from the reported total pressure measurements. Based on the derived partial pressures for KF(g), the enthalpy changes for the processes A) KF(cr) = KF(g), and B) KF(l) = KF(g) are calculated by the 2nd and 3rd law methods. Using the 3rd law $\Delta_r H°$(298.15 K) and $\Delta_f H°(298.15 \text{ K}) = -135\ 90$ and $-132.519 \text{ kcal·mol}^{-1}$ for KF(cr) and KF(l), respectively, we obtain the $\Delta_f H°$(298.15 K) for KF(g). The results are presented in the table below.

The dissociation energy of KF(g) has been determined as 117 ± 8 kcal mol$^{-1}$ by flame photometry by Page and Sugden,[7] and Bulewicz, Phillips, and Sugden,[8] yielding $\Delta_f H°(\text{KF, g, 298.15 K}) = -77.6 \pm 8 \text{ kcal·mol}^{-1}$. Barrow and Caunt[9] measured the fluctuation bands in the ultraviolet absorption spectra of KF and reported the upper limit for the $D_0°$(KF, g) value to be 121.8 kcal mol$^{-1}$ which leads to $\Delta_f H°(\text{KF, g, 298.15 K}) = -81.4 \text{ kcal·mol}^{-1}$ as the lower limit. Gaydon[1] reported $D_0° = 116.9 \pm 4\ 6 \text{ kcal·mol}^{-1}$ for KF(g). The corresponding value of $\Delta_f H°$(298.15 K) is calculated as $-77.5 \pm 4\ 6 \text{ kcal·mol}^{-1}$.

The enthalpy of formation for KF(g) at 298.15 K is adopted as .78.1±0.5 kcal·mol$^{-1}$.

| Source | Method | T/K | Data Points | Process | $\Delta_r H°$, kcal·mol$^{-1}$ 2nd law | $\Delta_r H°$, kcal·mol$^{-1}$ 3rd law | Drift cal K$^{-1}$·mol$^{-1}$ | $\Delta_f H°$(298.15 K) kcal·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| Wartenberg[1] | boiling point | 1624–1776 | 5 | B | 54.4±0.9 | 54.16 | −0.1±0.5 | −78.36 |
| Ruff[2] | boiling point | 1551–1773 | 6 | B | 58.1±2.5 | 54.14 | −2.4±1.5 | −78.38 |
| Niwa[3] | Knudsen–effusion | 913–973 | 6 | A | 56.2±0.3 | 55.67 | −0.6±0.3 | −80.23 |
| Naryshkin[4] | transpiration | 1023–1108 | 2 | A | — | 57.23 | — | −78.67 |
| | | 1188–1233 | 2** | B | — | 54.60 | — | −77.92 |
| Cantor[5] | boiling point | 1200–1500 | 7* | B | 54.4 | 54.38 | −0.02 | −78.14 |
| Pugh[6] | torsion–effusion | 910–1020 | 6* | A | 57.7 | 58.12 | 0.47 | −77.78 |

* Data points calculated from the given vapor pressure equation.
** Only the data point at 1233 K is adopted for evaluation.

## Heat Capacity and Entropy

The rotational transition spectrum of KF(g) has been measured in the millimeter– and submillimeter–wave region with a high resolution molecular–beam absorption spectrometer by Veazey and Gordy[15] From the derived potential constants the vibrational constants were calculated. The reported values for $\omega_e$, $\omega_e x_e$, $B_e$, $\alpha_e$ and $r_e$ are adopted.

Other values of $\omega_e$ reported are (in cm$^{-1}$) 390 ± 39,[11] 405 ± 25,[9] 429 ± 3,[12] and 426 ± 4.[13] The value of $\omega_e x_e$ has been determined as 1.45 cm$^{-1}$ by Barrow and Caunt,[9] and 2.4 cm$^{-1}$ by Ritchie and Lew[12] and Baikov and Vasilevskii.[13] Using the molecular beam electric resonance method, Green and Lew[14] measured the rotational transitions between the J = 0 and J = 1 states of $K^{39}F$ and reported the following values: $B_e = 0.27994 \text{ cm}^{-1}$, $\alpha_e = 0.002335 \text{ cm}^{-1}$, and $r_e = 2.17144 \pm 0.00005$ Å which are in excellent agreement with the adopted values. By use of the same method, Grabner and Hughes[11] investigated the rotational Stark spectrum of $K^{39}F$ and reported the K–F bond distance for the zeroth vibrational state as 2.55 ± 0.06 Å.

## References

[1] H. von Wartenberg and H. Schulz, Z. Electrochem. **27**, 568 (1921).
[2] O. Ruff, G. Schmidt, and S. Mugdan, Z. anorg. allgem. Chem. **123**, 83 (1922).
[3] K. Niwa, J. Fac. Sci. Hokkaido Imp. University, Ser. III 2, 201 (1938).
[4] I. I. Naryshkin, Zh. Fiz. Khim. **13**, 528 (1939).
[5] S. Cantor and F. Blankenship, paper presented at the American Chemical Society meeting, Chicago, September 7–12, (1958).

Continued on page 1214

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ (J·K$^{-1}$mol$^{-1}$) | S° (J·K$^{-1}$mol$^{-1}$) | $-[G°-H°(T_r)]/T$ (J·K$^{-1}$mol$^{-1}$) | $H°-H°(T_r)$ (kJ·mol$^{-1}$) | $\Delta_f H°$ (kJ·mol$^{-1}$) | $\Delta_f G°$ (kJ·mol$^{-1}$) | log $K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0. | 0. | INFINITE | −9.453 | −324.729 | −324.729 | INFINITE |
| 100 | 29.837 | 191.161 | 256.478 | −6.532 | −324.993 | −332.031 | 173.435 |
| 200 | 33.260 | 212.918 | 229.781 | −3.373 | −325.893 | −338.713 | 88.463 |
| 250 | 34.438 | 220.474 | 227.187 | −1.678 | −326.325 | −341.868 | 71.429 |
| 298.15 | 35.228 | 226.612 | 226.612 | 0. | −326.770 | −344.822 | 60 411 |
| 300 | 35.253 | 226.830 | 226.612 | 0.065 | −326.789 | −344.934 | 60.058 |
| 350 | 35.826 | 232.309 | 227.044 | 1.843 | −329.697 | −347.821 | 51.909 |
| 400 | 36.242 | 237.122 | 228.009 | 3.645 | −330.297 | −350.369 | 45.753 |
| 450 | 36.553 | 241.409 | 229.264 | 5.465 | −330.874 | −352.843 | 40.957 |
| 500 | 36.793 | 245.273 | 230.675 | 7.299 | −331.433 | −355.254 | 37.113 |
| 600 | 37.141 | 252.015 | 233.686 | 10.997 | −332.511 | −359.916 | 31.333 |
| 700 | 37.385 | 257.759 | 236.725 | 14.724 | −333.556 | −364 400 | 27.192 |
| 800 | 37.570 | 262.764 | 239.673 | 18 472 | −334.590 | −368 736 | 24.076 |
| 900 | 37.719 | 267.198 | 242.490 | 22.237 | −335.635 | −372.942 | 21.645 |
| 1000 | 37.846 | 271.179 | 245.163 | 26.015 | −336.714 | −377 030 | 19.694 |
| 1100 | 37.958 | 274.791 | 247.695 | 29.806 | −416.803 | −376.397 | 17.874 |
| 1200 | 38.060 | 278.098 | 250.093 | 33.607 | −416.953 | −372.717 | 16.224 |
| 1300 | 38.155 | 281.148 | 252.366 | 37.417 | −417 106 | −369 024 | 14.828 |
| 1400 | 38.244 | 283.979 | 254.524 | 41.237 | −417.260 | −365.320 | 13 630 |
| 1500 | 38.329 | 286.621 | 256.577 | 45 066 | −417 417 | −361.604 | 12.592 |
| 1600 | 38.412 | 289.097 | 258.533 | 48.903 | −417.574 | −357.878 | 11 684 |
| 1700 | 38.492 | 291.428 | 260.400 | 52.748 | −417.734 | −354.143 | 10.881 |
| 1800 | 38.570 | 293.631 | 262.185 | 56.601 | −417.896 | −350.397 | 10.168 |
| 1900 | 38.647 | 295.718 | 263.896 | 60.462 | −418.060 | −346.643 | 9.530 |
| 2000 | 38.722 | 297.702 | 265.537 | 64.331 | −418.227 | −342.880 | 8 955 |
| 2100 | 38.797 | 299.593 | 267.114 | 68.207 | −418.396 | −339.108 | 8 435 |
| 2200 | 38.871 | 301.400 | 268.632 | 72.090 | −418.567 | −335.329 | 7.962 |
| 2300 | 38.944 | 303.129 | 270.094 | 75.981 | −418.743 | −331.541 | 7.530 |
| 2400 | 39.017 | 304.788 | 271.506 | 79.879 | −418.921 | −327.746 | 7.133 |
| 2500 | 39.089 | 306.383 | 272.869 | 83.784 | −419.105 | −323.943 | 6.768 |
| 2600 | 39.160 | 307.917 | 274.188 | 87.697 | −419.294 | −320.133 | 6.432 |
| 2700 | 39.232 | 309.396 | 275.464 | 91.616 | −419.490 | −316.315 | 6.119 |
| 2800 | 39.303 | 310.824 | 276.702 | 95.543 | −419.694 | −312.490 | 5.830 |
| 2900 | 39.374 | 312.205 | 277.902 | 99.477 | −419.909 | −308.658 | 5.560 |
| 3000 | 39.444 | 313.541 | 279.068 | 103.418 | −420.135 | −304.818 | 5.307 |
| 3100 | 39.515 | 314.835 | 280.201 | 107.366 | −420.376 | −300.970 | 5.071 |
| 3200 | 39.585 | 316.091 | 281.303 | 111.321 | −420.635 | −297 114 | 4.850 |
| 3300 | 39.655 | 317.310 | 282.376 | 115.283 | −420.905 | −293.251 | 4 642 |
| 3400 | 39.725 | 318.495 | 283.421 | 119.252 | −421.203 | −289.378 | 4.446 |
| 3500 | 39 795 | 319.648 | 284.440 | 123.228 | −421.526 | −285.496 | 4.261 |
| 3600 | 39.865 | 320.770 | 285.433 | 127.211 | −421.880 | −281.605 | 4.086 |
| 3700 | 39.935 | 321.863 | 286.403 | 131.201 | −422.269 | −277.703 | 3.920 |
| 3800 | 40.004 | 322.929 | 287.350 | 135.198 | −422.696 | −273.790 | 3.764 |
| 3900 | 40.074 | 323.969 | 288.276 | 139.202 | −423.167 | −269.865 | 3.614 |
| 4000 | 40.143 | 324.984 | 289.181 | 143.213 | −423.679 | −265.929 | 3.473 |
| 4100 | 40.213 | 325.976 | 290.067 | 147.230 | −424.245 | −261.979 | 3.338 |
| 4200 | 40.282 | 326.946 | 290.933 | 151.255 | −424.872 | −258.013 | 3.209 |
| 4300 | 40.351 | 327.895 | 291.782 | 155.287 | −425.561 | −254 033 | 3.086 |
| 4400 | 40.421 | 328.823 | 292.613 | 159.325 | −426.040 | −250.062 | 2.969 |
| 4500 | 40 490 | 329.733 | 293.428 | 163.371 | −426.800 | −246.054 | 2.856 |
| 4600 | 40.559 | 330.623 | 294.227 | 167.423 | −427.624 | −242.029 | 2.748 |
| 4700 | 40.628 | 331.496 | 295.011 | 171.483 | −428.496 | −237.986 | 2.645 |
| 4800 | 40.697 | 332.352 | 295.780 | 175.549 | −429.329 | −233.937 | 2.546 |
| 4900 | 40.766 | 333.192 | 296.535 | 179.622 | −430.335 | −229.856 | 2.450 |
| 5000 | 40.835 | 334.016 | 297.276 | 183 702 | −431.413 | −225.754 | 2.358 |
| 5100 | 40.904 | 334.826 | 298.004 | 187.789 | −432.564 | −221.629 | 2.270 |
| 5200 | 40.973 | 335.621 | 298.720 | 191.883 | −433.790 | −217.481 | 2.185 |
| 5300 | 41.042 | 336.402 | 299.424 | 195.984 | −435.090 | −213.309 | 2.102 |
| 5400 | 41.111 | 337.170 | 300.116 | 200.091 | −436.466 | −209.112 | 2.023 |
| 5500 | 41.180 | 337.925 | 300.796 | 204.206 | −437.917 | −204.889 | 1.946 |
| 5600 | 41.249 | 338.667 | 301.466 | 208.327 | −439.442 | −200.638 | 1.871 |
| 5700 | 41.318 | 339.398 | 302.125 | 212.456 | −440.697 | −196.407 | 1.800 |
| 5800 | 41.387 | 340.117 | 302.774 | 216.591 | −442.325 | −192.108 | 1.730 |
| 5900 | 41.456 | 340.825 | 303.413 | 220.733 | −444.020 | −187.779 | 1.662 |
| 6000 | 41.525 | 341.523 | 304.042 | 224.882 | −445.779 | −183.421 | 1.597 |

PREVIOUS. June 1969 (1 atm) CURRENT June 1969 (1 bar)

## Lithium Fluoride (LiF) CRYSTAL $M_r = 25.939403$ Lithium Fluoride (LiF) $F_1Li_1(cr)$

$S°(298.15\ K) = 35.660 \pm 0\,021\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 1121.3 \pm 1.0\ K$

$\Delta_f H°(0\ K) = -614.369 \pm 0.8\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = 616.931 \pm 0.8\ kJ{\cdot}mol^{-1}$
$\Delta_{fus} H° = 27\,087 \pm 0\,021\ kJ{\cdot}mol^{-1}$

### Enthalpy of Formation

The enthalpies of solution and reaction of LiF(cr) in water and hydrochloric acid have been measured by many investigators. The reported $\Delta_{sln}H°$ values are listed in the table below. Using $\Delta_f H°(Li,^{+}\ aq,\ \infty,\ 298.15\ K) = -66.56\ kcal{\cdot}mol^{-1}$,[8] and $\Delta_f H°(F,^{-}\ aq,\ \infty,\ 298.15\ K) = -79\,82\ kcal{\cdot}mol^{-1}$,[9] we calculate the corresonding $\Delta_f H°(298.15\ K)$ values for LiF(cr). Based on the enthalpy of solution of LiOH(cr) in excess HF solution measured by Sinke,[7] the value, $\Delta_f H°(LiF,\ cr,\ 298.15\ K) = 146.65 \pm 0.5\ K\ cal{\cdot}mol^{-1}$ is derived. The value of $\Delta_f H°(298.15\ K)$ for LiF(cr) is adopted as $147.45 \pm 0.2\ kcal{\cdot}mol^{-1}$.

| Source | Solvent | $T/K$ | Concentration ($LiF{\cdot}nH_2O$) | $\Delta_s H°$, $kcal{\cdot}mol^{-1}$ | $\Delta_\infty H°$, $kcal{\cdot}mol^{-1}$* | $\Delta_f H°(298.15\ K)$, $kcal{\cdot}mol^{-1}$ |
|---|---|---|---|---|---|---|
| R.de Forcrand (1911)[1] | $H_2O$ | 288.2 | unavailable | 1.04 | – | – |
| Kolesov–Skuratov (1961)[2] | $H_2O$ | 294.7 | 3800 $H_2O$ | 1.25 ± 0.02 | 1.13 ± 0.05 | −147.50 |
| Wulff (1962)[3] | HCl | 298.2 | unavailable | unavailable | 1.10 ± 0.10 | −147.47 |
| Stephenson *et al.*(1964)[4] | $H_2O$ | 298.2 | 2780–5560 $H_2O$ | unavailable | 1.07 ± 0.05 | −147.44 |
| Cox and Harrop (1964)[5] | $H_2O$ | 298.2 | 60400 $H_2O$ | 1.059 ± 0.028 | 1.014 ± 0.055 | −147.38 |

*The enthalpy of dilution data of Parker[6] are used to convert $\Delta_s H°$ to $\Delta_\infty H°$.

### Heat Capacity and Entropy

Clusius, *et al.*[10] measured the low temperature heat capacities in the temperature range 19 to 272 K and Clusius and Eishenauer[11] from 10 to 111 K. Below 20 K a number of investigators have reported values of $\theta_D$, and the average value of $729 \pm 6$ is used here. The high temperature enthalpies from 298.15 K to the melting point 1121.3 K were measured by Douglas and Dever,[12] and Voskresenskaya *et al.*[13] All these data are taken and smoothed by computer to 400 K. Above 400 K the $C_p°$ values are obtained graphically by drawing a smooth line through the data points.

$S°(298.15\ K)$ is derived from the adopted low temperature heat capacities, based on $S°(20\ K) = 0.064\ cal{\cdot}K^{-1}\ mol^{-1}$.

### Fusion Data

Refer to the liquid table for details.

### Sublimation Data

The enthalpy of sublimation, $\Delta_{sub}H°(298.15\ K) = 276.144\ kJ{\cdot}mol^{-1}$, is calculated as the difference between $\Delta_f H°(298.15\ K)$ for LiF(g) and LiF(cr).

### References

[1] R. de Forcrand, Compt. Rend. 152, 27 (1911).
[2] V. P. Kolesov and S. M. Skuratov, Russ. J. Inorg. Chem. 6, 889 (1961).
[3] C. A. Wulff, Ph. D. Thesis, Massachusetts Institute of Technology, (1962).
[4] C. C. Stephenson, H. P. Hopkins and C. A. Wulff, J. Phys. Chem. 68, 1427 (1964).
[5] J. D. Cox and D. Harrop, Trans. Faraday Soc. 61, 1328 (1965).
[6] V. B. Parker, U. S. Nat. Bur. Stand., NSRDS NBS 2, (1965).
[7] G. C. Sinke, The Dow Chemical Company, Midland, Michigan, personal communication, (February 1959).
[8] S. R. Gunn and L. G. Green, J. Amer. Chem. Soc. 80, 4782 (1958).
[9] Derived from JANAF value of $\Delta_f H°(HF,\ g,\ 298.15\ K)$, 12–31–68.
[10] K. Clusius, J. Goldman, and A. Perlick, Z. Naturforsch. 49, 424 (1949).
[11] K. Clusius and W. Eishenauer, Z. Naturforsch. 2a, 715 (1956).
[12] T. B. Douglas and J. L. Dever, J. Amer. Chem. Soc. 76, 4826 (1954).
[13] N. K. Voskresenskaya, V. A. Sokolov, E. I. Banashek, and N. E. Shmidt, Akad. Nauk SSSR, Izvest. Sect. Fiz. Khim. Anal. 27, 233 (1956).

Enthalpy Reference Temperature = $T_r$ = 298.15 K     Standard State Pressure = $p°$ = 0.1 MPa

|  | $J{\cdot}K^{-1}mol^{-1}$ |  |  | $kJ{\cdot}mol^{-1}$ |  |  |  |
|---|---|---|---|---|---|---|---|
| $T/K$ | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | $\log K_f$ |
| 0 | 0. | 0. | INFINITE | −6.473 | −614.369 | −614.369 | INFINITE |
| 100 | 12.816 | 4.858 | 65.944 | −6.109 | −615.953 | −607.186 | 317.162 |
| 200 | 32.803 | 20.690 | 39.225 | −3.707 | −616.858 | −597.965 | 156.172 |
| 298.15 | 41.815 | 35.660 | 35.660 | 0. | −616.931 | −588.660 | 103.131 |
| 300 | 41.936 | 35.919 | 35.661 | 0.077 | −616.928 | −588.485 | 102.464 |
| 400 | 46.543 | 48.706 | 37.373 | 4.533 | −616.682 | −579.039 | 75.615 |
| 500 | 49.329 | 59.401 | 40.738 | 9.331 | −619.500 | −569.345 | 59 479 |
| 600 | 51.589 | 68.597 | 44.633 | 14.378 | −619.173 | −559.341 | 48.695 |
| 700 | 53.723 | 76.711 | 48.647 | 19.645 | −618.607 | −549.410 | 40.997 |
| 800 | 55.731 | 84.016 | 52.619 | 25.118 | −617.835 | −539.575 | 35.231 |
| 900 | 57.697 | 90.695 | 56.483 | 30.790 | −616.881 | −529.848 | 30.752 |
| 1000 | 59.580 | 96.871 | 60.217 | 36.654 | −615.749 | −520.237 | 27.174 |
| 1100 | 61.505 | 102.642 | 63.814 | 42.710 | −614.434 | −510.748 | 24.253 |
| 1121.300 | 61.883 | 103.825 | 64.563 | 44.02 | --- CRYSTAL <--> LIQUID --- |  |  |
| 1200 | 63.245 | 108.068 | 67.278 | 48.948 | −612.944 | −501.386 | 21.825 |
| 1300 | 64.892 | 113.196 | 70.615 | 55.356 | −611.294 | −492.155 | 19.775 |
| 1400 | 66.445 | 118.063 | 73.832 | 61.923 | −609.487 | −483.058 | 18.023 |
| 1500 | 67.906 | 122.697 | 76.936 | 68.642 | −607.532 | −474.094 | 16.509 |
| 1600 | 69.274 | 127.124 | 79.936 | 75.502 | −605.436 | −465.266 | 15.189 |
| 1700 | 70.549 | 131.363 | 82.837 | 82.494 | −748.444 | −449.397 | 13.808 |
| 1800 | 71.731 | 135.429 | 85.647 | 89.608 | −745.339 | −431.895 | 12.533 |
| 1900 | 72.821 | 139.337 | 88.370 | 96.837 | −742.129 | −414.569 | 11.397 |
| 2000 | 73.817 | 143.098 | 91.013 | 104.169 | −738.820 | −397.414 | 10.379 |
| 2100 | 74.720 | 146.722 | 93.580 | 111.597 | −735.423 | −380.427 | 9.463 |
| 2200 | 75.530 | 150.217 | 96.076 | 119 110 | −731.944 | −363.603 | 8.633 |
| 2300 | 76.248 | 153.590 | 98.503 | 126.700 | −728.394 | −346.940 | 7.879 |
| 2400 | 76.872 | 156.849 | 100.867 | 134.357 | −724.780 | −330.432 | 7.192 |
| 2500 | 77.404 | 159.998 | 103.170 | 142.071 | −721.112 | −314.076 | 6.562 |

PREVIOUS: December 1963     CURRENT: December 1968

## Lithium Fluoride (LiF) LIQUID $M_r = 25.939403$

$S°(298.15\ K) = [42.962]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [-598.651]\ kJ \cdot mol^{-1}$

$T_{fus} = 1121.3 \pm 1.0\ K$ $\Delta_{fus} H° = 27.087 \pm 0.021\ kJ \cdot mol^{-1}$

### Enthalpy of Formation

$\Delta_f H°$(LiF, l, 298.15 K) is calculated from $\Delta_f H°$(LiF, cr, 298 15 K) by adding the enthalpy of fusion, $\Delta_{fus} H°$, and the difference in enthalpy, $H°$(1121.3 K)–$H°$(298 15 K), between the crystal and liquid.

### Heat Capacity and Entropy

Douglas and Dever[1] and Voskresenskaya *et al.*[2] have measured the enthalpies of LiF liquid to 1200 and 1400 K, respectively. Using the reported enthalpy data, a constant heat capacity is derived for each set. The adopted $C_p°$ for LiF(l) is the mean of the two derived heat capacities, and is extended arbitrarily to the temperatures above $T_{vap}$ and below $T_{fus}$. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

### Fusion Data

The melting point has been determined by many investigators See the table below for details. The adopted value, 1121.3±1 0 K, is that reported by Douglas and Dever.[1] The heat of melting is the mean of the $\Delta_{fus} H°$ values reported by Douglas and Dever[1] and Voskresenskaya *et al.*[2]

| $T_{fus}$/K | Source |
|---|---|
| 1115 | von Wartenberg and Schulz[3] |
| 1115 | Petit and Cremieu[4] |
| 1119 | Flood *et al.*[5] |
| 1120 | Goryacheva *et al.*[6] |
| 1121 | Haendler *et al.*[7] |
| 1121.2 | Mateiko and Bukhalova[8] |
| 1121.3 | Douglas and Dever[9] |
| 1123 | Bukhalova and Sementsova[10] |

### Vaporization Data

$T_{vap}$ = 1990 K is the temperature at which the partial pressures of LiF(g), $Li_2F_2$(g), and $Li_3F_3$(g), in equilibrium with LiF(l), equal one atmosphere. The vapor composition at the boiling point is evaluated as LiF 69%, $Li_2F_2$ 26 6%, and $Li_3F_3$ 4.4%. The heat required to vaporize one mole of liquid to form 0.739 mole of vapor mixture of the above composition at $T_{vap}$ is calculated to be 35.08 kcal·mol$^{-1}$ (146.775 kJ·mol$^{-1}$).

The value of $T_{vap}$ for LiF(l) has been reported to be 1943 and 1949 K by Ruff *et al.*[3] and von Wartenberg and Schulz,[1] respectively, which were obtained by extrapolation of their vapor pressure data, measured by the boiling point method.

### References

[1] T. B Douglas and J. L. Dever, J Am. Chem. Soc 76, 4826 (1954).
[2] N. K. Voskresenskaya, V A. Sokolov, E. I. Banashek, and N. E. Shmidt, Akad. Nauk SSSR, Izvest. Sekt. Fiz. Khim. Anal. 27, 233 (1956).
[3] H von Wartenberg and H. Schulz, Z. Elektrochem. 27, 568 (1921).
[4] G. Petit and A Cremieu, Compt. Rend. 243, 360 (1956).
[5] H. Flood, V. Fykse, and S. Urnes, Z. Elektrochem. 59 364 (1955).
[6] V P. Goryacheva, A. G. Bergman, and A. G. Kislova, Zh. Neorg. Khim. 4, 2744 (1959).
[7] H. M. Haendler, P. S. Sennett, and C. M. Wheeler, J. Electrochem. Soc. 106, 264 (1959).
[8] Z A. Mateiko and G. A Bukhalova, Zh. Neorg. Khim. 4, 1649 (1959).
[9] T. B. Douglas and J. L. Dever, J. Am. Chem. Soc. 76, 4826 (1954).
[10] G. A. Bukhalova and D. V. Sementsova, Russ. J. Inorg. Chem. 10, 1027 (1965).
[11] O. Ruff, G. Schmidt, and S. Mugdan, Z. anorg. allgem. Chem. 123, 83 (1922).

## Lithium Fluoride (LiF) $F_1Li_1(l)$

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298 15 | 64.183 | 42.962 | 42 962 | 0. | −598.651 | −572.558 | 100.310 |
| 300 | 64 183 | 43.359 | 42.964 | 0 119 | −598.607 | −572.396 | 99.663 |
| 400 | 64.183 | 61.824 | 45.481 | 6.537 | −596.399 | −564.003 | 73.651 |
| 500 | 64.183 | 76.146 | 50.235 | 12.955 | −597.597 | −555.814 | 58.065 |
| 600 | 64.183 | 87.847 | 55.558 | 19.374 | −595.898 | −547.617 | 47 674 |
| 700 | 64 183 | 97.741 | 60.896 | 25 792 | −594.181 | −539.705 | 40.273 |
| 800 | 64.183 | 106.312 | 66.049 | 32.210 | −592.464 | −532.040 | 34 739 |
| 900 | 64.183 | 113.871 | 70 951 | 38.628 | −590.764 | −524.589 | 30.446 |
| 1000 | 64.183 | 120.634 | 75.587 | 45.047 | −589.077 | −517.327 | 27.022 |
| 1100 | 64 183 | 126 751 | 79 965 | 51.465 | −587.399 | −510.234 | 24.229 |
| 1121.300 | 64.183 | 127.982 | 80.865 | 52.832 | --- CRYSTAL <--> LIQUID --- | | |
| 1200 | 64.183 | 132.335 | 84.100 | 57.883 | −585 730 | −503.292 | 21.908 |
| 1300 | 64 183 | 137.473 | 88.010 | 64.301 | −584.069 | −496.490 | 19.949 |
| 1400 | 64.183 | 142.229 | 91 715 | 70.720 | −582.412 | −489.815 | 18.275 |
| 1500 | 64.183 | 146 657 | 95.232 | 77.138 | −580 757 | −483.259 | 16.829 |
| 1600 | 64.183 | 150.800 | 98.577 | 83.556 | −579.102 | −476.813 | 15.566 |
| 1700 | 64.183 | 154 691 | 101 765 | 89.974 | −722.684 | −463.294 | 14.235 |
| 1800 | 64.183 | 158.359 | 104.808 | 96.393 | −720.276 | −448.106 | 13.004 |
| 1900 | 64.183 | 161.829 | 107.718 | 102.811 | −717.875 | −433.051 | 11.905 |
| 2000 | 64.183 | 165.122 | 110.507 | 109.229 | −715.481 | −418.122 | 10 920 |
| 2100 | 64.183 | 168.253 | 113 183 | 115.647 | −713.093 | −403.313 | 10.032 |
| 2200 | 64.183 | 171.239 | 115.754 | 122.066 | −710.710 | −388.617 | 9.227 |
| 2300 | 64 183 | 174.092 | 118.229 | 128.484 | −708.331 | −374.030 | 8.494 |
| 2400 | 64.183 | 176.823 | 120 614 | 134 902 | −705.955 | −359.546 | 7.825 |
| 2500 | 64.183 | 179.443 | 122.915 | 141.320 | −703.583 | −345.161 | 7.212 |
| 2600 | 64.183 | 181 961 | 125.138 | 147 739 | −701.214 | −330.871 | 6.647 |
| 2700 | 64.183 | 184.383 | 127 288 | 154.157 | −698.848 | −316.672 | 6.126 |
| 2800 | 64 183 | 186.717 | 129.369 | 160.575 | −696.484 | −302.560 | 5.644 |
| 2900 | 64.183 | 188 969 | 131.385 | 166 993 | −694.124 | −288.533 | 5.197 |
| 3000 | 64.183 | 191.145 | 133.341 | 173.412 | −691.768 | −274.588 | 4 781 |

PREVIOUS December 1963 CURRENT. December 1968

## Lithium Fluoroide (LiF) CRYSTAL-LIQUID

0 to 1121.3 K crystal
above 1121.3 K liquid

Refer to individual tables for details

## $M_r$ = 25.939403 Lithium Fluoride (LiF) $F_1Li_1(cr,l)$

Enthalpy Reference Temperature = $T_r$ = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

|  | J·K⁻¹mol⁻¹ |  |  | kJ·mol⁻¹ |  |  |  |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −6.473 | −614.369 | −614.369 | INFINITE |
| 100 | 12.816 | 4.858 | 65.944 | −6.109 | −615.953 | −607.186 | 317.162 |
| 200 | 32.803 | 20.690 | 39.225 | −3.707 | −616.858 | −597.965 | 156.172 |
| 298.15 | 41.815 | 35.660 | 35.660 | 0. | −616.931 | −588.660 | 103.131 |
| 300 | 41.936 | 35.919 | 35.661 | 0.077 | −616.928 | −588.485 | 102.464 |
| 400 | 46.543 | 48.706 | 37.373 | 4.533 | −616.682 | −579.039 | 75.615 |
| 500 | 49.329 | 59.401 | 40.738 | 9.331 | −619.500 | −569.345 | 59.479 |
| 600 | 51.589 | 68.597 | 44.633 | 14.378 | −619.173 | −559.341 | 48.695 |
| 700 | 53.723 | 76.711 | 48.647 | 19.645 | −618.607 | −549.410 | 40.997 |
| 800 | 55.731 | 84.016 | 52.619 | 25.118 | −617.835 | −539.575 | 35.231 |
| 900 | 57.697 | 90.695 | 56.483 | 30.790 | −616.881 | −529.848 | 30.752 |
| 1000 | 59.580 | 96.871 | 60.217 | 36.654 | −615.749 | −520.237 | 27.174 |
| 1100 | 61.505 | 102.642 | 63.814 | 42.710 | −614.434 | −510.748 | 24.253 |
| 1121.300 | 61.883 | 103.825 | 64.563 | 44.024 | CRYSTAL <--> LIQUID |  |  |
| 1121.300 | 64.183 | 127.982 | 64.563 | 71.111 | TRANSITION |  |  |
| 1200 | 64.183 | 132.335 | 68.867 | 76.162 | −585.730 | −503.292 | 21.908 |
| 1300 | 64.183 | 137.473 | 73.949 | 82.581 | −584.069 | −496.490 | 19.949 |
| 1400 | 64.183 | 142.229 | 78.659 | 88.999 | −582.412 | −489.815 | 18.275 |
| 1500 | 64.183 | 146.657 | 83.046 | 95.417 | −580.757 | −483.259 | 16.829 |
| 1600 | 64.183 | 150.800 | 87.152 | 101.835 | −579.102 | −476.813 | 15.566 |
| 1700 | 64.183 | 154.691 | 91.012 | 108.254 | −722.684 | −463.294 | 14.235 |
| 1800 | 64.183 | 158.359 | 94.653 | 114.672 | −720.276 | −448.106 | 13.004 |
| 1900 | 64.183 | 161.829 | 98.098 | 121.090 | −717.875 | −433.051 | 11.905 |
| 2000 | 64.183 | 165.122 | 101.367 | 127.508 | −715.481 | −418.122 | 10.920 |
| 2100 | 64.183 | 168.253 | 104.478 | 133.927 | −713.093 | −403.313 | 10.032 |
| 2200 | 64.183 | 171.239 | 107.446 | 140.345 | −710.710 | −388.617 | 9.227 |
| 2300 | 64.183 | 174.092 | 110.282 | 146.763 | −708.331 | −374.030 | 8.494 |
| 2400 | 64.183 | 176.823 | 112.998 | 153.181 | −705.955 | −359.546 | 7.825 |
| 2500 | 64.183 | 179.443 | 115.604 | 159.600 | −703.583 | −345.161 | 7.212 |
| 2600 | 64.183 | 181.961 | 118.108 | 166.018 | −701.214 | −330.871 | 6.647 |
| 2700 | 64.183 | 184.383 | 120.518 | 172.436 | −698.848 | −316.672 | 6.126 |
| 2800 | 64.183 | 186.717 | 122.841 | 178.854 | −696.485 | −302.560 | 5.644 |
| 2900 | 64.183 | 188.969 | 125.082 | 185.273 | −694.124 | −288.533 | 5.197 |
| 3000 | 64.183 | 191.145 | 127.248 | 191.691 | −691.768 | −274.588 | 4.781 |

PREVIOUS: CURRENT: December 1968

Lithium Fluoride (LiF) $F_1Li_1(cr,l)$

## Lithium Fluoride (LiF) IDEAL GAS $M_r = 25.939403$ Lithium Fluoride (LiF) $F_1Li_1(g)$

$\Delta_fH°(0\ K) = -340.575 \pm 8.4\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -340.787 \pm 8.4\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = 200.278 \pm 0.008\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

| Electronic Level and Quantum Weight<br>State | $\epsilon_i$, $cm^{-1}$ | $g_i$ |
|---|---|---|
| $^1\Sigma$ | 0 | 1 |

$\omega_e = 914.33\ cm^{-1}$ $\omega_ex_e = 8.00\ cm^{-1}$ $\sigma = 1$
$B_e = 1.3588\ cm^{-1}$ $\alpha_e = 0.0203\ cm^{-1}$ $r_e = 1.5631 Å$

### Enthalpy of Formation

The molecular species produced on vaporization of lithium fluoride have been studied by many investigators during the last ten years. The occurrence of dimer and trimer molecules in addition to the monomer has been established by use of mass spectrometric,[4 7 8] torsion effusion,[3 6] molecular beam[9 10] and transpiration[11] methods. To evaluate $\Delta_{vap}H°$(LiF, g) we have used a trial and error variation of $\Delta_{sub}H°$ and $\Delta_{vap}H°$ for the monomer, dimer and trimer in order to obtain reasonable agreement with the observed total pressures, 997–1939 K.[1 2,3 5 6] Using as guidelines these total pressures and the equilibrium data for dimer and trimer (refer to these tables), we adopt $\Delta_{sub}H°$(298.15 K) = 66.0, 69.57 and 79 73 and $\Delta_{vap}H°$(298 15 K) = 61.63, 60.83 and 66.62 kcal·mol$^{-1}$ for LiF, $Li_2F_2$ and $Li_3F_3$, respectively. The adopted value $\Delta_{sub}H°$(1000 K) = 63 1 kcal·mol$^{-1}$ is in agreement with the reported values: 64.8 ± 2[12], 63.6 ± 1[6] and 63.0 ± 1.5[8] kcal·mol$^{-1}$ at 1000 K.

A 2nd and 3rd law analysis of the total pressure data is given below Monomer pressures for this analysis are obtained by deducing dimer and trimer pressures calcualted from JANAF free energy functions and the adopted values of $\Delta_{sub}H°$(298.15 K) and $\Delta_{vap}H°$(298.15 K).

The vapor pressure data reported by Eisenstadt *et al.*[9 10] are too low and so not consistent with the others and are not used for evaluation. The transpiration data of Sense and Stone[11] and Knudsen effusion data of Evseev *et al.*[13] are not considered for analysis because of the complications involved in converting the report apparent pressures to the real total pressures of the gaseous mixtures containing monomer, dimer and trimer.

Herzberg[14] and Gaydon[15] reported the dissociation energies ($D_0^\circ$) of LiF(g) to be <6.6 and 5.95 ± 0.3 eV, respectively. Using these $D_0^\circ$ values, we derive $\Delta_fH°$(LiF, g, 298.15 K) as −95.9 and −80.9 ± 6.9 kcal·mol$^{-1}$ By use of flame photometric method, Page and Sugden[16] and Bulewicz *et al.*[17] gave $D_0^\circ$ = 141 and 136 ± 8 kcal·mol$^{-1}$, yielding $\Delta_fH°$(LiF, g, 298.15 K) = −84.7 and −79.7 ± 8 kcal·mol$^{-1}$.

| Source | T/K | Method | Reaction* | Data Points | $\Delta_rH°$(298.15 K), kcal·mol$^{-1}$ 2nd law | 3rd law | Drift cal K$^{-1}$·mol$^{-1}$ | $\Delta_fH°$(298 15 K) kcal·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| von Wartenberg (1921)[1] | 1626–1820 | boiling point | I | 5 | 67.6±2.4 | 61.4 | −3.6±1.4 | −81.68 |
| Ruff (1922)[2] | 1671–1939 | boiling point | I | 14 | 65.8±0.7 | 60.8 | −2.7±0.4 | −82.28 |
| Pugh (1958)*[3] | 1020–1120 | torsion effusion | II | 6 | 69.1 | 66.8 | −2.2 | −80.65 |
| Porter (1958)[4] | 1073 | mass spectrometry | II | 1 | – | 67.7 | – | −79.75 |
| Cantor (1958)*[5] | 1328–1575 | boiling point | I | 10 | 64.5 | 61.6 | −2.0 | −81.48 |
| Hildenbrand (1964)*[6] | 997–1119 | torsion effusion | II | 24 | 69.9 | 66.8 | −3.0 | −80.65 |
|  | 1125–1159 | torsion effusion | I | 19 | 67.1 | 62.3 | −4.2 | −80.78 |

*Data points are calculated from the given vapor pressure equation.
Reaction I. LiF(l) = LiF(g); II. LiF(cr) = LiF(g).

### Heat Capacity and Entropy

The infrared spectrum of LiF(g) and microwave spectrum of $Li^6F$ have been observed by Vidale[19] and Wharten and Klemperer,[21] respectively. The reported vibrational and rotational constants for $Li^7F$ and $Li^6F(g)$ are adopted and corrected to the average isotopic species. Veazey and Gordy[18] measured the rotational transitions of $Li^7F$ with a high resolution molecular beam absorption spectrometer. By use of the electric resonance method of molecular beam spectroscopy, Braunstein and Trischka[22] observed the transitions between $v = 0$ and $v = 1$ vibrational states. The infrared spectrum of LiF(g) have also been measured by Vasilevskii and Baikov.[20]

### References

[1] H. von Wartenberg and H. Schulz, Z. Electrochem. 27, 568 (1921).
[2] O. Ruff, G. Schmidt, and S. Mugdan, Z. anorg. allg. Chem. 123, 83 (1922).
[3] A. C. P. Pugh and R. F. Barrow, Trans. Faraday Soc. 54, 671 (1958).
[4] R. F. Porter and R. C. Schoonmaker, J. Chem. Phys. 29, 1070, (1958); 30, 283 (1959).
[5] S. Cantor and F. Blankenship, paper presented at American Chemical Society meeting at Chicago, (September 7–12, 1958).
[6] D. L. Hildenbrand, W. F Hall, F. Ju, and N. D. Potter, J. Chem. Phys. 40, 2882 (1964).
[7] J. Berkowitz and W. A. Chupka, J. Chem. Phys. 29, 653 (1958).

Continued on page 1214

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p^\circ$ (J·K$^{-1}$mol$^{-1}$) | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ (kJ·mol$^{-1}$) | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0. | 0. | INFINITE | −8.823 | −340.575 | −340.575 | INFINITE |
| 100 | 29 119 | 167 860 | 227.033 | −5.917 | −339.618 | −347.151 | 181.333 |
| 200 | 29.683 | 188.144 | 203.084 | −2.988 | −339.995 | −354.593 | 92.610 |
| 250 | 30.438 | 194.845 | 200.788 | −1.486 | −340.372 | −358.200 | 74.842 |
| 298 15 | 31.287 | 200.278 | 200.278 | 0. | −340.787 | −361.597 | 63.350 |
| 300 | 31.320 | 200.471 | 200.278 | 0.058 | −340.803 | −361.726 | 62.982 |
| 350 | 32.185 | 205.365 | 200.663 | 1.646 | −341.273 | −365.177 | 54.500 |
| 400 | 32.965 | 209.715 | 201.527 | 3.275 | −341.797 | −368.557 | 48.129 |
| 450 | 33.641 | 213.638 | 202.659 | 4.941 | −342.388 | −371.867 | 43.165 |
| 500 | 34.215 | 217.213 | 203.938 | 6.637 | −346.050 | −374.801 | 39.155 |
| 600 | 35.110 | 223.534 | 206.691 | 10.106 | −347.301 | −380.431 | 33.120 |
| 700 | 35.756 | 228.998 | 209.496 | 13.651 | −348.457 | −385.861 | 28 793 |
| 800 | 36.234 | 233.805 | 212.240 | 17.252 | −349.557 | −391.128 | 25.538 |
| 900 | 36 600 | 238.095 | 214.879 | 20.894 | −350.633 | −396.260 | 22.998 |
| 1000 | 36 888 | 241.967 | 217.397 | 24.569 | −351.689 | −401.273 | 20.960 |
| 1100 | 37.122 | 245.494 | 219.794 | 28.270 | −352.729 | −406.181 | 19.288 |
| 1200 | 37.318 | 248 733 | 222.072 | 31.992 | −353 756 | −410.995 | 17.890 |
| 1300 | 37.484 | 251.726 | 224.240 | 35.733 | −354.773 | −415.723 | 16.704 |
| 1400 | 37.630 | 254.510 | 226.303 | 39.489 | −355.778 | −420.374 | 15.684 |
| 1500 | 37.759 | 257.110 | 228.271 | 43.258 | −356.771 | −424.953 | 14.798 |
| 1600 | 37.876 | 259.551 | 230.151 | 47.040 | −357.753 | −429.467 | 14.021 |
| 1700 | 37 983 | 261.850 | 231.949 | 50.833 | −503.960 | −426.743 | 13.112 |
| 1800 | 38.082 | 264.024 | 233.671 | 54 636 | −504.167 | −422.195 | 12.252 |
| 1900 | 38.175 | 266.086 | 235.323 | 58.449 | −504.372 | −417.635 | 11.482 |
| 2000 | 38.263 | 268.046 | 236.911 | 62.271 | −504.574 | −413.065 | 10.788 |
| 2100 | 38.347 | 269.915 | 238.438 | 66.102 | −504.774 | −408.484 | 10.160 |
| 2200 | 38.427 | 271 701 | 239.910 | 69.940 | −504.970 | −403.894 | 9.590 |
| 2300 | 38.504 | 273 411 | 241.329 | 73.787 | −505.163 | −399.296 | 9.068 |
| 2400 | 38.579 | 275.051 | 242.701 | 77.641 | −505.352 | −394.689 | 8.590 |
| 2500 | 38.652 | 276.627 | 244.026 | 81.503 | −505.536 | −390.074 | 8.150 |
| 2600 | 38.723 | 278.145 | 245.310 | 85.372 | −505.717 | −385.452 | 7.744 |
| 2700 | 38 793 | 279.607 | 246.553 | 89.247 | −505.893 | −380.823 | 7.367 |
| 2800 | 38.861 | 281.020 | 247.759 | 93.130 | −506.065 | −376.188 | 7.018 |
| 2900 | 38.928 | 282.384 | 248.929 | 97.019 | −506.234 | −371.546 | 6.692 |
| 3000 | 38.994 | 283.705 | 250.067 | 100.916 | −506.399 | −366.899 | 6.388 |
| 3100 | 39.059 | 284.985 | 251.173 | 104.818 | −506.562 | −362.246 | 6.104 |
| 3200 | 39.124 | 286.226 | 252.249 | 108.727 | −506.723 | −357.588 | 5 837 |
| 3300 | 39.188 | 287.431 | 253.297 | 112.643 | −506.884 | −352.925 | 5.586 |
| 3400 | 39.251 | 288.602 | 254.318 | 116.565 | −507.044 | −348.257 | 5.350 |
| 3500 | 39.314 | 289.740 | 255.314 | 120.493 | −507.206 | −343.585 | 5.128 |
| 3600 | 39.376 | 290.849 | 256.286 | 124.428 | −507.371 | −338.908 | 4.917 |
| 3700 | 39.438 | 291.928 | 257.234 | 128.368 | −507.539 | −334.226 | 4.718 |
| 3800 | 39.500 | 292.981 | 258.161 | 132.315 | −507.713 | −329.539 | 4.530 |
| 3900 | 39.561 | 294.008 | 259.067 | 136.268 | −507.893 | −324.848 | 4.351 |
| 4000 | 39.622 | 295.010 | 259.953 | 140.227 | −508.081 | −320.152 | 4.181 |
| 4100 | 39 682 | 295.989 | 260.820 | 144.193 | −508.279 | −315.452 | 4 019 |
| 4200 | 39.743 | 296.946 | 261.669 | 148.164 | −508.488 | −310.746 | 3.865 |
| 4300 | 39.803 | 297.882 | 262.500 | 152.141 | −508.711 | −306.036 | 3 718 |
| 4400 | 39.863 | 298.798 | 263.315 | 156.124 | −508.927 | −301.321 | 3.577 |
| 4500 | 39.922 | 299.694 | 264.114 | 160.114 | −509.171 | −296.600 | 3 443 |
| 4600 | 39.982 | 300.572 | 264.897 | 164.109 | −509.435 | −291.873 | 3.314 |
| 4700 | 40.041 | 301.433 | 265.665 | 168.110 | −509.718 | −287.141 | 3 191 |
| 4800 | 40.101 | 302.277 | 266.419 | 172.117 | −510.021 | −282.402 | 3 073 |
| 4900 | 40.160 | 303.104 | 267.159 | 176.130 | −510.347 | −277.657 | 2.960 |
| 5000 | 40.219 | 303 916 | 267.886 | 180.149 | −510.697 | −272.904 | 2.851 |
| 5100 | 40.278 | 304.713 | 268.600 | 184.174 | −511.069 | −268.145 | 2.746 |
| 5200 | 40.336 | 305.496 | 269.303 | 188.205 | −511.473 | −263.378 | 2.646 |
| 5300 | 40.395 | 306.265 | 269.993 | 192.241 | −511.907 | −258.603 | 2.549 |
| 5400 | 40.454 | 307.020 | 270.671 | 196.284 | −512.373 | −253.819 | 2.455 |
| 5500 | 40.512 | 307.763 | 271.339 | 200.332 | −512.874 | −249.027 | 2.365 |
| 5600 | 40.570 | 308 494 | 271.996 | 204.386 | −513.411 | −244.225 | 2.278 |
| 5700 | 40.629 | 309.212 | 272.643 | 208.446 | −513.986 | −239 413 | 2.194 |
| 5800 | 40.687 | 309.919 | 273.279 | 212.512 | −514.601 | −234.591 | 2.113 |
| 5900 | 40.745 | 310.615 | 273.906 | 216.583 | −515.258 | −229.757 | 2.034 |
| 6000 | 40.803 | 311.301 | 274.524 | 220.661 | −515.959 | −224.912 | 1.958 |

PREVIOUS· December 1968 (1 atm) CURRENT December 1968 (1 bar)

## Lithium Hypofluorite (LIOF) IDEAL GAS $M_r = 41.938803$ Lithium Hypofluorite (LIOF) $F_1Li_1O_1(g)$

$S°(298.15\ K) = [246.022]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [89.499 \pm 41.8]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-92.048 \pm 41.8]\ kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ |
|---|
| [800](1) |
| [500](1) |
| [950](1) |

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: $C_s$
Bond Distance: Li–O = [1.59] Å; F–O = [1.41] Å
Bond Angle: F–O–Li = [104]°
Product of the Moments of Inertia: $I_A I_B I_C = [4.21997 \times 10^{-116}]\ g^3 \cdot cm^6$

### Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°$(LiFO, g, 298.15 K), is calculated from $\Delta_r H°(298.15\ K) = 139\ kcal \cdot mol^{-1}$ for the reaction LiFO(g) = Li(g) + F(g) + O(g) where the value of $\Delta_r H°(298.15\ K)$ is estimated to be the sum of the F–O and Li–O bond energies. The values of the F–O and Li–O bond energies are obtained from those in $F_2O(g)$ and $Li_2O(g)$ molecules, respectively.

### Heat Capacity and Entropy

The F–O and Li–O bond distances are assumed to be the same as those in $F_2O(g)$ and $Li_2O(g)$ molecules, respectively. The F–O–Li bond angle and vibrational frequencies are estimated by comparison with the corresponding values for the same oxide molecules. The three principal moments of inertia are: $I_A = 1.2732 \times 10^{-39}$, $I_B = 5.1556 \times 10^{-39}$, and $I_C = 6.4288 \times 10^{-39}\ g \cdot cm^2$.

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −10.827 | −89.499 | −89.499 | INFINITE |
| 100 | 33.594 | 205.644 | 280.612 | −7.497 | −89.569 | −92.216 | 48.168 |
| 200 | 37.671 | 229.966 | 249.788 | −3.964 | −90.799 | −94.413 | 24.658 |
| 250 | 40.466 | 238.672 | 246.717 | −2.011 | −91.454 | −95.240 | 19.899 |
| 298.15 | 43.031 | 246.022 | 246.022 | 0. | −92.048 | −95.915 | 16.804 |
| 300 | 43.124 | 246.289 | 246.023 | 0.080 | −92.070 | −95.939 | 16.704 |
| 350 | 45.452 | 253.116 | 246.557 | 2.296 | −92.650 | −96.537 | 14.407 |
| 400 | 47.406 | 259.317 | 247.770 | 4.619 | −93.227 | −97.053 | 12.674 |
| 450 | 49.017 | 264.997 | 249.373 | 7.031 | −93.830 | −97.496 | 11.317 |
| 500 | 50.336 | 270.232 | 251.201 | 9.515 | −97.475 | −97.562 | 10.192 |
| 600 | 52.306 | 279.595 | 255.171 | 14.654 | −98.637 | −97.468 | 8.485 |
| 700 | 53.656 | 287.765 | 259.257 | 19.956 | −99.663 | −97.190 | 7.252 |
| 800 | 54.607 | 294.996 | 263.281 | 25.372 | −100.616 | −96.771 | 6.319 |
| 900 | 55.296 | 301.469 | 267.171 | 30.869 | −101.540 | −96.235 | 5.585 |
| 1000 | 55.809 | 307.323 | 270.898 | 36.425 | −102.446 | −95.597 | 4.993 |
| 1100 | 56.200 | 312.662 | 274.456 | 42.027 | −103.340 | −94.869 | 4.505 |
| 1200 | 56.504 | 317.565 | 277.846 | 47.662 | −104.228 | −94.059 | 4.094 |
| 1300 | 56.744 | 322.098 | 281.078 | 53.325 | −105.113 | −93.176 | 3 744 |
| 1400 | 56.937 | 326.310 | 284.160 | 59.010 | −105.997 | −92.225 | 3.441 |
| 1500 | 57.095 | 330.244 | 287.103 | 64.712 | −106.879 | −91.210 | 3.176 |
| 1600 | 57.225 | 333.933 | 289.916 | 70.428 | −107.760 | −90.137 | 2.943 |
| 1700 | 57.334 | 337.406 | 292.608 | 76.156 | −253.878 | −81.832 | 2.514 |
| 1800 | 57.425 | 340.686 | 295.189 | 81.894 | −254.008 | −71.709 | 2.081 |
| 1900 | 57.503 | 343.793 | 297.666 | 87.640 | −254.149 | −61.577 | 1.693 |
| 2000 | 57.570 | 346.744 | 300.047 | 93.394 | −254.300 | −51.438 | 1.343 |
| 2100 | 57.628 | 349.554 | 302.338 | 99.154 | −254.463 | −41.291 | 1.027 |
| 2200 | 57.678 | 352.236 | 304.545 | 104.919 | −254.637 | −31.135 | 0.739 |
| 2300 | 57.722 | 354.801 | 306.675 | 110.689 | −254.822 | −20.972 | 0.476 |
| 2400 | 57.760 | 357.258 | 308.732 | 116.464 | −255.017 | −10.801 | 0.235 |
| 2500 | 57.794 | 359.617 | 310.720 | 122.241 | −255.223 | −0.621 | 0.013 |
| 2600 | 57.825 | 361.884 | 312.645 | 128.022 | −255.439 | 9.567 | −0.192 |
| 2700 | 57.852 | 364.067 | 314.509 | 133.806 | −255.666 | 19.764 | −0.382 |
| 2800 | 57.876 | 366.172 | 316.317 | 139.593 | −255.903 | 29.970 | −0.559 |
| 2900 | 57.898 | 368.203 | 318.071 | 145.381 | −256.151 | 40.183 | −0.724 |
| 3000 | 57.918 | 370.166 | 319.775 | 151.172 | −256.410 | 50.406 | −0.878 |
| 3100 | 57.935 | 372.065 | 321.432 | 156.965 | −256.681 | 60.638 | −1.022 |
| 3200 | 57.952 | 373.905 | 323.043 | 162.759 | −256.964 | 70.879 | −1.157 |
| 3300 | 57.966 | 375.689 | 324.611 | 168.555 | −257.260 | 81.128 | −1.284 |
| 3400 | 57.980 | 377.419 | 326.139 | 174.352 | −257.569 | 91.387 | −1.404 |
| 3500 | 57.992 | 379.100 | 327.628 | 180.151 | −257.893 | 101.655 | −1.517 |
| 3600 | 58 004 | 380 734 | 329.081 | 185.951 | −258.231 | 111.933 | −1.624 |
| 3700 | 58.014 | 382.323 | 330.499 | 191.752 | −258.587 | 122.220 | −1.725 |
| 3800 | 58.024 | 383.871 | 331.883 | 197.554 | −258.959 | 132.517 | −1.822 |
| 3900 | 58.033 | 385.378 | 333.235 | 203.356 | −259.351 | 142.824 | −1.913 |
| 4000 | 58.041 | 386.847 | 334.557 | 209.160 | −259.762 | 153.141 | −2.000 |
| 4100 | 58.049 | 388.281 | 335.850 | 214.965 | −260.195 | 163.469 | −2.083 |
| 4200 | 58.056 | 389.679 | 337.115 | 220.770 | −260.651 | 173.808 | −2.162 |
| 4300 | 58.062 | 391.046 | 338.354 | 226.576 | −261.131 | 184.158 | −2.237 |
| 4400 | 58.069 | 392.381 | 339.566 | 232.382 | −261.618 | 194.518 | −2.309 |
| 4500 | 58.074 | 393.686 | 340.755 | 238.189 | −262.143 | 204.890 | −2.378 |
| 4600 | 58.080 | 394.962 | 341.919 | 243.997 | −262.699 | 215.274 | −2.445 |
| 4700 | 58.085 | 396.211 | 343.061 | 249.805 | −263.286 | 225.671 | −2.508 |
| 4800 | 58.090 | 397.434 | 344.181 | 255.614 | −263.905 | 236.081 | −2.569 |
| 4900 | 58.094 | 398.632 | 345.280 | 261.423 | −264.559 | 246.505 | −2.628 |
| 5000 | 58.098 | 399.806 | 346.359 | 267.233 | −265.249 | 256.941 | −2.684 |
| 5100 | 58.102 | 400.956 | 347.418 | 273.043 | −265.972 | 267.392 | −2.739 |
| 5200 | 58.106 | 402.084 | 348.459 | 278.853 | −266.741 | 277.857 | −2.791 |
| 5300 | 58.110 | 403.191 | 349.481 | 284.664 | −267.552 | 288.338 | −2.842 |
| 5400 | 58.113 | 404.278 | 350.486 | 290.475 | −268.409 | 298.835 | −2.891 |
| 5500 | 58.116 | 405.344 | 351.474 | 296.287 | −269.314 | 309.347 | −2.938 |
| 5600 | 58.119 | 406.391 | 352.445 | 302.098 | −270.269 | 319.877 | −2.984 |
| 5700 | 58.122 | 407.420 | 353.400 | 307.910 | −271.276 | 330.424 | −3.028 |
| 5800 | 58.125 | 408.431 | 354.340 | 313.723 | −272.338 | 340.990 | −3.071 |
| 5900 | 58.127 | 409.424 | 355.266 | 319.535 | −273.458 | 351.573 | −3.113 |
| 6000 | 58.130 | 410.401 | 356.177 | 325.348 | −274.637 | 362.177 | −3.153 |

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$S°(298\ 15\ K) = 221\ 085 \pm 0.08\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -236.371 \pm 8.4\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -236.814 \pm 8.4\ kJ{\cdot}mol^{-1}$

| State | $T_0$, cm$^{-1}$ | $g_i$ | $\omega_e$, cm$^{-1}$ | $\omega_ex_e$, cm$^{-1}$ | $B_e$, cm$^{-1}$ | $\alpha_e$, cm$^{-1}$ | $r_e$, Å |
|---|---|---|---|---|---|---|---|
| | Electronic Levels and Molecular Constants | | | | | | |
| $X^2\Sigma^+$ | 0 | 2 | 719.56 | 4.91 | 1.7498 | | |
| $A^2\pi$ | 27829.60 | 4 | 743.89 | 3.95 | 0.51711 | 0.00324 | 1.7485 |
| $B^2\Sigma^+$ | 37187.45 | 2 | 759.94 | 5.57 | 0.53542 | 0.00507 | 1.7183 |
| $C^2\Sigma^+$ | 42589.64 | 2 | 820.77 | 5.01 | 0.54792 | 0.00445 | 1.6986 |

## Enthalpy of Formation

We calculated $\Delta_fH°$(MgF, g, 298.15 K) = −56.6 ± 2.0 kcal·mol$^{-1}$ from an adopted. $\Delta_aH°$(MgF, 298 15 K) = 110.7 ± 2 kcal·mol$^{-1}$ which is derived from a 3rd law analysis of three sets of mass spectral–equilibrium data reported by Murad *et al.*[1] and Hildenbrand.[2] Also included in the analysis are independent mass spectrometer–equilibrium measurements on MgF(g) by Ehlert.[3, 4]

| Source | Reaction | Data Points | T/K | $\Delta_rH°$(298.15 K), kcal·mol$^{-1}$ 2nd law | 3rd law | Drift cal K$^{-1}$·mol$^{-1}$ | $\Delta_fH°$(298 15 K)[c] kcal·mol$^{-1}$ | $D_0°$(298.15 K) kcal·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| Murad *et al.*[1] | (A) | 4 | 1546–1585 | 6.2 | 5.6[b]±1.3 | −0.4±26 | −57.5±2.0 | 111.6 |
| Hildenbrand[2] Set 1 | (B) | 4 | 1280–1345 | 22.1 | 25.8±0.7 | 2.9±8.7 | −56.3±0.8 | 110.4 |
| Set 2 | (B) | 7 | 1413–1493 | 24.3 | 26.58±0.2 | 1.6±3.7 | −55.9±0.7 | 110.0 |
| Ehlert[3] | (B) | 5 | 1205–1253 | −90.0 | −31.5±2.1 | 47±18 | −53.5±1.5 | 107.6 |
| Ehlert *et al.*[4] | (C) | 5 | 1238–1301 | 63.0 | 47 6±26 | −12.2±26 | −53.7±2.0 | 107.8 |
| Ehlert *et al.*[4] | (D) | 5 | 1238–1301 | −91.9 | −126.7±1.8 | −28.3±17 | −53.4±1.0 | 107.5 |

Reactions: (A) Tl(g) + MgF(g) = TlF(g) + Mg(g) (B) Mg(g) + $MgF_2$(g) = 2 MgF(g) (C) $AlF_3$(g) + 2 Mg(g) = AlF(g) + 2 MgF(g)
(D) 2 MgF(g) = Mg(g) + $MgF_2$(cr)

[a] One point rejected due to failure of a statistical test.

[b] Free–energy functions (FEF) for TlF(g) are calculated from spectral data,[5] FEF for Tl(g) are from Hultgren.[6]

[c] 3rd law Values, all auxillary $\Delta_fH°$(298.15 K) from JANAF Thermochemical Table[8] except for Tl and TlF.[7]

We dismiss the measurements of Ehlert[3] and Ehlert *et al.*[4] since our analyses show that their equilibrium data most likely contain temperature dependent errors. Furthermore, their results[3, 4] yield $D_0°$ values which are less than that predicted by the Rittner ionic model. Krasnov and Karaseva[9] have applied this potential function to all the alkaline earth monohalides and found that it establishes a lower limit for $D_0°$. Recalculation of their results[9] sets $\Delta_aH°$(MgF, 298.15 K) > 110.4 kcal·mol$^{-1}$. Application of this ionic model to MgF is justified since the spin densities calculated from the ESR spectra[10] of matrix–isolated MgF show that the molecule is indeed highly ionic.

Trends in the well–established values of the ratio $\Delta_aH°$(MX,298.15 K)/$\Delta_aH°$($MX_2$,298.15 K) for the majority of the alkaline earth halides[8] suggests a value for MgF/$MgF_2$ which is less than or equal to 0.45. This sets the upper limit of $\Delta_aH°$(MgF, 298.15 K) at 111 kcal·mol$^{-1}$ when $\Delta_aH°$($MgF_2$, 298.15 K) = 246.7 kcal·mol$^{-1}$.[8] If $MgF_2$(g) is linear then the maximum $\Delta_aH°$(298 15 K) value increases to 112.6 kcal·mol$^{-1}$ suggesting a possible uncertainty in the adopted $D_0°$ of ±2 kcal·mol$^{-1}$. Our adopted results give $\Delta_aH°$(MgF, 298.15 K)/$\Delta_a$H($MgF_2$, 298.15 K) = $0.44_9$.

Our selected thermochemical $\Delta_aH°$(298.15 K) value converted to 0 K is 4.76 eV (109.8 kcal·mol$^{-1}$). Other values for $D_0°$ which were considered but believed less reliable are (all in ev 4 0,[11] 5.0 or 4.7[11] and 4.2.[12] These spectroscopic values have been derived from linear Birge–Sponer extrapolations of the ground state ($X^2\Sigma^+$) and first excited state ($^2\pi$) vibrational levels We obtain $D_0° = 3.2_2$ eV from a linear Birge–Sponer extrapolation with our adopted ground state vibrational constants This value adjusts to 3.59 eV when corrected for the ionicity[2] of the Mg–F bond. The corrected $D_0°$ value is 1.2 eV less than the thermochemical result. This discrepancy is most likely due to the use of an inaccurate value for the anharmonic constant, $\omega_ex_e$, in the Birge–Sponer extrapolation. The use of lower reported values[12, 15] for $\omega_ex_e$ brings the spectroscopic and thermochemical $D_0°$ values into much better agreement but leaves the thermodynamic functions for MgF unaltered. In addition, Singh *et al.*[10] have employed a method to fit an electronegative potential energy function to the expermimental potential energy curves which yields $D_0°$ = 4.45 eV. This value agrees with our results within probable error limits.

## Heat Capacity and Entropy

The electronic levels and vibrational–rotational constants are taken from the compilation of Rosen.[5] Values of these constants, tabulated for $Mg^{24}F$, are corrected for the natural isotopic abundances of magnesium. The value of $\alpha_e$ listed by Rosen for the $C^2\Sigma^+$ state is incorrect. The rotational constants are based on an analysis[14] of the rotational structure in the bands of the A–X, B–X, and C–X systems. Barrow and Beale[14] used the Pekeris relation[12] to calculate $\omega_ex_e$ values from their spectroscopic $\alpha_e$'s. These $\omega_ex_e$ values were combined with $\Delta G_{1/2}$ values to give $\omega_e$. These estimates of $\omega_e$ and $\omega_ex_e$ differ somewhat from those obtained from a vibrational analysis[15] of band head measurements.

Continued on page 1214

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ (J·K$^{-1}$mol$^{-1}$) | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ (kJ·mol$^{-1}$) | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0. | 0 | INFINITE | −8.968 | −236.371 | −236.371 | INFINITE |
| 100 | 29.142 | 188.032 | 248.620 | −6.059 | −235.558 | −244 892 | 127.919 |
| 200 | 30.463 | 208.521 | 223.998 | −3.095 | −236.066 | −254.077 | 66.358 |
| 250 | 31.569 | 215.437 | 221.616 | −1.545 | −236.438 | −258.537 | 54.018 |
| 298.15 | 32.569 | 221.085 | 221.085 | 0. | −236.814 | −262.759 | 46.034 |
| 300 | 32.605 | 221.287 | 221.086 | 0.060 | −236.829 | −262.920 | 45.778 |
| 350 | 33.481 | 226.381 | 221.486 | 1 713 | −237.233 | −267.237 | 39.883 |
| 400 | 34.194 | 230.900 | 222.386 | 3.406 | −237.649 | −271.495 | 35.454 |
| 450 | 34.768 | 234.962 | 223.561 | 5.130 | −238.078 | −275.700 | 32.002 |
| 500 | 35.229 | 238.649 | 224.888 | 6.881 | −238.523 | −279.857 | 29.236 |
| 600 | 35.912 | 245.137 | 227.737 | 10.440 | −239.468 | −288.036 | 25.076 |
| 700 | 36.381 | 250.710 | 230.630 | 14.056 | −240.500 | −296.050 | 22.092 |
| 800 | 36.720 | 255.591 | 233.452 | 17.712 | −241.637 | −303.910 | 19.843 |
| 900 | 36.975 | 259.932 | 236.157 | 21.397 | −242.897 | −311.620 | 18.086 |
| 1000 | 37 175 | 263.838 | 238.733 | 25.105 | −252.890 | −318.470 | 16.635 |
| 1100 | 37.338 | 267.389 | 241.179 | 28.831 | −254.455 | −324.952 | 15.431 |
| 1200 | 37.474 | 270.644 | 243.501 | 32.572 | −256.018 | −331.292 | 14.421 |
| 1300 | 37.592 | 273.649 | 245.706 | 36.325 | −257.580 | −337.501 | 13.561 |
| 1400 | 37.695 | 276.438 | 247.803 | 40.090 | −386.551 | −340.423 | 12.701 |
| 1500 | 37.787 | 279.042 | 249.800 | 43.864 | −386.761 | −337.121 | 11.740 |
| 1600 | 37.872 | 281 484 | 251.704 | 47.647 | −386.971 | −333.805 | 10.898 |
| 1700 | 37.950 | 283.782 | 253.524 | 51.438 | −387.181 | −330.475 | 10 154 |
| 1800 | 38.023 | 285.953 | 255.266 | 55.237 | −387.391 | −327 134 | 9.493 |
| 1900 | 38.092 | 288.011 | 256.936 | 59.042 | −387.600 | −323.780 | 8 901 |
| 2000 | 38.157 | 289.966 | 258.539 | 62.855 | −387.807 | −320.416 | 8.368 |
| 2100 | 38.221 | 291.830 | 260.080 | 66.674 | −388.010 | −317.042 | 7.886 |
| 2200 | 38.281 | 293.609 | 261.564 | 70.499 | −388.209 | −313.657 | 7 447 |
| 2300 | 38.341 | 295.312 | 262.995 | 74.330 | −388.402 | −310.264 | 7 046 |
| 2400 | 38.398 | 296.945 | 264.375 | 78.167 | −388.587 | −306.863 | 6.679 |
| 2500 | 38.454 | 298.514 | 265.710 | 82.010 | −388.764 | −303 454 | 6.340 |
| 2600 | 38.510 | 300 023 | 267.001 | 85.858 | −388.930 | −300.038 | 6.028 |
| 2700 | 38.564 | 301.477 | 268.251 | 89.712 | −389.086 | −296.616 | 5.738 |
| 2800 | 38.619 | 302.881 | 269.463 | 93.571 | −389.230 | −293 189 | 5 470 |
| 2900 | 38.672 | 304.237 | 270.639 | 97.435 | −389.361 | −289.757 | 5.219 |
| 3000 | 38.726 | 305.549 | 271.780 | 101.305 | −389.480 | −286.320 | 4.985 |
| 3100 | 38.779 | 306.820 | 272.890 | 105.180 | −389.587 | −282.880 | 4.766 |
| 3200 | 38.833 | 308 052 | 273.970 | 109.061 | −389.682 | −279.436 | 4.561 |
| 3300 | 38.887 | 309.247 | 275.021 | 112.947 | −389.766 | −275.989 | 4.369 |
| 3400 | 38.941 | 310.409 | 276.045 | 116.838 | −389.840 | −272.540 | 4.187 |
| 3500 | 38.997 | 311.539 | 277.043 | 120.735 | −389.906 | −269.089 | 4.016 |
| 3600 | 39.053 | 312.638 | 278.016 | 124.638 | −389.964 | −265.637 | 3.854 |
| 3700 | 39.110 | 313.709 | 278.967 | 128.546 | −390.017 | −262.182 | 3 701 |
| 3800 | 39.169 | 314 753 | 279.895 | 132.460 | −390.066 | −258.727 | 3.556 |
| 3900 | 39.230 | 315.771 | 280.802 | 136.380 | −390.114 | −255.270 | 3.419 |
| 4000 | 39.292 | 316.765 | 281.688 | 140.306 | −390.162 | −251.811 | 3.288 |
| 4100 | 39.357 | 317.736 | 282.556 | 144.238 | −390.213 | −248.352 | 3.164 |
| 4200 | 39.423 | 318.685 | 283 405 | 148.177 | −390.270 | −244.891 | 3.046 |
| 4300 | 39.492 | 319.613 | 284.236 | 152.123 | −390.333 | −241.429 | 2.933 |
| 4400 | 39.563 | 320.522 | 285.050 | 156.076 | −390 406 | −237.966 | 2.825 |
| 4500 | 39 637 | 321.412 | 285.849 | 160.036 | −390.491 | −234.500 | 2.722 |
| 4600 | 39.714 | 322.284 | 286.631 | 164.003 | −390.590 | −231.033 | 2.623 |
| 4700 | 39.794 | 323.139 | 287.399 | 167 979 | −390.706 | −227.563 | 2.529 |
| 4800 | 39 877 | 323.978 | 288.152 | 171.962 | −390.840 | −224.090 | 2.439 |
| 4900 | 39.963 | 324.801 | 288.892 | 175.954 | −390.995 | −220.615 | 2.352 |
| 5000 | 40.052 | 325.609 | 289.618 | 179.955 | −391.172 | −217.136 | 2.268 |
| 5100 | 40.145 | 326 403 | 290.332 | 183.965 | −391.374 | −213.653 | 2.188 |
| 5200 | 40.241 | 327.184 | 291.033 | 187.984 | −391.603 | −210 166 | 2.111 |
| 5300 | 40.340 | 327.951 | 291.722 | 192.013 | −391.859 | −206.675 | 2.037 |
| 5400 | 40.443 | 328.706 | 292.400 | 196.052 | −392.146 | −203.178 | 1.965 |
| 5500 | 40.549 | 329.449 | 293.067 | 200.101 | −392.464 | −199.676 | 1.896 |
| 5600 | 40.659 | 330.181 | 293.723 | 204.162 | −392.814 | −196.167 | 1.830 |
| 5700 | 40.772 | 330.901 | 294.369 | 208.233 | −393.199 | −192.653 | 1.765 |
| 5800 | 40.888 | 331.611 | 295.005 | 212.316 | −393.620 | −189.131 | 1.703 |
| 5900 | 41.008 | 332.311 | 295 632 | 216 411 | −394.077 | −185.601 | 1.643 |
| 6000 | 41.131 | 333 002 | 296.249 | 220.518 | −394.573 | −182.063 | 1.585 |

PREVIOUS: June 1976 (1 atm)    CURRENT: June 1976 (1 bar)

## Magnesium Fluoride, Ion (MgF$^+$) IDEAL GAS $M_r = 43.302854$ Magnesium Fluoride, Ion (MgF$^+$) $F_1Mg_1^+(g)$

$S°(298.15\ K) = [215.330 \pm 8.4]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_fH°(0\ K) = 506.533 \pm 46.0\ kJ\cdot mol^{-1}$
$\Delta_fH°(298.15\ K) = [512.289]\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights

| State | $\epsilon_i$, cm$^{-1}$ | $g_i$ | State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|---|---|---|
| $X^1\Sigma^+$ | 0 | [1] | $B^1\Sigma^+$ | [20000] | [1] |
| $^3\Pi$ | [2600] | [6] | $^3\Pi$ | [28000] | [3] |
| $A^1\Pi$ | [3500] | [2] | $^3\Delta$ | [29000] | [6] |
| $^3\Sigma^+$ | [15000] | [3] | $D^1\Delta$ | [30000] | [2] |

$\omega_e = [718.5]\ cm^{-1}$
$\omega_ex_e = [4.90]\ cm^{-1}$
$\sigma = 1$

$B_e = [0.5162]\ cm^{-1}$
$\alpha_e = [0.00463]\ cm^{-1}$
$r_e = [1.75]\ Å$

### Enthalpy of Formation

MgF$^+$ ionization–efficiency curves obtained from mass spectral observations on the MgF$_2$[1] and MgF$_2$–Al[2] systems are of the two–process type. Evidence[1 2] has been presented which shows that the low–energy portion (<13 eV) of the curve arises from the direct ionization (A) of MgF(g). These curves also show an inflection point at higher energies (~14 eV) which has been interpreted[1-3] as due to the onset of the dissociative ionization (B) of MgF$_2$(g). The appearance potentials, in eV, which have been observed for these two processes from measurements on various MgF$_2$ systems are tabulated below.

| Source | Year | System | (A) Direct Ionization | (B) Dissociative Ionization |
|---|---|---|---|---|
| Berkowitz and Marquart[4] | 1962 | MgF$_2$ | | 13.5±0.4 |
| Green *et al.*[1] | 1964 | MgF$_2$ | | 13 6±0.3 |
| Ehlert *et al.*[2] | 1964 | MgF$_2$–Al | 7.8±0.3 | 13.7±0.4 |
| Murad *et al.*[5] | 1966 | MgF$_2$–Tl–Pd | 8.0±0.5 | |
| Hildenbrand[6] | 1968 | MgF$_2$–Cu | 7.5±0.3 | |
| Hildenbrand[3] | 1968 | MgF$_2$ | 7.5±0.5 | |

(A) $MgF(g) + e^- \rightarrow MgF^+(g) + 2\ e^-$ (B) $MgF_2(g) + e^- \rightarrow MgF^+(g) + F(g) + 2\ e^-$

Both sets of data show the normal scatter ( 0.5 eV) expected for such measurements. The mean value (7.7 ± 0.4 eV) of the four AP's for the direct ionization (A) is supported by the spectroscopic ionization potential of 7.68 eV.[7] We adopt $\Delta_rH° = 177.56 \pm\ 9$ kcal·mol$^{-1}$ (7.7 eV) for process (A), and we obtain $\Delta_fH°(MgF,^+ g) = 121.1 \pm 11.0$ kcal·mol$^{-1}$ when the $\Delta_rH°$ value is combined with $\Delta_fH°(MgF, g) = -56.5 \pm 2.0$ kcal mol.$^{-1}$[8] The fragmentation process (B) is likely to involve unknown kinetic energy factors and would not be expected to yield as reliable $\Delta_fH°$ value as obtained from direct ionization. However, the mean value (13.58 ± 0.5 eV) of the four AP's for process (B) leads to $\Delta_fH°(MgF^+, g, 0\ K) = 121.5 \pm 13.0$ kcal·mol$^{-1}$ which is in remarkably good with the $\Delta_fH°$ value from direct ionization (121.1 kcal·mol$^{-1}$). This implies that the excess kinetic energy of the fragment MgF$^+$ is small.

### Heat Capacity and Entropy

The bond dissociation energy for MgF$^+$ (108.6 kcal·mol$^{-1}$) is nearly the same as that for MgF(109.8 kcal·mol$^{-1}$)[8] which implies that the bonding in these two molecules is quite similar. Thus, it is reasonable to assume that $r_e(MgF^+) = r_e(MgF)$. We adopt the measured $r_e$ value (1.75 Å) for MgF.[8] $B_e$ is calculated from the adopted value for $r_e$. The value of $\omega_e$ is obtained from Badger's rule[9] which is written in the form $\omega_e^2 = 3.159 \times 10^6/\mu\ (r_e = d_{ij})$.[3] Molecular data[8] for NaF, MgF, and MgO are used to determine the constant $d_{ij}$. Barrow and Caunt[10] have shown that the product $x_e^{1/2}$ is fairly constant within a group of similar molecules. We assume $x_e(MgF^+) = x_e(MgF)$ since $^{1/2}(MgF^+) = {}^{1/2}(MgF)$. These estimates of $\omega_e$ and $\omega_ex_e$ are only slightly different from those observed for MgF.[8] $\alpha_e$ is obtained from the other constants assuming a Morse potential function.

Novikov and Gurvich[11] have observed a band system in the emission spectrum of MgF near 54000 cm$^{-1}$. An analysis of the vibrational structure showed that the system did not belong to any of those known for MgF, and they[11] assigned it to the $^1\Sigma-^1\Sigma$ transition of MgF$^+$. Band systems have appeared in the absorption spectra[12, 13] of MgF which are now known to arise from AlF. A comparison of the vibrational constants reported by Novikov and Gurvich[11] with those for AlF[8] strongly suggests that this system is the $B^1\Sigma-X^1\Sigma$ transition of AlF. Barrow[14] has come to the same conclusion.

MgF$^+$ (8 valence elecrons) is isoelectronic with the alkaline earth monoxides. We estimate the electronic states and levels for MgF$^+$ by analogy with those for these isoelectronic molecules,[8] particularly MgO. The $^1\pi-^3\pi$ splitting of MgO has recently been reported as 900 ± 200 cm.$^{-1}$.[15] We believe that our adopted electronic entropies represent minimal values. Probable upper limits for the electronic contributions can be established by decreasing the two lowest triplet levels to 1000 cm$^{-1}$ ($^3\pi$) and 5000 cm$^{-1}$ ($^3\Sigma$) and neglecting the other excited states. This increases the entropy to 65.1 and 78.6 cal K$^{-1}$·mol$^{-1}$ at 1000 K and 4000 K, respectively. The enthalpy is much more uncertain, approaching ±3.0 kcal·mol$^{-1}$ at temperatures in excess of 2000 K.

Continued on page 1214

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −8.969 | 506.533 | | |
| 100 | 29.142 | 182.270 | 242.875 | −6.060 | | | |
| 200 | 30.469 | 202.761 | 218.245 | −3.097 | | | |
| 250 | 31.580 | 209.679 | 215.862 | −1.546 | | | |
| 298.15 | 32.605 | 215.330 | 215.330 | 0. | 512.289 | 481.805 | −84 410 |
| 300 | 32.643 | 215.532 | 215.331 | 0.060 | 512.313 | 481.616 | −83.857 |
| 350 | 33.621 | 220.638 | 215.732 | 1.717 | 512.952 | 476.449 | −71.106 |
| 400 | 34.589 | 225.191 | 216.635 | 3.422 | 513.588 | 471.191 | −61.531 |
| 450 | 35.646 | 229.324 | 217.819 | 5.178 | 514.229 | 465.853 | −54.075 |
| 500 | 36.868 | 233.142 | 219.162 | 6.990 | 514.885 | 460.443 | −48.102 |
| 600 | 39.885 | 240.119 | 222.084 | 10.821 | 516.291 | 449.425 | −39.126 |
| 700 | 43.407 | 246.529 | 225.123 | 14.984 | 517.884 | 438.157 | −32.696 |
| 800 | 46.861 | 252.555 | 228.179 | 19.500 | 519 687 | 426.647 | −27.857 |
| 900 | 49.709 | 258.246 | 231.207 | 24.336 | 521.655 | 414.900 | −24.080 |
| 1000 | 51.662 | 263.593 | 234.181 | 29.412 | 515.109 | 403.642 | −21.084 |
| 1100 | 52.688 | 268.572 | 237.084 | 34.637 | 517.121 | 392.398 | −18.633 |
| 1200 | 52.931 | 273.172 | 239.902 | 39.923 | 519.183 | 380.969 | −16.583 |
| 1300 | 52.600 | 277.399 | 242.626 | 45.204 | 521.226 | 369.368 | −14.841 |
| 1400 | 51.901 | 281.273 | 245.251 | 50.431 | 395.797 | 360.779 | −13.461 |
| 1500 | 51.001 | 284.824 | 247.772 | 55.577 | 399.038 | 358.164 | −12.472 |
| 1600 | 50.020 | 288.084 | 250.191 | 60.629 | 402.175 | 355.336 | −11.601 |
| 1700 | 49.035 | 291.087 | 252.510 | 65.581 | 405.204 | 352.315 | −10.825 |
| 1800 | 48.095 | 293.863 | 254.731 | 70.437 | 408.131 | 349.119 | −10.131 |
| 1900 | 47.225 | 296.439 | 256.859 | 75.203 | 410.960 | 345.763 | −9.506 |
| 2000 | 46.436 | 298.841 | 258.899 | 79.885 | 413.701 | 342.261 | −8.939 |
| 2100 | 45.731 | 301.090 | 260.855 | 84.493 | 416.365 | 338.623 | −8.423 |
| 2200 | 45.107 | 303.202 | 262.732 | 89.034 | 418.961 | 334.860 | −7.951 |
| 2300 | 44.559 | 305.195 | 264.536 | 93.517 | 421.498 | 330.980 | −7.517 |
| 2400 | 44.081 | 307.081 | 266.269 | 97.948 | 423.986 | 326.991 | −7.117 |
| 2500 | 43.665 | 308.872 | 267.938 | 102.335 | 426.432 | 322.899 | −6.747 |
| 2600 | 43.306 | 310.577 | 269.545 | 106.683 | 428.844 | 318.710 | −6.403 |
| 2700 | 42.997 | 312.206 | 271.095 | 110.998 | 431.229 | 314.428 | −6.083 |
| 2800 | 42.732 | 313.765 | 272.592 | 115.284 | 433.590 | 310.059 | −5.784 |
| 2900 | 42.506 | 315.260 | 274.037 | 119.545 | 435.935 | 305.606 | −5.505 |
| 3000 | 42.315 | 316.698 | 275.436 | 123.786 | 438.265 | 301.072 | −5.242 |
| 3100 | 42.154 | 318.082 | 276.789 | 128.009 | 440.585 | 296.461 | −4.995 |
| 3200 | 42.021 | 319.419 | 278.101 | 132.218 | 442.896 | 291.775 | −4.763 |
| 3300 | 41.913 | 320.710 | 279.372 | 136.414 | 445.201 | 287.017 | −4.543 |
| 3400 | 41.825 | 321.960 | 280.607 | 140.601 | 447.501 | 282.189 | −4.335 |
| 3500 | 41.757 | 323.171 | 281.806 | 144.780 | 449.796 | 277.293 | −4.138 |
| 3600 | 41.706 | 324.347 | 282.971 | 148.953 | 452.087 | 272.332 | −3.951 |
| 3700 | 41.670 | 325.489 | 284.105 | 153.122 | 454.373 | 267.307 | −3.774 |
| 3800 | 41.648 | 326.600 | 285.208 | 157.288 | 456.654 | 262.221 | −3.604 |
| 3900 | 41.638 | 327.682 | 286.284 | 161.452 | 458.929 | 257.075 | −3.443 |
| 4000 | 41.639 | 328.736 | 287.332 | 165.616 | 461.197 | 251.870 | −3.289 |
| 4100 | 41.651 | 329.764 | 288.354 | 169.780 | 463.457 | 246.609 | −3.142 |
| 4200 | 41.671 | 330.768 | 289.352 | 173.946 | 465.707 | 241.293 | −3.001 |
| 4300 | 41.700 | 331.749 | 290.327 | 178.114 | 467.944 | 235.923 | −2.866 |
| 4400 | 41.736 | 332.708 | 291.279 | 182.286 | 470.169 | 230.501 | −2.736 |
| 4500 | 41.780 | 333.646 | 292.210 | 186.462 | 472.379 | 225.029 | −2.612 |
| 4600 | 41.829 | 334.565 | 293.121 | 190.642 | 474.571 | 219.508 | −2.493 |
| 4700 | 41.884 | 335.465 | 294.013 | 194.828 | 476.744 | 213.940 | −2.378 |
| 4800 | 41.944 | 336.348 | 294.885 | 199.019 | 478.896 | 208.326 | −2.267 |
| 4900 | 42.009 | 337.213 | 295.740 | 203.217 | 481.026 | 202.667 | −2.160 |
| 5000 | 42.079 | 338.063 | 296.578 | 207.421 | 483.130 | 196.965 | −2.058 |
| 5100 | 42.152 | 338.897 | 297.400 | 211.633 | 485.209 | 191.221 | −1.958 |
| 5200 | 42.229 | 339.716 | 298.206 | 215.852 | 487.258 | 185.436 | −1.863 |
| 5300 | 42.309 | 340.521 | 298.997 | 220.079 | 489.278 | 179.613 | −1.770 |
| 5400 | 42.393 | 341.313 | 299.773 | 224.314 | 491.266 | 173.751 | −1.681 |
| 5500 | 42.479 | 342.091 | 300.535 | 228.557 | 493.222 | 167.853 | −1.594 |
| 5600 | 42.567 | 342.858 | 301.284 | 232.810 | 495.142 | 161.920 | −1.510 |
| 5700 | 42.658 | 343.612 | 302.020 | 237.071 | 497.025 | 155.953 | −1.429 |
| 5800 | 42.751 | 344.354 | 302.744 | 241.341 | 498.870 | 149.953 | −1.350 |
| 5900 | 42.845 | 345 086 | 303.455 | 245.621 | 500.676 | 143.922 | −1.274 |
| 6000 | 42.941 | 345.807 | 304.155 | 249.910 | 502.441 | 137.860 | −1.200 |

PREVIOUS· December 1975 (1 atm) CURRENT: December 1975 (1 bar)

**Molybdenum Fluoride (MoF)** **IDEAL GAS** $M_r = 114.938403$ **Molybdenum Fluoride (MoF)** $F_1Mo_1(g)$

$D_0^\circ = [451.454 \pm 16.7]\ kJ\cdot mol^{-1}$
$S^\circ(298.15\ K) = [246.399 \pm 8.4]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H^\circ(0\ K) = [282.853 \pm 12.6]\ kJ\cdot mol^{-1}$
$\Delta_f H^\circ(298.15\ K) = 282.838 \pm 12.6\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights

| $\epsilon_i$, cm$^{-1}$ | $g_i$ | $\epsilon_i$, cm$^{-1}$ | $g_i$ | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|---|---|---|
| 0 | [6] | [15199] | [6] | [15890] | [2] |
| [11783] | [2] | [15331] | [8] | [16796] | [2] |
| [12034] | [4] | [15428] | [10] | [16947] | [8] |
| [12417] | [6] | [15447] | [12] | [17174] | [4] |
| [12900] | [8] | [15691] | [6] | [17344] | [6] |
| [13461] | [10] | [15699] | [4] | | |

$\omega_e = [700]\ cm^{-1}$
$B_e = [0.3209]\ cm^{-1}$
$\omega_e x_e = [3.05]\ cm^{-1}$
$\alpha_e = [0.0019]\ cm^{-1}$
$\sigma = 1$
$r_e = [1.82]$ Å

## Enthalpy of Formation

The adopted enthalpy of formation at 298.15 K is that derived by Brewer[1] from the high temperature mass spectrometric measurements of equilibria among gaseous molybdenum fluorides by Hildenbrand [2054–2242 K].[2] The value of $\Delta_f H^\circ(0\ K)$ combined with JANAF data[3] for Mo(g) and F(g) gives $D_0^\circ(MoF) = 107.9 \pm 4\ kcal\cdot mol^{-1}$.

## Heat Capacity and Entropy

We use the ground state vibrational frequency of 700 cm$^{-1}$ estimated by Hildenbrand[2] and adopted by Brewer.[1] The Mo–F bond distance, 1.82 Å, is the Mo–F bond distance in $MoF_6(g)$ used by Brewer.[1] The electronic contributions are assumed to be the same as those for the free gaseous $Mo^+$ ion, as suggested by Brewer.[1] All states up to 17344 cm$^{-1}$ as listed by Moore[4] are included in the calculation. Our thermodynamic functions differ slightly from those reported by Brewer[1] because of the use of non zero values for $\omega_e x_e$ and $\alpha_e$. The estimates for $\omega_e x_e$ and $\alpha_e$ are based on the empirical correlations of Calder and Ruedenberg.[5]

This table is based on the critical analysis of data existing in 1978 by Brewer.[1]

## References

[1] L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication, Sept. 1978, of preliminary draft of review was submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.
[2] D. L. Hildenbrand, J. Chem. Phys. 65, 614 (1976).
[3] JANAF Thermochemical Tables: Mo(g), 3–31–78; F(g), 9–30–65.
[4] C. E. Moore, U.S. Nat. Bur. Stand., NSRDS NBS 34 (1970); NSRDS NBS 35, Vol. III, 1971 [Reprint of NBS Circular 467, Vol. III, 1958].
[5] G. V. Calder and K. Ruedenberg, J. Chem. Phys. 49, 5399 (1968).

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p^\circ$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −8.982 | 282.853 | 282.853 | INFINITE |
| 100 | 29.145 | 213.279 | 274.009 | −6.073 | 283.818 | 271.711 | −141.927 |
| 200 | 30.549 | 233.795 | 249.321 | −3.105 | 283.479 | 259.681 | −67.822 |
| 250 | 31.674 | 240.733 | 246.931 | −1.550 | 283.165 | 253.767 | −53.022 |
| 298.15 | 32.671 | 246.399 | 246.399 | 0. | 282.838 | 248.134 | −43.472 |
| 300 | 32.706 | 246.601 | 246.399 | 0.060 | 282.826 | 247.919 | −43.166 |
| 350 | 33.567 | 251 710 | 246.801 | 1.718 | 282.475 | 242.129 | −36.136 |
| 400 | 34.260 | 256.239 | 247.703 | 3.414 | 282.114 | 236.389 | −30.869 |
| 450 | 34.812 | 260.307 | 248.881 | 5.142 | 281.743 | 230.696 | −26.778 |
| 500 | 35.253 | 263.999 | 250.211 | 6.894 | 281.362 | 225.044 | −23.510 |
| 600 | 35 897 | 270.487 | 253.065 | 10.453 | 280.568 | 213.854 | −18.618 |
| 700 | 36.334 | 276.055 | 255.961 | 14.066 | 279.733 | 202.801 | −15.133 |
| 800 | 36.645 | 280.928 | 258.783 | 17.716 | 278.857 | 191.870 | −12.528 |
| 900 | 36.875 | 285.258 | 261.489 | 21.393 | 277.940 | 181.051 | −10.508 |
| 1000 | 37.053 | 289.153 | 264.064 | 25.089 | 276.979 | 170.337 | −8.897 |
| 1100 | 37.195 | 292 692 | 266.508 | 28.802 | 275.969 | 159.721 | −7.585 |
| 1200 | 37.313 | 295.933 | 268.827 | 32.527 | 274.903 | 149.200 | −6.495 |
| 1300 | 37.416 | 298.924 | 271.029 | 36.264 | 273.774 | 138 770 | −5.576 |
| 1400 | 37.511 | 301.700 | 273.121 | 40.010 | 272.575 | 128.430 | −4.792 |
| 1500 | 37.605 | 304.291 | 275.114 | 43.766 | 271.300 | 118.177 | −4.115 |
| 1600 | 37.707 | 306.722 | 277.014 | 47.532 | 269 944 | 108.013 | −3.526 |
| 1700 | 37.825 | 309.011 | 278.830 | 51.308 | 268.503 | 97.936 | −3.009 |
| 1800 | 37.967 | 311.177 | 280.567 | 55.097 | 266.971 | 87.946 | −2.552 |
| 1900 | 38.144 | 313.234 | 282.233 | 58.903 | 265.346 | 78.044 | −2.146 |
| 2000 | 38.363 | 315.196 | 283.832 | 62.728 | 263.624 | 68.231 | −1.782 |
| 2100 | 38 634 | 317.074 | 285.371 | 66.577 | 261.803 | 58.505 | −1.455 |
| 2200 | 38 965 | 318.879 | 286.853 | 70 457 | 259.882 | 48.869 | −1.160 |
| 2300 | 39.362 | 320.619 | 288.284 | 74.372 | 257.859 | 39.323 | −0.893 |
| 2400 | 39.830 | 322.304 | 289.666 | 78.331 | 255.733 | 29 866 | −0.650 |
| 2500 | 40.373 | 323.941 | 291.005 | 82.341 | 253.502 | 20.501 | −0.428 |
| 2600 | 40.993 | 325.536 | 292.302 | 86.408 | 251.153 | 11.226 | −0.226 |
| 2700 | 41.688 | 327.096 | 293.562 | 90.542 | 248.656 | 2.045 | −0.040 |
| 2800 | 42.457 | 328 626 | 294.787 | 94.749 | 245.958 | −7.040 | 0.131 |
| 2900 | 43.296 | 330.130 | 295.980 | 99.036 | 207.102 | −15.974 | 0.288 |
| 3000 | 44.198 | 331 613 | 297.143 | 103.410 | 205.820 | −23.645 | 0.412 |
| 3100 | 45 157 | 333.078 | 298.279 | 107.877 | 204 644 | −31.274 | 0.527 |
| 3200 | 46.163 | 334.527 | 299.389 | 112.443 | 203.581 | −38.867 | 0.634 |
| 3300 | 47.206 | 335.964 | 300.476 | 117.111 | 202.636 | −46.428 | 0.735 |
| 3400 | 48.277 | 337.389 | 301.540 | 121.885 | 201.812 | −53.963 | 0.829 |
| 3500 | 49.363 | 338.804 | 302.585 | 126.767 | 201.112 | −61.475 | 0.917 |
| 3600 | 50.453 | 340.210 | 303.610 | 131.758 | 200.538 | −68.969 | 1.001 |
| 3700 | 51.537 | 341.607 | 304.618 | 136.857 | 200.090 | −76.449 | 1.079 |
| 3800 | 52.603 | 342.995 | 305.610 | 142.064 | 199.766 | −83.919 | 1.154 |
| 3900 | 53.640 | 344.375 | 306.586 | 147.377 | 199.565 | −91.381 | 1.224 |
| 4000 | 54.640 | 345 746 | 307.548 | 152.791 | 199.482 | −98.840 | 1.291 |
| 4100 | 55.593 | 347.107 | 308.497 | 158.303 | 199.515 | −106.298 | 1.354 |
| 4200 | 56.491 | 348.458 | 309.432 | 163.908 | 199.656 | −113.759 | 1.415 |
| 4300 | 57.330 | 349.797 | 310.355 | 169.599 | 199.902 | −121.224 | 1.473 |
| 4400 | 58.102 | 351.124 | 311.267 | 175.372 | 200.244 | −128.695 | 1.528 |
| 4500 | 58.805 | 352.438 | 312.167 | 181.218 | 200.676 | −136.176 | 1.581 |
| 4600 | 59.436 | 353.737 | 313.057 | 187.130 | 201.190 | −143.667 | 1.631 |
| 4700 | 59.992 | 355.021 | 313.936 | 193 102 | 201.780 | −151.170 | 1.680 |
| 4800 | 60.474 | 356.290 | 314.805 | 199.126 | 202.436 | −158.687 | 1.727 |
| 4900 | 60.882 | 357.541 | 315.664 | 205.195 | 203.151 | −166.217 | 1.772 |
| 5000 | 61.217 | 358.774 | 316.514 | 211.300 | −387.467 | −168.032 | 1.755 |
| 5100 | 61.481 | 359.989 | 317.355 | 217.436 | −388.335 | −163.635 | 1.676 |
| 5200 | 61.677 | 361.185 | 318.186 | 223.594 | −389.314 | −159.219 | 1.599 |
| 5300 | 61.808 | 362.361 | 319.009 | 229.769 | −390.406 | −154.784 | 1.525 |
| 5400 | 61.879 | 363.517 | 319.822 | 235.954 | −391.619 | −150.327 | 1.454 |
| 5500 | 61.892 | 364.653 | 320.627 | 242.143 | −392.955 | −145.847 | 1.385 |
| 5600 | 61.853 | 365 768 | 321.423 | 248.330 | −394.419 | −141.341 | 1.318 |
| 5700 | 61 765 | 366.862 | 322.211 | 254.512 | −396.011 | −136.808 | 1.254 |
| 5800 | 61.632 | 367 935 | 322.990 | 260.682 | −397.735 | −132.246 | 1.191 |
| 5900 | 61.459 | 368 987 | 323.761 | 266.837 | −399.591 | −127.653 | 1.130 |
| 6000 | 61 251 | 370.019 | 324.523 | 272.973 | −401.584 | −123.028 | 1.071 |

PREVIOUS December 1978 (1 atm)    CURRENT· December 1978 (1 bar)

**Molybdenum Fluoride (MoF)** $F_1Mo_1(g)$

# Fluoroimidogen (NF) IDEAL GAS $M_r = 33.005103$ Fluoroimidogen (NF) $F_1N_1(g)$

$S°(298.15\text{ K}) = 215.276\text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0\text{ K}) = 248.953 \pm 33\text{ kJ·mol}^{-1}$
$\Delta_f H°(298.15\text{ K}) = 248.948 \pm 33\text{ kJ·mol}^{-1}$

| Electronic Level and Quantum Weight | | |
|---|---|---|
| State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
| [$^3\Sigma$] | 0 | 3 |

$\omega_e = 1115\text{ cm}^{-1}$ $\omega_e x_e = [12.175]\text{ cm}^{-1}$ $\sigma = 1$
$B_e = [.923]\text{ cm}^{-1}$ $\alpha_e = [.0120]\text{ cm}^{-1}$ $r_e = [1.51\text{ Å}]$

## Enthalpy of Formation

The enthalpy of formation is obtained by taking an average of two estimates of the dissociation energy of NF. The first estimate of 3.15 eV (72.4 kcal·mol$^{-1}$) was obtained from Price *et al.*[1] The second estimate of 70.4 kcal·mol$^{-1}$ is obtained by taking one half the dissociation energy of $NF_2(g)$ calculated from JANAF values. The $\Delta_f H°(298.15\text{ K})$ for NF(g) was then calculated with auxiliary JANAF data from a dissociation energy of 71.4 kcal·mol$^{-1}$.

## Heat Capacity and Entropy

The $\omega_e$ value was obtained from infrared studies of Milligan and Jacox.[2] The $r_e$ value was estimated from Guggenheimer's[3] relation for single bonded molecules. The anharmonicity constant $x_e$ is estimated by assuming the separation of the vibrational levels to be a linear function of the vibrational quantum number. The $\alpha_e$ value is then calculated using the Morse potential function; $B_e$ is determined from the bond length. The ground state configuration is assumed to be the same as that in NBr.

## References

[1] W. C. Price, T. R. Passmore and D. M. Roessler, Disc. Faraday Soc. 35, 201 11 (1963).
[2] D. E. Milligan and M. E. Jacox, J. Chem. Phys. 40, 2461 (1964).
[3] K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −8.745 | 248.953 | 248.953 | INFINITE |
| 100 | 29.108 | 183.197 | 241.576 | −5.838 | 248.953 | 247.142 | −129.094 |
| 200 | 29.318 | 203.404 | 218.012 | −2.922 | 248.949 | 245.332 | −64.074 |
| 250 | 29.745 | 209.987 | 215.772 | −1.446 | 248.946 | 244.429 | −51.071 |
| 298.15 | 30.345 | 215.276 | 215.276 | 0. | 248.948 | 243.558 | −42.670 |
| 300 | 30.370 | 215.464 | 215.276 | 0 056 | 248.948 | 243.525 | −42.401 |
| 350 | 31.089 | 220.199 | 215.649 | 1.592 | 248.962 | 242.620 | −36.209 |
| 400 | 31.813 | 224.397 | 216.485 | 3.165 | 248.989 | 241.713 | −31.564 |
| 450 | 32.492 | 228.184 | 217.578 | 4.773 | 249.030 | 240.801 | −27.951 |
| 500 | 33.106 | 231.640 | 218.814 | 6.413 | 249.084 | 239.884 | −25.060 |
| 600 | 34.122 | 237.770 | 221.475 | 9.777 | 249.220 | 238.031 | −20.722 |
| 700 | 34.893 | 243.090 | 224.191 | 13.229 | 249.375 | 236.154 | −17.622 |
| 800 | 35.480 | 247.790 | 226.853 | 16.749 | 249.536 | 234.255 | −15.295 |
| 900 | 35.933 | 251.996 | 229.417 | 20.321 | 249.692 | 232.335 | −13.484 |
| 1000 | 36.291 | 255.801 | 231.868 | 23.933 | 249.839 | 230.399 | −12.035 |
| 1100 | 36.578 | 259.274 | 234.204 | 27.577 | 249.974 | 228.448 | −10.848 |
| 1200 | 36.815 | 262.467 | 236.428 | 31.247 | 250.097 | 226.486 | −9.859 |
| 1300 | 37.013 | 265.422 | 238.546 | 34.938 | 250.207 | 224.513 | −9.021 |
| 1400 | 37.182 | 268.171 | 240.565 | 38.648 | 250.305 | 222.533 | −8.303 |
| 1500 | 37.329 | 270.742 | 242.492 | 42.374 | 250.391 | 220.546 | −7.680 |
| 1600 | 37.459 | 273.155 | 244.334 | 46.114 | 250.467 | 218.554 | −7.135 |
| 1700 | 37.575 | 275.430 | 246.097 | 49.865 | 250.533 | 216.558 | −6.654 |
| 1800 | 37.679 | 277.580 | 247.787 | 53.628 | 250.591 | 214.558 | −6.226 |
| 1900 | 37.775 | 279.620 | 249.409 | 57.401 | 250.643 | 212.554 | −5.844 |
| 2000 | 37.864 | 281.560 | 250.969 | 61.183 | 250.690 | 210.548 | −5.499 |
| 2100 | 37.947 | 283.409 | 252.470 | 64.974 | 250.735 | 208.540 | −5.187 |
| 2200 | 38.024 | 285 177 | 253.916 | 68.772 | 250.779 | 206.530 | −4.904 |
| 2300 | 38.098 | 286.868 | 255.313 | 72.578 | 250.824 | 204.517 | −4.645 |
| 2400 | 38.168 | 288.491 | 256.662 | 76.392 | 250.873 | 202.503 | −4.407 |
| 2500 | 38.235 | 290.051 | 257.966 | 80.212 | 250.928 | 200.487 | −4.189 |
| 2600 | 38.299 | 291.552 | 259.229 | 84.039 | 250.990 | 198.468 | −3.987 |
| 2700 | 38.362 | 292.998 | 260.453 | 87.872 | 251.062 | 196.446 | −3.800 |
| 2800 | 38.422 | 294.395 | 261.641 | 91.711 | 251.146 | 194.422 | −3.627 |
| 2900 | 38.481 | 295.744 | 262.793 | 95.556 | 251.242 | 192.394 | −3.465 |
| 3000 | 38.538 | 297.049 | 263.914 | 99.407 | 251.352 | 190.363 | −3.315 |
| 3100 | 38.594 | 298.314 | 265.003 | 103.264 | 251.479 | 188.328 | −3.173 |
| 3200 | 38.649 | 299.540 | 266.063 | 107.126 | 251.622 | 186.289 | −3.041 |
| 3300 | 38.704 | 300.730 | 267.096 | 110.993 | 251.782 | 184.245 | −2.916 |
| 3400 | 38.757 | 301.886 | 268.102 | 114.867 | 251.961 | 182.196 | −2.799 |
| 3500 | 38.809 | 303.011 | 269.084 | 118.745 | 252.158 | 180.141 | −2.688 |
| 3600 | 38.861 | 304.105 | 270.041 | 122.628 | 252.375 | 178.080 | −2.584 |
| 3700 | 38.912 | 305.170 | 270.976 | 126.517 | 252.611 | 176.013 | −2.485 |
| 3800 | 38.962 | 306.209 | 271.890 | 130.411 | 252.868 | 173.940 | −2.391 |
| 3900 | 39.013 | 307.221 | 272.783 | 134.309 | 253.144 | 171.859 | −2.302 |
| 4000 | 39.062 | 308.210 | 273.656 | 138.213 | 253.440 | 169.771 | −2.217 |
| 4100 | 39.111 | 309.175 | 274.511 | 142.122 | 253.756 | 167.676 | −2.136 |
| 4200 | 39.160 | 310.118 | 275.347 | 146.035 | 254.092 | 165.572 | −2.059 |
| 4300 | 39.209 | 311.040 | 276.167 | 149.954 | 254.447 | 163.460 | −1.986 |
| 4400 | 39.257 | 311.942 | 276.970 | 153.877 | 254.822 | 161.340 | −1.915 |
| 4500 | 39.305 | 312.825 | 277.757 | 157.805 | 255.216 | 159.211 | −1.848 |
| 4600 | 39.352 | 313.689 | 278.528 | 161.738 | 255.628 | 157.073 | −1.784 |
| 4700 | 39.400 | 314.536 | 279.286 | 165.676 | 256.059 | 154.926 | −1.722 |
| 4800 | 39.447 | 315.366 | 280.029 | 169.618 | 256.508 | 152.770 | −1.662 |
| 4900 | 39.494 | 316.180 | 280.758 | 173.565 | 256.975 | 150.604 | −1.605 |
| 5000 | 39.541 | 316.978 | 281.475 | 177.517 | 257.459 | 148.428 | −1.551 |
| 5100 | 39.588 | 317.761 | 282.178 | 181.473 | 257.960 | 146.242 | −1.498 |
| 5200 | 39.634 | 318.531 | 282.870 | 185.434 | 258.477 | 144.047 | −1.447 |
| 5300 | 39.680 | 319.286 | 283.550 | 189.400 | 259.010 | 141.841 | −1.398 |
| 5400 | 39.727 | 320.028 | 284.219 | 193.370 | 259.560 | 139.625 | −1.351 |
| 5500 | 39.773 | 320.758 | 284.877 | 197.345 | 260.124 | 137.399 | −1.305 |
| 5600 | 39.819 | 321.475 | 285.524 | 201.325 | 260.704 | 135.162 | −1.261 |
| 5700 | 39.865 | 322.180 | 286.161 | 205.309 | 261.298 | 132.915 | −1.218 |
| 5800 | 39.911 | 322.873 | 286.788 | 209.298 | 261.905 | 130.658 | −1.177 |
| 5900 | 39.956 | 323.556 | 287.405 | 213.291 | 262.527 | 128.390 | −1.137 |
| 6000 | 40.002 | 324.228 | 288.013 | 217.289 | 263.161 | 126.111 | −1.098 |

PREVIOUS June 1965 (1 atm) CURRENT: June 1965 (1 bar)

## Nitrosyl Fluoride (ONF) IDEAL GAS $M_r = 49.004503$

$S°(298.15\text{ K}) = 248.082\text{ J K}^{-1}\cdot\text{mol}^{-1}$

$\Delta_f H°(0\text{ K}) = -63.300 \pm 1.7\text{ kJ}\cdot\text{mol}^{-1}$
$\Delta_f H°(298.15\text{ K}) = -65\,689 \pm 1.7\text{ kJ}\cdot\text{mol}^{-1}$

| Vibrational Levels and Degeneracies $\nu$, cm$^{-1}$ |
|---|
| 1844.03(1) |
| 521 |
| 765.85(1) |

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: $C_s$
Bond Distances: N–O = 1.13 Å; N–F = 1.52 Å
Bond Angle: O–N–F = 110.2°
Product of the Moments of Inertia: $I_A I_B I_C = 49.6113 \times 10^{-117}\text{ g}^3\cdot\text{cm}^6$

### Enthalpy of Formation

For the reaction $2NO(g) + F_2(g) \rightarrow 2ONF(g)$, Johnston and Bertin[1] report $\Delta_r H°(298\ 15\text{ K}) = 74\ 8 \pm 0.8\text{ kcal}\cdot\text{mol}^{-1}$, determined calorimetrically. This yields $15.7 \pm 0.4\text{ kcal}\cdot\text{mol}^{-1}$ for $\Delta_f H°(298.15\text{ K})$.

### Heat Capacity and Entropy

Stephenson and Jones,[2] report the frequencies, obtained from the infrared spectrum, and moments of inertia, obtained from the microwave spectrum. The principal moments of inertia are: $I_A = 0.8778 \times 10^{-39}$, $I_B = 7.0919 \times 10^{-39}$, and $I_C = 7.9697 \times 10^{-39}\text{ g}\cdot\text{cm}^2$.

### References

[1] H S. Johnston and H. J. Bertin, J. Amer. Chem. Soc. **81**, 6402 (1959).
[2] C. V. Stephenson and E. A Jones, J. Chem. Phys. **20**, 135 (1952).

## Nitrosyl Fluoride (ONF) $F_1N_1O_1(g)$

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −10 701 | −63.300 | −63.300 | INFINITE |
| 100 | 33.534 | 208.247 | 281.961 | −7.371 | −64.328 | −59.978 | 31.329 |
| 200 | 37.177 | 232.429 | 251.737 | −3.862 | −65.193 | −55.267 | 14.434 |
| 250 | 39.427 | 240.969 | 248.753 | −1.946 | −65.485 | −52 750 | 11.021 |
| 298.15 | 41.348 | 248.082 | 248.082 | 0. | −65.689 | −50.277 | 8.808 |
| 300 | 41.416 | 248.338 | 248.083 | 0.077 | −65.695 | −50.182 | 8.737 |
| 350 | 43.115 | 254.854 | 248.594 | 2.191 | −65.842 | −47.584 | 7.101 |
| 400 | 44.574 | 260.708 | 249.748 | 4.384 | −65.942 | −44.968 | 5.872 |
| 450 | 45.850 | 266.034 | 251.266 | 6.645 | −66.005 | −42.342 | 4.915 |
| 500 | 46.980 | 270.924 | 252.991 | 8.967 | −66.041 | −39.711 | 4.149 |
| 600 | 48.895 | 279.665 | 256.725 | 13.764 | −66.052 | −34.442 | 2.998 |
| 700 | 50.437 | 287.322 | 260.561 | 18.733 | −66.007 | −29.177 | 2.177 |
| 800 | 51.678 | 294.141 | 264.340 | 23.841 | −65.927 | −23.921 | 1.562 |
| 900 | 52.678 | 300.288 | 267.998 | 29.061 | −65.826 | −18.676 | 1.084 |
| 1000 | 53.486 | 305.881 | 271.511 | 34.370 | −65.712 | −13.443 | 0.702 |
| 1100 | 54.142 | 311.011 | 274.872 | 39.753 | −65.593 | −8.222 | 0.390 |
| 1200 | 54 679 | 315.746 | 278.083 | 45 195 | −65.473 | −3.012 | 0.131 |
| 1300 | 55.122 | 320.140 | 281.152 | 50.686 | −65.355 | 2.188 | −0.088 |
| 1400 | 55 491 | 324.239 | 284.085 | 56.217 | −65.243 | 7.380 | −0.275 |
| 1500 | 55 799 | 328.079 | 286.891 | 61.782 | −65.138 | 12.563 | −0.437 |
| 1600 | 56.060 | 331.688 | 289.579 | 67.375 | −65.042 | 17.740 | −0.579 |
| 1700 | 56.282 | 335.094 | 292.157 | 72.992 | −64.956 | 22.911 | −0.704 |
| 1800 | 56.472 | 338.316 | 294.633 | 78.630 | −64.880 | 28.078 | −0.815 |
| 1900 | 56.636 | 341.374 | 297.013 | 84.286 | −64.815 | 33.240 | −0.914 |
| 2000 | 56.778 | 344.283 | 299.304 | 89 957 | −64.760 | 38.400 | −1.003 |
| 2100 | 56.902 | 347.056 | 301.513 | 95.641 | −64.715 | 43.556 | −1.083 |
| 2200 | 57.011 | 349.706 | 303.644 | 101.337 | −64.678 | 48.712 | −1.157 |
| 2300 | 57.107 | 352.242 | 305.702 | 107.043 | −64.648 | 53.865 | −1.223 |
| 2400 | 57.192 | 354 674 | 307.692 | 112.758 | −64.624 | 59 017 | −1.284 |
| 2500 | 57.267 | 357.011 | 309.618 | 118 481 | −64.604 | 64.168 | −1.341 |
| 2600 | 57.335 | 359.258 | 311.485 | 124.211 | −64.586 | 69.319 | −1.393 |
| 2700 | 57.395 | 361.423 | 313.294 | 129.947 | −64.569 | 74.469 | −1.441 |
| 2800 | 57.450 | 363.511 | 315.051 | 135.690 | −64.552 | 79.618 | −1.485 |
| 2900 | 57.499 | 365.528 | 316.757 | 141.437 | −64.532 | 84.766 | −1.527 |
| 3000 | 57.544 | 367.478 | 318 415 | 147.189 | −64.509 | 89.914 | −1.566 |
| 3100 | 57.584 | 369.366 | 320.029 | 152.946 | −64.481 | 95.061 | −1.602 |
| 3200 | 57.621 | 371.195 | 321.599 | 158.706 | −64.447 | 100.207 | −1.636 |
| 3300 | 57.655 | 372.968 | 323.129 | 164.470 | −64.406 | 105.352 | −1.668 |
| 3400 | 57.686 | 374.690 | 324.620 | 170.237 | −64.357 | 110.496 | −1.698 |
| 3500 | 57 714 | 376.363 | 326.075 | 176.007 | −64.299 | 115 637 | −1.726 |
| 3600 | 57.740 | 377.989 | 327.494 | 181.780 | −64.233 | 120.778 | −1.752 |
| 3700 | 57.764 | 379.571 | 328.881 | 187.555 | −64.157 | 125.915 | −1 778 |
| 3800 | 57.786 | 381.112 | 330.235 | 193.332 | −64.071 | 131.052 | −1.801 |
| 3900 | 57.807 | 382.613 | 331.559 | 199.112 | −63 975 | 136.186 | −1.824 |
| 4000 | 57.826 | 384.077 | 332.854 | 204.894 | −63.869 | 141.316 | −1.845 |
| 4100 | 57.844 | 385.505 | 334.120 | 210 677 | −63.752 | 146.444 | −1.866 |
| 4200 | 57.860 | 386.899 | 335.360 | 216.462 | −63.625 | 151.570 | −1.885 |
| 4300 | 57 876 | 388.261 | 336.575 | 222.249 | −63.489 | 156.692 | −1.903 |
| 4400 | 57.890 | 389.591 | 337.765 | 228.037 | −63.342 | 161 811 | −1.921 |
| 4500 | 57.904 | 390.893 | 338.931 | 233.827 | −63.185 | 166.926 | −1.938 |
| 4600 | 57.916 | 392.165 | 340 074 | 239.618 | −63.020 | 172.037 | −1.954 |
| 4700 | 57.928 | 393.411 | 341.196 | 245.410 | −62.846 | 177.146 | −1.969 |
| 4800 | 57.939 | 394.631 | 342.297 | 251.204 | −62.663 | 182.250 | −1.983 |
| 4900 | 57.950 | 395.826 | 343.377 | 256.998 | −62.473 | 187.351 | −1.997 |
| 5000 | 57 959 | 396.996 | 344.438 | 262.794 | −62.276 | 192.447 | −2.010 |
| 5100 | 57 969 | 398.144 | 345.480 | 268.590 | −62.072 | 197.540 | −2.023 |
| 5200 | 57.977 | 399.270 | 346.503 | 274.387 | −61.863 | 202.628 | −2.035 |
| 5300 | 57.986 | 400.374 | 347.509 | 280.185 | −61.648 | 207.712 | −2.047 |
| 5400 | 57.993 | 401.458 | 348.498 | 285.984 | −61.430 | 212.792 | −2.058 |
| 5500 | 58.001 | 402.523 | 349 471 | 291.784 | −61.207 | 217.868 | −2.069 |
| 5600 | 58.008 | 403.568 | 350.428 | 297.585 | −60.983 | 222.941 | −2.080 |
| 5700 | 58.015 | 404.594 | 351.369 | 303.386 | −60.756 | 228.008 | −2.089 |
| 5800 | 58.021 | 405.603 | 352.295 | 309.187 | −60.529 | 233.073 | −2.099 |
| 5900 | 58.027 | 406.595 | 353.207 | 314.990 | −60.303 | 238.132 | −2.108 |
| 6000 | 58.033 | 407.571 | 354.105 | 320.793 | −60.077 | 243.189 | −2.117 |

PREVIOUS. June 1961 (1 atm) CURRENT June 1961 (1 bar)

Nitrosyl Fluoride (ONF) $F_1N_1O_1(g)$

## Nitryl Fluoride ($NO_2F$) IDEAL GAS $M_r$ = 65.003903 Nitryl Fluoride ($NO_2F$) $F_1N_1O_2(g)$

$S°(298.15\ K) = 260.250\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 102.881 \pm 20.9\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -108.784 \pm 20.9\ kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|
| 1312(1) | 1793(1) |
| 822(1) | 570(1) |
| 460(1) | 742(1) |

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group. $C_{2v}$
Bond Distances N–F = 1.40 Å; N–O = 1.21 Å
Bond Angles: O–N–O = 129.5°; F–N–O = 115.25°
Product of the Moments of Inertia: $I_A I_B I_C = 6.400639 \times 10^{-115}\ g^3 \cdot cm^6$

### Enthalpy of Formation

The enthalpy of reaction at 25°C for direct synthesis of nitryl fluoride from nitrogen dioxide with fluorine ($NO_2(g) + 1/2\ F_2(g) = NO_2F(g)$) has been measured calorimetrically as −33.9 kcal·mol$^{-1}$ by Breazeale and MacLaren.[1] The enthalpy of formation, $\Delta_f H°(298.15\ K) = -26.0$ kcal mol$^{-1}$, for $NO_2F(g)$ was then drived. The values of $\Delta_f H°(298.15\ K) = -20 \pm 5$ and $-19 \pm 2$ kcal·mol$^{-1}$ were issued in their second and third quarterly technical reports and have been quoted in the literature by Tschuikow–Roux.[2]

Hetherington and Robinson[3] quoted $\Delta_f H° = 26$ kcal·mol$^{-1}$ (presumably it has a minus sign) for $NO_2F(g)$ which was derived from the heat of solution measured by Nichols and Robinson.[4]

### Heat Capacity and Entropy

Smith and Magnuson[5] have measured the moments of inertia from microwave spectrum of $NO_2F(g)$. In order to calculate the bond distances, given as N–F = 1.35 Å and N–O = 1.23 Å, the bond angle O–N–O was assumed to be 125°. The selected bond distances and angle were obtained from Clayton *et al.*[6] Clayton *et al.* assumed the bond angle O–N–O in $NO_2F(g)$ should be the same as that in $NO_2Cl(g)$ and then calculated the bond distances N–F and N–O from Smith and Magnuson[5] data of the moments of inertia.

The selected vibrational frequencies were obtained from the infrared and Raman spectra measurements by Dodd *et al.*[7]

The three principal moments of inertia are: $I_A = 6.3641 \times 10^{-39}$, $I_B = 7.3394 \times 10^{-39}$, and $I_C = 13.7034 \times 10^{-39}\ g \cdot cm^2$.

### References

[1] J. D. Breazeale and R. O. MacLaren, "Thermochemistry of Oxygen Fluorine Bonding", Final Tech. Summary Report, Contract No. Nonr 3433(00), ARPA Order No. 184–62, United Technology Corporation, Sunnyvale, Calif., (March 1963).
[2] E. Tschuikow Roux, J. Phys. Chem. 66, 1636 (1962).
[3] G. Hetherington and P. L. Robinson, Special Publication No. 10, The Chem. Soc., London, (1957).
[4] Nichols and Robinson, personal communication to Hetherington and Robinson.
[5] D. F. Smith and D. W. Magnuson, Phys. Rev. 87, 226 (1952).
[6] L. Clayton, Q. Williams, and T. Weatherly, J. Chem. Phys. 30, 1328 (1959).
[7] R. Dodd, J. Rolfe and L. Woodward, Trans. Faraday Soc. 52, 145 (1956).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log K$_f$ |
| 0 | 0. | 0. | INFINITE | −11.528 | −102.881 | −102.881 | INFINITE |
| 100 | 33.929 | 216.706 | 298.630 | −8.192 | −105.355 | −93.186 | 48.675 |
| 200 | 41.239 | 242.134 | 264.542 | −4.482 | −107.475 | −80.141 | 20.931 |
| 250 | 45.801 | 251.830 | 261.049 | −2.305 | −108.235 | −73.215 | 15.298 |
| 298.15 | 49.865 | 260.250 | 260.250 | 0. | −108.784 | −66.418 | 11.636 |
| 300 | 50.013 | 260.559 | 260.251 | 0.092 | −108.802 | −66.155 | 11.519 |
| 350 | 53.744 | 268.555 | 260.874 | 2.688 | −109.205 | −59.013 | 8.807 |
| 400 | 57.010 | 275.950 | 262.302 | 5.459 | −109.475 | −51.823 | 6.767 |
| 450 | 59.862 | 282.833 | 264.206 | 8.382 | −109.635 | −44.606 | 5.178 |
| 500 | 62.352 | 289.272 | 266.394 | 11.439 | −109.706 | −37.376 | 3.905 |
| 600 | 66.424 | 301.017 | 271.205 | 17.887 | −109.646 | −22.912 | 1.995 |
| 700 | 69.537 | 311.500 | 276.226 | 24.692 | −109.393 | −8.474 | 0.632 |
| 800 | 71.933 | 320.949 | 281.236 | 31.771 | −109.011 | 5.918 | −0.386 |
| 900 | 73.795 | 329.534 | 286.133 | 39.061 | −108.541 | 20.256 | −1.176 |
| 1000 | 75.256 | 337.387 | 290.871 | 46.516 | −108.013 | 34.539 | −1.804 |
| 1100 | 76.417 | 344.616 | 295.433 | 54.102 | −107.445 | 48.767 | −2.316 |
| 1200 | 77.351 | 351.307 | 299.814 | 61.792 | −106.851 | 62.942 | −2.740 |
| 1300 | 78.110 | 357.529 | 304.017 | 69.567 | −106.241 | 77.067 | −3.097 |
| 1400 | 78.734 | 363.342 | 308.049 | 77.410 | −105.623 | 91.145 | −3.401 |
| 1500 | 79.252 | 368.792 | 311.919 | 85.310 | −105.004 | 105 178 | −3.663 |
| 1600 | 79.687 | 373.921 | 315.635 | 93.257 | −104.387 | 119.170 | −3.890 |
| 1700 | 80.054 | 378.763 | 319.207 | 101.245 | −103.777 | 133.123 | −4.090 |
| 1800 | 80.366 | 383.348 | 322.645 | 109.266 | −103.176 | 147.041 | −4.267 |
| 1900 | 80.635 | 387.701 | 325.955 | 117.317 | −102.586 | 160.926 | −4.424 |
| 2000 | 80.867 | 391.843 | 329.147 | 125.392 | −102.008 | 174.780 | −4.565 |
| 2100 | 81 069 | 395.793 | 332.227 | 133.489 | −101.442 | 188.605 | −4.691 |
| 2200 | 81.245 | 399.569 | 335.203 | 141.605 | −100.889 | 202.405 | −4.806 |
| 2300 | 81.400 | 403.184 | 338.081 | 149.737 | −100.348 | 216.178 | −4.910 |
| 2400 | 81.537 | 406.651 | 340.866 | 157.884 | −99.819 | 229.929 | −5.004 |
| 2500 | 81.659 | 409.982 | 343.564 | 166.044 | −99.299 | 243.658 | −5.091 |
| 2600 | 81.767 | 413.187 | 346.181 | 174.216 | −98.788 | 257.366 | −5.171 |
| 2700 | 81.865 | 416.275 | 348.720 | 182.397 | −98.285 | 271.055 | −5.244 |
| 2800 | 81.952 | 419.254 | 351.186 | 190.588 | −97.788 | 284.725 | −5.312 |
| 2900 | 82.031 | 422.131 | 353.583 | 198.788 | −97.295 | 298.377 | −5.374 |
| 3000 | 82.102 | 424.913 | 355.915 | 206.994 | −96.806 | 312.013 | −5.433 |
| 3100 | 82.167 | 427.606 | 358.184 | 215.208 | −96.318 | 325.632 | −5.487 |
| 3200 | 82.225 | 430.216 | 360.395 | 223.427 | −95.832 | 339.235 | −5.537 |
| 3300 | 82.279 | 432.747 | 362.549 | 231.653 | −95.345 | 352.823 | −5.585 |
| 3400 | 82.328 | 435.204 | 364.650 | 239.883 | −94.856 | 366.397 | −5.629 |
| 3500 | 82.374 | 437.591 | 366.700 | 248.118 | −94.366 | 379.956 | −5.671 |
| 3600 | 82.415 | 439.912 | 368.702 | 256.358 | −93.872 | 393.501 | −5.710 |
| 3700 | 82.453 | 442.171 | 370.657 | 264.601 | −93.375 | 407.032 | −5.746 |
| 3800 | 82.489 | 444.370 | 372.568 | 272.848 | −92.874 | 420.551 | −5.781 |
| 3900 | 82.521 | 446.513 | 374.437 | 281.099 | −92.368 | 434.056 | −5.814 |
| 4000 | 82.552 | 448.603 | 376.265 | 289.352 | −91.858 | 447.547 | −5.844 |
| 4100 | 82.580 | 450.642 | 378.054 | 297.609 | −91.342 | 461.026 | −5.874 |
| 4200 | 82.606 | 452.632 | 379.806 | 305.868 | −90.822 | 474.492 | −5.901 |
| 4300 | 82.631 | 454.576 | 381.522 | 314.130 | −90.297 | 487.946 | −5.927 |
| 4400 | 82.653 | 456.476 | 383.204 | 322.394 | −89.767 | 501.386 | −5.952 |
| 4500 | 82.675 | 458.334 | 384.853 | 330.661 | −89.233 | 514.816 | −5.976 |
| 4600 | 82.695 | 460.151 | 386.471 | 338.929 | −88.695 | 528.233 | −5.998 |
| 4700 | 82.713 | 461.930 | 388.057 | 347.200 | −88.154 | 541.639 | −6.020 |
| 4800 | 82.731 | 463.671 | 389.614 | 355.472 | −87.610 | 555.033 | −6.040 |
| 4900 | 82.748 | 465.377 | 391.143 | 363.746 | −87.064 | 568.416 | −6.059 |
| 5000 | 82.763 | 467.049 | 392.645 | 372.021 | −86.517 | 581.788 | −6.078 |
| 5100 | 82.778 | 468.688 | 394.120 | 380.298 | −85.970 | 595.149 | −6.096 |
| 5200 | 82.792 | 470.296 | 395.569 | 388.577 | −85.424 | 608.498 | −6.112 |
| 5300 | 82.805 | 471.873 | 396.994 | 396.857 | −84.879 | 621.838 | −6.129 |
| 5400 | 82.817 | 473.421 | 398.395 | 405.138 | −84.338 | 635.167 | −6.144 |
| 5500 | 82.829 | 474.940 | 399.773 | 413.420 | −83.800 | 648.485 | −6.159 |
| 5600 | 82.840 | 476.433 | 401.129 | 421.704 | −83.268 | 661.796 | −6.173 |
| 5700 | 82 850 | 477.899 | 402.463 | 429.988 | −82.743 | 675.095 | −6.187 |
| 5800 | 82.860 | 479.340 | 403.776 | 438.274 | −82.226 | 688.387 | −6.200 |
| 5900 | 82.870 | 480 757 | 405.069 | 446.560 | −81.719 | 701.667 | −6.212 |
| 6000 | 82.879 | 482 150 | 406.342 | 454.848 | −81.223 | 714.942 | −6.224 |

PREVIOUS. December 1965 (1 atm) CURRENT: December 1965 (1 bar)

## Fluorine Nitrate (FNO$_3$) IDEAL GAS $M_r = 81.003303$ Fluorine Nitrate (FONO$_2$) $F_1N_1O_3(g)$

$S°(298.15\ K) = [292.933]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = [18.049 \pm 2.1]\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [10.460 \pm 2.1]\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|
| [1300](1) | [760](1) |
| [800](1) | [980](1) |
| [680](1) | [370](1) |
| [1700](1) | [130](1) |
| [450](1) | |

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: $C_s$
Bond Distances. O–N = 1.29 ± 0.05 Å; N–O' = 1.39 ± 0.05 Å; O'–F = 1.42 ± 0.05 Å
Bond Angles: O–N–O = 125° ± 5°; F–O'–N = 105° ± 5°
Angle between NO'F plane and $O_2NO'$ plane = 90°
Product of the Moments of Inertia: $I_A I_B I_C = 3.88611 \times 10^{-114}\ g^3{\cdot}cm^6$

### Enthalpy of Formation

The value, 2.5 ± 0.5 kcal·mol$^{-1}$, for the enthalpy of formation of $FNO_3(g)$ was obtained from Anderson, *et al.*[1] The value of $\Delta_f H°$ reported by Talakin, *et al.*[2] was 4.2 ± 0.9 kcal·mol$^{-1}$ at 294 K.

### Heat Capacity and Entropy

Vibrational frequencies were estimated by comparison with those of $HNO_3(g)$ reported by Palm and Kilpatrick.[3] Bond distances and angles were taken from Pauling and Brockway.[4] The three principal moments of inertia are: $I_A = 8.8638 \times 10^{-39}$, $I_B = 18.5651 \times 10^{-39}$, and $I_C = 23.6154 \times 10^{-39}\ g{\cdot}cm^2$. The possible existence of restricted internal rotation in the molecule was not considered Thus the calculated values of $C_p°$ and $S°$ may be low.

### References

[1] R. Anderson, *et al.*, "Thermochemistry of Oxygen Fluorine Bonding," UTC 2002 QT4, United Technology Corporation, Sunnyvale, California, (March 1, 1961 through February 28, 1962).
[2] O. G. Talakin, *et al.*, Russ. J. Phys. Chem., 36, 561 (1962).
[3] A. Palm and M. Kilpatrick, J. Chem. Phys. 23, 1562 (1955).
[4] L. Pauling and L. O. Brockway, J. Amer. Chem. Soc. 59, 13 (1937).

Enthalpy Reference Temperature = $T_r$ = 298.15 K  Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log K$_f$ |
| 0 | 0. | 0. | INFINITE | −14.184 | 18.049 | 18.049 | INFINITE |
| 100 | 41.294 | 237.188 | 342.626 | −10.544 | 14.427 | 33.213 | −17.349 |
| 200 | 53.333 | 269.363 | 298.527 | −5.833 | 11.852 | 53.088 | −13.865 |
| 250 | 59.618 | 281.944 | 293.975 | −3.008 | 11.011 | 63.501 | −13.268 |
| 298.15 | 65.223 | 292.933 | 292.933 | 0. | 10.460 | 73.664 | −12.906 |
| 300 | 65.427 | 293.337 | 292.934 | 0.121 | 10.443 | 74.056 | −12.894 |
| 350 | 70.594 | 303.819 | 293.750 | 3.524 | 10.109 | 84.688 | −12.639 |
| 400 | 75.105 | 313.547 | 295.624 | 7.169 | 9.967 | 95.354 | −12.452 |
| 450 | 79.008 | 322.624 | 298.125 | 11.025 | 9.980 | 106.028 | −12.307 |
| 500 | 82.371 | 331.127 | 301.005 | 15.061 | 10.118 | 116.693 | −12.191 |
| 600 | 87.757 | 346.645 | 307.344 | 23.581 | 10.670 | 137.962 | −12.011 |
| 700 | 91.766 | 360.489 | 313.965 | 32.567 | 11.477 | 159.116 | −11.873 |
| 800 | 94.781 | 372.949 | 320.573 | 41.901 | 12.446 | 180.143 | −11.762 |
| 900 | 97.080 | 384.251 | 327.030 | 51.499 | 13.521 | 201.041 | −11.668 |
| 1000 | 98.860 | 394.575 | 333.276 | 61.300 | 14.663 | 221.816 | −11.586 |
| 1100 | 100.258 | 404.066 | 339.286 | 71.258 | 15.850 | 242.475 | −11.514 |
| 1200 | 101.372 | 412.839 | 345.054 | 81.342 | 17.063 | 263.023 | −11.449 |
| 1300 | 102.271 | 420.990 | 350.586 | 91.526 | 18.290 | 283.470 | −11.390 |
| 1400 | 103.006 | 428.597 | 355.889 | 101.791 | 19.523 | 303.823 | −11.336 |
| 1500 | 103.613 | 435.725 | 360.976 | 112.123 | 20.753 | 324.086 | −11.286 |
| 1600 | 104.120 | 442.429 | 365.860 | 122.510 | 21.976 | 344.269 | −11.239 |
| 1700 | 104.546 | 448.754 | 370.552 | 132.944 | 23.187 | 364.375 | −11.196 |
| 1800 | 104.909 | 454.740 | 375.064 | 143.417 | 24.382 | 384.410 | −11.155 |
| 1900 | 105.219 | 460.421 | 379.408 | 153.924 | 25.559 | 404.379 | −11.117 |
| 2000 | 105.487 | 465.825 | 383.595 | 164.460 | 26.716 | 424.287 | −11.081 |
| 2100 | 105.719 | 470.977 | 387.634 | 175.020 | 27.852 | 444.138 | −11.047 |
| 2200 | 105.922 | 475.900 | 391.535 | 185.602 | 28.968 | 463.936 | −11.015 |
| 2300 | 106.100 | 480.613 | 395.307 | 196.204 | 30.062 | 483.682 | −10.985 |
| 2400 | 106.258 | 485.132 | 398.956 | 206.822 | 31.136 | 503.381 | −10.956 |
| 2500 | 106.397 | 489.472 | 402.490 | 217.455 | 32.191 | 523.036 | −10.928 |
| 2600 | 106.521 | 493.648 | 405.917 | 228.101 | 33.229 | 542.649 | −10.902 |
| 2700 | 106.632 | 497.670 | 409.241 | 238.758 | 34.250 | 562.223 | −10.877 |
| 2800 | 106.732 | 501.550 | 412.469 | 249.427 | 35.255 | 581.760 | −10.853 |
| 2900 | 106.822 | 505.297 | 415.605 | 260.105 | 36.248 | 601.259 | −10.830 |
| 3000 | 106.903 | 508.919 | 418.656 | 270.791 | 37.228 | 620.726 | −10.808 |
| 3100 | 106.977 | 512.426 | 421.624 | 281.485 | 38.198 | 640.161 | −10.787 |
| 3200 | 107.044 | 515.824 | 424.515 | 292.186 | 39.159 | 659.563 | −10.766 |
| 3300 | 107.106 | 519.118 | 427.332 | 302.894 | 40.113 | 678.935 | −10.747 |
| 3400 | 107.162 | 522.317 | 430.079 | 313.607 | 41.061 | 698.280 | −10.728 |
| 3500 | 107.213 | 525.424 | 432.759 | 324.326 | 42.003 | 717.595 | −10.710 |
| 3600 | 107.260 | 528.445 | 435.375 | 335.050 | 42.941 | 736.885 | −10.692 |
| 3700 | 107.304 | 531.384 | 437.931 | 345.778 | 43.876 | 756.148 | −10.675 |
| 3800 | 107.344 | 534.246 | 440.428 | 356.510 | 44.808 | 775.387 | −10.658 |
| 3900 | 107.381 | 537.035 | 442.869 | 367.247 | 45.739 | 794.601 | −10.642 |
| 4000 | 107.416 | 539.754 | 445.258 | 377.986 | 46.668 | 813.790 | −10.627 |
| 4100 | 107.448 | 542.407 | 447.595 | 388.730 | 47.595 | 832.957 | −10.612 |
| 4200 | 107.477 | 544.997 | 449.883 | 399.476 | 48.522 | 852.101 | −10.597 |
| 4300 | 107.505 | 547.526 | 452.125 | 410.225 | 49.448 | 871.223 | −10.583 |
| 4400 | 107.531 | 549.998 | 454.321 | 420.977 | 50.372 | 890.323 | −10.569 |
| 4500 | 107.555 | 552.414 | 456.474 | 431.731 | 51.295 | 909.402 | −10.556 |
| 4600 | 107.578 | 554.779 | 458.586 | 442.488 | 52.216 | 928.460 | −10.543 |
| 4700 | 107.599 | 557.092 | 460.657 | 453.247 | 53.134 | 947.500 | −10.530 |
| 4800 | 107.619 | 559.358 | 462.690 | 464.008 | 54.050 | 966.519 | −10.518 |
| 4900 | 107.638 | 561.577 | 464.685 | 474.771 | 54.960 | 985.520 | −10.506 |
| 5000 | 107.656 | 563.752 | 466.645 | 485.535 | 55.866 | 1004.502 | −10.494 |
| 5100 | 107.672 | 565.884 | 468.570 | 496.302 | 56.765 | 1023.466 | −10.482 |
| 5200 | 107.688 | 567.975 | 470.462 | 507.070 | 57.657 | 1042.411 | −10.471 |
| 5300 | 107.703 | 570.026 | 472.321 | 517.839 | 58.540 | 1061.342 | −10.460 |
| 5400 | 107.717 | 572.040 | 474.149 | 528.610 | 59.412 | 1080.253 | −10.449 |
| 5500 | 107.730 | 574.016 | 475.947 | 539.383 | 60.273 | 1099.149 | −10.439 |
| 5600 | 107.743 | 575.958 | 477.715 | 550.156 | 61.119 | 1118.031 | −10.429 |
| 5700 | 107.755 | 577.865 | 479.456 | 560.931 | 61.950 | 1136.896 | −10.418 |
| 5800 | 107.766 | 579.739 | 481.169 | 571.707 | 62.764 | 1155.749 | −10.409 |
| 5900 | 107.777 | 581.581 | 482.855 | 582.484 | 63.559 | 1174.585 | −10.399 |
| 6000 | 107.787 | 583.393 | 484.516 | 593.263 | 64.331 | 1193.411 | −10.390 |

PREVIOUS. March 1963 (1 atm)  CURRENT. March 1963 (1 bar)

## Sodium Fluoride (NaF) CRYSTAL $M_r$ = 41.988173 Sodium Fluoride (NaF) $F_1Na_1(cr)$

$S°(298.15\ K) = 51.212 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1269 \pm 2\ K$

$\Delta_f H°(0\ K) = -573.013 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -575.384 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 33.346\ kJ \cdot mol^{-1}$

### Enthalpy of Formation

The enthalpies of solution and reaction of NaF(cr) have been determined by many investigators. Incorporating their reported data with auxiliary $\Delta_f H°$(298.15 K) values,[1,2] we calculate the corresponding values of $\Delta_f H°$(NaF, cr, 298.15 K). The results are presented in the table below. The adopted $\Delta_f H°$(NaF, cr, 298.15 K) is −137.52 ± 0.2 kcal·mol⁻¹ (−575.384 ± 0.8 kJ·mol⁻¹).

| Source | Reaction* | T/K | Concentration $NaF \cdot nH_2O$ | No. of Determination | $\Delta_r H°$(298.15 K) kcal·mol⁻¹ | $\Delta_f H°$(298.15 K) kcal·mol⁻¹ |
|---|---|---|---|---|---|---|
| Guntz (1884)[1] | A | 285 | 400 | 1 | 0.13 | −137.42 |
| Latimer–Jolly (1953)[2] | A | 298 | 1850 | 2 | 0.23±0.01 | −137.52 |
| Hepler *et al*. (1953)[3] | A | 298 | 1540 | 1 | 0.22±0.01 | −137.51 |
| Davies–Benson (1965)[4] | A | 298 | 222 | 1 | 0.24±0.01 | −137.53 |
| Thomsen (1882)[5] | B | 291 |  | 2 | 16.24±0.15 | −137.38 |
| Wartenberg–Fitzner (1926)[6] | C | 293 | — | 1 | −39.3 ±0.1 | −137.62 |
| Schmitz–Schumaker (1947)[7] | C | 291 | — | 1 | −39.5 | −137.82 |
| Coughlin (1958)[8] | D | 298 |  | 6 | −1 40±0.06 | −137.58 |
| Vorob'yev–Skuratov (1960)[9] | E | 298 | — | 5 | −325.5 ±2.2 | −137.13 |

*Reaction A) $NaF(cr) = NaF(n\ H_2O)$ and $\Delta_r H°(298\ 15\ K) = \Delta_{sol} H°$; B) $NaOH(H_2O, 200\ K) + HF(H_2O, 200\ K) + H_2O(NaF401\ H_2O)$;
C) $NaCl(cr) + 1/2\ F_2(g) = NaF(cr) + 1/2\ Cl_2(g)$, D) $NaCl(cr) + HF(H_2O, 5.716\ K) = NaF(cr) + HCl(H_2O, 2.731K)$;
E) $4\ Na(cr) + CF_4(g) = 4\ NaF(cr) + C$ (graphite).

### Heat Capacity and Entropy

The low temperature heat capacities, 0.05–15 K and 54.01 –295 86 K, were measured by Harrison *et al*.[10] and King,[11] respectively. These two sets of data are joined smoothly with the high temperature heat capacities at 298 K which were derived from the enthalpy measurements, 406.1–1282.2 K, determined by O'Brien and Kelley.[12] The $C_p°$ values above 1282.2 K are obtained by linear extrapolation $S°$(298.15 K) is calculated using the adopted low temperature heat capacities and $S°$(54 K) = 0.555 cal K⁻¹·mol⁻¹.

Frank[13] commented that the temperature measurements of O'Brien and Kelley[12] seemed to be about 20 K high at 1000 with a smaller error at lower temperatures. A correction for the assumed error in the temperature measurement was used in the previous JANAF table. However, Douglas and Ditmars[14] have questioned this correction, since new enthalpy data for $AlF_3$ yielded $C_p°$ values in better agreement with the original $C_p°$ values of O'Brien and Kelley than with the corrected values of Frank. The α → β transition of $AlF_3(cr)$ was found in the range 723–6 K, while O'Brien and Kelley selected 727 K based on a point at 728.1 K in the β region and a point at 724.9 K in the pretransition region. Frank's correction yields an error of 9 at 727 K, yet the true error appears to be negligible (≤2) for $AlF_3(cr)$ Based on the above reasoning and the comparison of the $C_p°$ curve of NaF(cr) with those of NaCl(cr), LiCl(cr) and LiF(cr) in the temperature range 300–1300 K, we adopt the high temperature enthalpy data of O'Brien and Kelley without any correction.

The low temperature heat capacities in the temperature ranges 81–190 and 198–273 K were also measured by Koref;[15] and high temperature enthalpies at temperatures 288–1073 and 290–1287 K were reported by Krestovnikov and Karetnikov,[16] and Lyashenko,[17] respectively. They are not used for evaluation.

### Fusion Data

Refer to the liquid table for details.

### Sublimation Data

$\Delta_{sub} H°$(298.15 K) = 284.93 kJ·mol⁻¹ is calculated as the difference between $\Delta_f H°$(298 15 K) for NaF(g) and NaF(cr).

### References

[1] A. Guntz, Ann. Chim. Phys. [6] 3, 5 (1884).
[2] W. M. Latimer and W. L. Jolly, J. Amer. Chem. Soc. 75, 1548 (1953).
[3] L. G. Hepler, W. L. Jolly, and W. M. Latimer, J. Amer. Chem. Soc. 75, 2809 (1953).
[4] D. H. Davies and G. C. Benson, Can. J. Chem. 43, 3100 (1965).
[5] J. Thomsen, Thermochemische Untersuchungen, Vol. I, J. Barth Verlag, Leipzig, p. 157, (1882).
[6] H. Wartenberg and O. Fitzner, Z. anorg. allgem. Chem. 151, 313 (1926).
[7] H. Schmitz and H. J. Schumacher, Z. Naturforsch. 2A, 362 (1947).
[8] J. P. Coughlin, J. Amer. Chem. Soc. 80, 1802 (1958).
[9] A. F. Vorob'yev and S. M. Skuratov, Russ. J. Inorg. Chem. 5, 679 (1960).

Continued on page 1214

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ (J·K⁻¹mol⁻¹) | $S°$ (J·K⁻¹mol⁻¹) | $-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹) | $H°-H°(T_r)$ (kJ·mol⁻¹) | $\Delta_f H°$ (kJ·mol⁻¹) | $\Delta_f G°$ (kJ·mol⁻¹) | log $K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0. | 0. | INFINITE | −8.488 | −573.013 | −573.013 | INFINITE |
| 100 | 22.836 | 11.067 | 88.086 | −7.702 | −575.020 | −565.226 | 295.244 |
| 200 | 40.811 | 33.606 | 55.340 | −4.347 | −575.585 | −555.101 | 144.978 |
| 298.15 | 46.852 | 51.212 | 51.212 | 0. | −575.384 | −545 081 | 95.496 |
| 300 | 46.924 | 51.502 | 51.213 | 0.087 | −575.378 | −544.892 | 94.874 |
| 400 | 49.597 | 65.409 | 53.091 | 4.927 | −577.769 | −534.566 | 69.807 |
| 500 | 51.262 | 76.664 | 56.716 | 9.974 | −577.506 | −523.791 | 54.720 |
| 600 | 52.677 | 86.136 | 60.850 | 15 171 | −577.062 | −513.087 | 44.668 |
| 700 | 54.124 | 94.363 | 65.063 | 20.510 | −576.451 | −502.471 | 37.495 |
| 800 | 55.710 | 101.692 | 69.191 | 26.001 | −575.674 | −491.953 | 32.121 |
| 900 | 57.492 | 108.355 | 73.178 | 31.659 | −574.730 | −481.543 | 27.948 |
| 1000 | 59.505 | 114.514 | 77.007 | 37.507 | −573.615 | −471.247 | 24.615 |
| 1100 | 61.756 | 120.289 | 80.682 | 43.568 | −572.322 | −461.071 | 21.894 |
| 1200 | 64.266 | 125.768 | 84.213 | 49.866 | −667.607 | −448.581 | 19.526 |
| 1269.000 | 66.149 | 129.412 | 86.572 | 54.364 | --- CRYSTAL <--> LIQUID --- |  |  |
| 1300 | 66.944 | 131.018 | 87.612 | 56.427 | −665.009 | −430.433 | 17.295 |
| 1400 | 69.162 | 136.065 | 90.894 | 63.239 | −662.172 | −412.494 | 15.390 |
| 1500 | 70.626 | 140.892 | 94.068 | 70.236 | −659.158 | −394.764 | 13.747 |
| 1600 | 71.128 | 145.469 | 97.139 | 77.328 | −656.059 | −377.238 | 12.316 |
| 1700 | 71.128 | 149.781 | 100.110 | 84.441 | −652.948 | −359.907 | 11.059 |
| 1800 | 71.128 | 153.846 | 102.983 | 91.554 | −649.844 | −342.759 | 9.947 |
| 1900 | 71.128 | 157.692 | 105.762 | 98.666 | −646.747 | −325.783 | 8.956 |
| 2000 | 71.128 | 161.340 | 108.451 | 105.779 | −643.655 | −308.971 | 8.069 |
| 2100 | 71.128 | 164.811 | 111.053 | 112.892 | −640.566 | −292.312 | 7.271 |
| 2200 | 71.128 | 168.120 | 113.572 | 120.005 | −637.481 | −275.801 | 6.548 |
| 2300 | 71.128 | 171.281 | 116.013 | 127.118 | −634.396 | −259.430 | 5.892 |
| 2400 | 71.128 | 174.309 | 118.379 | 134.230 | −631.312 | −243.193 | 5.293 |
| 2500 | 71.128 | 177.212 | 120.675 | 141.343 | −628.227 | −227.085 | 4.745 |
| 2600 | 71.128 | 180.002 | 122.903 | 148.456 | −625.140 | −211.101 | 4.241 |
| 2700 | 71.128 | 182.686 | 125.068 | 155.569 | −622.051 | −195.235 | 3.777 |
| 2800 | 71.128 | 185.273 | 127.172 | 162.682 | −618.958 | −179.483 | 3.348 |
| 2900 | 71.128 | 187.769 | 129.219 | 169.794 | −615.863 | −163.842 | 2.951 |
| 3000 | 71.128 | 190.180 | 131.211 | 176.907 | −612.765 | −148.308 | 2.582 |

PREVIOUS: December 1963 CURRENT: December 1968

Sodium Fluoride (NaF) $F_1Na_1(cr)$

## Sodium Fluoride (NaF) LIQUID $M_r = 41.988173$

## Sodium Fluoride (NaF) $F_1Na_1(l)$

$S°(298.15\ K) = [73.464]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 1269 \pm 2\ K$

$\Delta_fH°(298.15\ K) = [-546.204]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 33.346\ kJ{\cdot}mol^{-1}$

### Enthalpy of Formation

$\Delta_fH°(NaF_3,l, 298.15\ K)$ is calculated from $\Delta_fH°(NaF, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1269\ K)–H°(298.15\ K)$, between the crystal and liquid.

### Heat Capacity and Entropy

The heat capacities of NaF(l) are derived from the enthalpy data, 1287.6–1746.5 K, determined by O'Brien and Kelley.[1] A glass transition temperature is assumed at 900 K. The heat capacities below 900 K are taken from those for NaF(cr). The $C_p°$ values above 1746.5 K are obtained by extrapolation. The entropy is calculated in a manner analogous to that used for the enthalpy formation.

### Fusion Data

The value of $T_{fus}$ has been reported as (K)· 1313,[2] 1285,[1] 1270,[3 4 5] 1269,[6] 1268,[7 8 9] 1267,[10, 11 12] 1265,[13] 1263,[14] and 1253.[15] We select $T_{fus} = 1269$ K. The value 1285 K reported by O'Brien and Kelley seems unreasonably high and is not adopted. The cause of this discrepancy is still unresolved.[17] The heat of melting is calculated as the difference between the adopted enthalpies for NaF(cr) and NaF(l) at 1269 K. Kelley[18] derived $\Delta_{fus}H°(1265\ K)$ to be 5.82 8.43 kcal·mol$^{-1}$, based on 13 sets of molten salts equilibrium data involving NaF. The value $\Delta_{fus}H°(1285\ K) = 8.03$ kcal·mol$^{-1}$ reported by O'Brien and Kelley is not used.

### Vaporization Data

$T_{vap} = 2060$ K is the temperature at which the partial pressures of NaF(g) and $Na_2F_2$(g) in equilibrium with NaF(l) equal one atmosphere. The vapor composition at $T_{vap}$ is evaluated as NaF 84.8% and $Na_2F_2$ 15.2% The heat required to vaporize one mole of liquid to form 0.868 mole of vapor mixture of the above composition at $T_{vap}$ is calculated to be 42.1 kcal·mol$^{-1}$ (176.146 kJ·mol$^{-1}$).

Ruff *et al.*[16] measured the vapor pressure of NaF(l) in the temperature range of 1699–1974 K and reported $T_{vap} = 1978$ K.

### References

[1] C. J. O'Brien and K.K. Kelley, J. Amer. Chem. Soc. 79, 5616 (1957).
[2] N. Puschin and A. Baskow, Z. Anorg. Chem. 81, 347 (1913).
[3] N. S. Kurnakow and S. F. Zemczuznyj, Z. Anorg. Chem. 52, 186 (1907).
[4] G. J. Landon and A. R. Ubbelohde, Proc. Roy. Soc. (London), 240A, 160 (1957).
[5] M. Rolin, Bull. Soc. Chim. France, 1960, 671 (1960).
[6] K. A. Sense, C. A. Alexander, R. E. Bowman, R. W. Stone, R. B. Filbert, Jr., J. Phys. Chem. 61, 384 (1957).
[7] H. S. Booth and B. A. Starrs, J. Phys. Chem. 35, 3553 (1931).
[8] M. A. Bredig, J. W. Johnson and W. T. Smith, Jr., J. Amer. Chem. Soc. 77, 307 (1955).
[9] S. Cantor, J. Phys Chem. 65, 2208 (1961).
[10] B. Porter and E. A. Brown, J. Amer. Ceram. Soc. 45, 49 (1962).
[11] N. W. F. Phillips, R. H. Singleton, and E. A. Hollingshead, J. Electrochem. Soc. 102, 690 (1955).
[12] J. Brynestad, K. Grjotheim, and S. Urnes, Metallurgia Ital. 52, No. 8, 495 (1960).
[13] W. Plato, Z. Physik. Chem. 58, 350 (1907).
[14] A. G. Bergman and E. P. Dergunov, Compt. Rend, Acad. Sci. U.R.S.S. 31, 753 (1941).
[15] O. Ruff and W. Plato, Ber. 36, 2363 (1903).
[16] O. Ruff, G. Schmidt and S. Mugdan, Z. anorg. allgem. Chem. 123, 83 (1922).
[17] K K. Kelley, U. S. Bur. Mines, Berkeley, California, personal communication, (May 31, 1963).
[18] K. K. Kelley, U. S. Bur. Mines Bull. 393, (1936).

Enthalpy Reference Temperature = $T_r$ = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 46.852 | 73.464 | 73 464 | 0.000 | −546.204 | −522.536 | 91.546 |
| 300 | 46.924 | 73.754 | 73.465 | 0 087 | −546 199 | −522.389 | 90.956 |
| 400 | 49.597 | 87.661 | 75.343 | 4.927 | −548.589 | −514.287 | 67.159 |
| 500 | 51.262 | 98.915 | 78.968 | 9.974 | −548.327 | −505.738 | 52.834 |
| 600 | 52.677 | 108.387 | 83.102 | 15.171 | −547.883 | −497.259 | 43.290 |
| 700 | 54.124 | 116.615 | 87.314 | 20.510 | −547.271 | −488.868 | 36 480 |
| 800 | 55.710 | 123.944 | 91.443 | 26.001 | −546.495 | −480.575 | 31.378 |
| 900 | 57.492 | 130.606 | 95.430 | 31.659 | −545.551 | −472.390 | 27.417 |
| 900.000 | 57.492 | 130.606 | 95.430 | 31.659 | GLASS <--> LIQUID | | |
| 900.000 | 76.525 | 130.606 | 95.430 | 31.659 | TRANSITION | | |
| 1000 | 74.099 | 138.538 | 99.353 | 39.185 | −542.757 | −464.413 | 24.258 |
| 1100 | 72.300 | 145.512 | 103.239 | 46.501 | −540.209 | −456.704 | 21.687 |
| 1200 | 70.961 | 151.744 | 107.026 | 53.662 | −634.632 | −446.778 | 19.448 |
| 1269.000 | 70.208 | 155.689 | 109.566 | 58.531 | --- CRYSTAL <--> LIQUID --- | | |
| 1300 | 69.873 | 157.380 | 110.686 | 60.702 | −631.555 | −431.249 | 17.328 |
| 1400 | 69.036 | 162.526 | 114.207 | 67.646 | −628.585 | −415.953 | 15.519 |
| 1500 | 68.367 | 167.266 | 117.589 | 74.515 | −625.699 | −400.866 | 13.959 |
| 1600 | 67.823 | 171.660 | 120.833 | 81.324 | −622.884 | −385.969 | 12.601 |
| 1700 | 67.362 | 175.758 | 123.944 | 88.083 | −620.127 | −371.247 | 11.407 |
| 1800 | 66.986 | 179.597 | 126.931 | 94.800 | −617.419 | −356.685 | 10.351 |
| 1900 | 66.651 | 183.210 | 129.798 | 101.481 | −614.752 | −342.273 | 9.410 |
| 2000 | 66.358 | 186.621 | 132.555 | 108.131 | −612.123 | −328.000 | 8.566 |
| 2100 | 66.107 | 189.852 | 135.207 | 114.754 | −609.525 | −313.858 | 7.807 |
| 2200 | 65.898 | 192.923 | 137.761 | 121.354 | −606.952 | −299.839 | 7.119 |
| 2300 | 65.731 | 195.848 | 140.224 | 127.936 | −604.399 | −285.936 | 6.494 |
| 2400 | 65.563 | 198.642 | 142.600 | 134.500 | −601.863 | −272.144 | 5.923 |
| 2500 | 65.438 | 201.316 | 144.896 | 141.050 | −599.341 | −258.458 | 5.400 |
| 2600 | 65.312 | 203.880 | 147.115 | 147.588 | −596.829 | −244.872 | 4.920 |
| 2700 | 65.187 | 206.342 | 149.264 | 154.112 | −594.328 | −231.383 | 4.476 |
| 2800 | 65.103 | 208.711 | 151.345 | 160.627 | −591.834 | −217.986 | 4.067 |
| 2900 | 65.019 | 210.995 | 153.363 | 167.133 | −589.345 | −204.679 | 3.687 |
| 3000 | 64.936 | 213.197 | 155.321 | 173.631 | −586.862 | −191.457 | 3.334 |
| 3100 | 64.852 | 215.325 | 157.222 | 180.120 | −584.385 | −178.317 | 3.005 |
| 3200 | 64.810 | 217.384 | 159.070 | 186.603 | −581.911 | −165.258 | 2.698 |
| 3300 | 64.726 | 219.376 | 160.868 | 193.080 | −579.442 | −152.276 | 2.410 |
| 3400 | 64.685 | 221.308 | 162.617 | 199.550 | −576.980 | −139.368 | 2.141 |
| 3500 | 64.643 | 223.183 | 164.321 | 206.016 | −574.523 | −126.533 | 1.888 |

PREVIOUS. June 1964 — CURRENT: December 1968

Sodium Fluoride (NaF) $F_1Na_1(l)$

## Sodium Fluoride (NaF) CRYSTAL-LIQUID

0 to 1269 K crystal
above 1269 K liquid

Refer to the individual tables for details.

## $M_r$ = 44988173 Sodium Fluoride (NaF) $F_1Na_1(cr,l)$

Enthalpy Reference Temperature = $T_r$ = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

|  | J·K⁻¹mol⁻¹ |  |  | kJ·mol⁻¹ |  |  |  |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −8.488 | −573.013 | −573.013 | INFINITE |
| 100 | 22.836 | 11.067 | 88.086 | −7.702 | −575.020 | −565.226 | 295.244 |
| 200 | 40.811 | 33.606 | 55.340 | −4.347 | −575.585 | −555.101 | 144.978 |
| 298.15 | 46.852 | 51.212 | 51.212 | 0. | −575.384 | −545.081 | 95.496 |
| 300 | 46.924 | 51.502 | 51.213 | 0.087 | −575.378 | −544.892 | 94.874 |
| 400 | 49.597 | 65 409 | 53.091 | 4.927 | −577.769 | −534.566 | 69.807 |
| 500 | 51.262 | 76.664 | 56.716 | 9.974 | −577.506 | −523.791 | 54.720 |
| 600 | 52.677 | 86.136 | 60.850 | 15.171 | −577.062 | −513.087 | 44.668 |
| 700 | 54.124 | 94.363 | 65.063 | 20.510 | −576.451 | −502 471 | 37 495 |
| 800 | 55.710 | 101.692 | 69.191 | 26.001 | −575.674 | −491.953 | 32.121 |
| 900 | 57.492 | 108.355 | 73.178 | 31.659 | −574.730 | −481.543 | 27.948 |
| 1000 | 59.505 | 114.514 | 77.007 | 37.507 | −573.615 | −471.247 | 24.615 |
| 1100 | 61.756 | 120.289 | 80.682 | 43.568 | −572.322 | −461.071 | 21.894 |
| 1200 | 64.266 | 125.768 | 84.213 | 49.866 | −667.607 | −448.581 | 19.526 |
| 1269.000 | 66.149 | 129.412 | 86.572 | 54.364 | CRYSTAL <--> LIQUID |  |  |
| 1269 000 | 70.208 | 155.689 | 86.572 | 87.710 |  | TRANSITION |  |
| 1300 | 69.873 | 157.380 | 88.240 | 89.882 | −631.555 | −431.249 | 17.328 |
| 1400 | 69.036 | 162.526 | 93.365 | 96.826 | −628.585 | −415.953 | 15.519 |
| 1500 | 68.367 | 167.266 | 98.136 | 103.695 | −625.699 | −400.866 | 13.959 |
| 1600 | 67.823 | 171.660 | 102.595 | 110.504 | −622.884 | −385.969 | 12.601 |
| 1700 | 67.362 | 175.758 | 106.780 | 117.262 | −620.127 | −371.247 | 11.407 |
| 1800 | 66.986 | 179.597 | 110.720 | 123.979 | −617.419 | −356.685 | 10.351 |
| 1900 | 66.651 | 183.210 | 114.441 | 130.661 | −614.752 | −342.273 | 9.410 |
| 2000 | 66.358 | 186.621 | 117.965 | 137.311 | −612.123 | −328.000 | 8.566 |
| 2100 | 66.107 | 189.852 | 121.312 | 143 934 | −609.525 | −313.858 | 7 807 |
| 2200 | 65.898 | 192.923 | 124.498 | 150.534 | −606.952 | −299.839 | 7 119 |
| 2300 | 65.731 | 195.848 | 127.537 | 157.115 | −604.399 | −285.936 | 6.494 |
| 2400 | 65.563 | 198.642 | 130.442 | 163.679 | −601.863 | −272.144 | 5.923 |
| 2500 | 65.438 | 201.316 | 133.224 | 170.229 | −599.341 | −258.458 | 5.400 |
| 2600 | 65.312 | 203.880 | 135.893 | 176.767 | −596.829 | −244.872 | 4.920 |
| 2700 | 65.187 | 206.342 | 138.456 | 183.292 | −594.328 | −231.383 | 4.476 |
| 2800 | 65.103 | 208.711 | 140.924 | 189.806 | −591.834 | −217.986 | 4.067 |
| 2900 | 65.019 | 210.995 | 143.301 | 196.312 | −589.345 | −204.679 | 3.687 |
| 3000 | 64.936 | 213.197 | 145.594 | 202.810 | −586.862 | −191.457 | 3.334 |
| 3100 | 64.852 | 215.325 | 147.809 | 209.299 | −584.385 | −178.317 | 3.005 |
| 3200 | 64.810 | 217 384 | 149.952 | 215.782 | −581.911 | −165.258 | 2.698 |
| 3300 | 64.726 | 219.376 | 152.025 | 222.259 | −579.442 | −152.276 | 2.410 |
| 3400 | 64.685 | 221.308 | 154.035 | 228.729 | −576.980 | −139.368 | 2.141 |
| 3500 | 64.643 | 223.183 | 155.984 | 235.196 | −574.523 | −126.533 | 1.888 |

PREVIOUS: CURRENT December 1968

**Sodium Fluoride (NaF)** **IDEAL GAS** **$M_r$ = 41.988173** **Sodium Fluoride (NaF)** **$F_1Na_1(g)$**

$S°(298.15\ K) = 217\ 610 \pm 0.008\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -288.819 \pm 2.1\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -290.453 \pm 2.1\ kJ{\cdot}mol^{-1}$

| Electronic Level and Quantum Weight<br>State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|
| $^1\Sigma$ | 0 | 1 |

$\omega_e = 536.10 \pm 0.35\ cm^{-1}$   $\omega_ex_e = 3.83 \pm 0.14\ cm^{-1}$   $\sigma = 1$
$B_e = 0.4369\ cm^{-1}$   $\sigma_e = 0.00456\ cm^{-1}$   $r_e = 1.99260$ Å

## Enthalpy of Formation

The total pressure of NaF(g) and $Na_2F_2$(g), in equilibrium with NaF(cr,l) at temperatures 1020–1974 K, have been determined by many investigators, using manometric,[1 2, 5] torsion–effusion,[6, 8] Knudsen effusion,[3 7] transpiration,[4] and molecular–beam velocity–selector[9 10] methods. In order to evaluate $\Delta_{vap}H°$(LiF, g) we have used a trial and error variation of $\Delta_{sub}H°$ and $\Delta_{vap}H°$ for the monomer and dimer such that the $\Delta_rH°$(298.15 K) values derived by the 2nd and 3rd law methods are in reasonable agreement.

Incorporating $\Delta_{sub}H°$(298.15 K) = 68.1 and 72.7, and $\Delta_{vap}H°$(298.15 K) = 61 12 and 58 75 kcal·mol$^{-1}$ for NaF and $Na_2F_2$, respectively, with JANAF functions for NaF(cr), NaF(l), NaF(g) and $Na_2F_2$(g), we derive the partial pressures of NaF monomer from the reported total pressures. Based on the calculated partial pressures of NaF(g), the corresponding enthalpy of vaporization are evaluated by the 2nd and 3rd law methods. Using the 3rd law $\Delta_rH°$(298.15 K) and $\Delta_fH°$(298 15 K) = −137.52 and −130.545 kcal mol$^{-1}$for NaF(cr) and NaF(l), we obtain values of $\Delta_fH°$(298.15 K) for NaF(g). The results are presented in the table below The $\Delta_fH°$(NaF, g, 298.15 K) value adopted is −69.42 kcal·mol$^{-1}$ (−290.453±2.1 kJ·mol$^{-1}$).

Gaydon[11] and Herzberg[12] reported $D_0^\circ$ = 114.2 ± 6.9 (4.95±0.3 eV) and < 122.2 kcal·mol$^{-1}$ (5.3 eV), respectivley Using JANAF $\Delta_fH°$(298.15 K) values for Na(g) and F(g), we obtain $\Delta_fH°$(NaF, g, 298.15 K) = −70.5 ± 5 8 and >−78.5 kcal·mol.$^{-1}$ Employing flame–photometric method, Bulewicz *et al*.[13] and Page and Sugden[14] derived $D_0^\circ$ = 121 ± 7 and 119–120 kcal·mol$^{-1}$ for NaF(g), which lead to $\Delta_fH°$(NaF, g, 298.15 K) = −77.3 ± 7 and −75 to −76 kcal·mol.$^{-1}$

| Source | T/K | Reaction** | Data Points | $\Delta_rH°$(298.15 K), kcal·mol$^{-1}$ 2nd law | 3rd law | Drift cal K$^{-1}$·mol$^{-1}$ | $\Delta_fH°$(298 15 K) kcal·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| vonWartenberg Schulz (1921)[1] | 1669–1830 | B | 5 | 67.76±0.11 | 59.90 | −4.5±0.1 | −70.65 |
| Ruff *et al*. (1922)[2] | 1699–1974 | B | 14 | 64.07±0.58 | 59.54 | −2.4±0.3 | −71.01 |
| Niwa (1938)[3] | 1053–1112 | A | 5 | 63.18±1.04 | 66.68 | 3 2±1.0 | −70.84 |
| Sense *et al*. (1957)[4] | 1208–1265 | A | 7 | 71.26±0.63 | 68.25 | −2.4±0.5 | −69.27 |
|  | 1274–1348 | B | 9 | 65.88±0.76 | 61.14 | −3.6±0.6 | −69.41 |
| Cantor Blankenship (1958)[5] | 1381–1592 | B | 6* | 66.13 | 60.84 | -3.6 | −69.71 |
| Pugh Barrow (1958)[6] | 1023–1166 | A | 7* | 68.13 | 68.14 | 0.0 | −69.38 |
| Porter Schoonmaker (1958)[7] | 1121 | A | 1 | – | 68.82 | – | −68.70 |
| Entner Neckel (1967)[8] | 1016–1236 | A | 6* | 68.54±0.10 | 67.74 | −0 7±0.1 | −69.78 |

*Data points calculated from a given total pressure equation.
**Reaction A) NaF(cr) = NaF(g) B) NaF(l) = NaF(g).

## Heat Capacity and Entropy

Veazey and Gordy[15] have measured the rotational transitions of NaF in the millimeter– and sub–millimeter–wave region with a high resolution molecular–beam absorption spectrometer. The derived values of $\omega_e$, $\omega_ex_e$, $B_e$, $\alpha_e$ and $r_e$ are adopted here.

Using the molecular beam electric resonance method, Bauer and Lew[16] measured the transition between the J = 0 and J = 1 rotational levels of $Na^{23}F^{19}$ in the three lowest vibrational states. Radio–frequency transitions for $Na^{23}F^{19}$ have been observed by Hollowell *et al.*[19] Infrared spectra of NaF have been analyzed by Snelson and Pitzer,[17] Ritchie and Lew,[18] and Baikov and Vasilevskii.[20] The molecular constants derived by the above authors are similar to the values adopted, except the value $\omega_e$= 550 cm$^{-1}$ [17] which is different from the value 536.1 cm$^{-1}$ reported by Veazey and Gordy.[15]

## References

[1] H. von Wartenberg and H Schulz, Z. Elektrochem. **27**, 568 (1921).
[2] O. Ruff, G. Schmidt, and S. Mugdan, Z. anorg. allg. Chem. **123**, 83 (1922).
[3] K. Niwa, J. Fac. Sci. Hokkaido Imp Univ. Ser. III, **2**, 201 (1938).
[4] K. A. Sense, C. A. Alexander, R. E. Bowman, R. W. Stone, and R. B. Filbert, Jr., J Phys. Chem. Phys. Chem. **61**, 384 (1957).
[5] S. Cantor and F. Blankenship, paper presented at the American Chemical Society at Chicago, (September 7–12, 1958).
[6] A. C. P. Pugh and R. F. Barrow, Trans. Faraday Soc. **54**, 671 (1958).
[7] R. F. Porter and R. C. Schoonmaker, J. Chem. Phys. **29**, 1070 (1958).

Continued on page 1214

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

|  | J·K$^{-1}$mol$^{-1}$ |  |  | kJ·mol$^{-1}$ |  |  |  |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −9.225 | −288.819 | −288.819 | INFINITE |
| 100 | 29.357 | 183.316 | 246.446 | −6.313 | −288.700 | −296.132 | 154.683 |
| 200 | 31.978 | 204.387 | 220.675 | −3.258 | −289.565 | −303.238 | 79.198 |
| 250 | 33.261 | 211.666 | 218.168 | −1.626 | −290.009 | −306.605 | 64.062 |
| 298.15 | 34.215 | 217.610 | 217.610 | 0. | −290.453 | −309.761 | 54.269 |
| 300 | 34.247 | 217.821 | 217.610 | 0.063 | −290.471 | −309.881 | 53.955 |
| 350 | 34 984 | 223.159 | 218.030 | 1.795 | −290.987 | −313.077 | 46.724 |
| 400 | 35.538 | 227.868 | 218.971 | 3.559 | −294.207 | −315.987 | 41.264 |
| 450 | 35.962 | 232.079 | 220.198 | 5.347 | −294.815 | −318.673 | 36.991 |
| 500 | 36.293 | 235.886 | 221.579 | 7.153 | −295.396 | −321.293 | 33.565 |
| 600 | 36.773 | 242.548 | 224.535 | 10.808 | −296 494 | −326.367 | 28.413 |
| 700 | 37.103 | 248.243 | 227.525 | 14.503 | −297.528 | −331.264 | 24.719 |
| 800 | 37.348 | 253.214 | 230.432 | 18.226 | −298.518 | −336.015 | 21.940 |
| 900 | 37.541 | 257.625 | 233.213 | 21.971 | −299.488 | −340.644 | 19.770 |
| 1000 | 37.699 | 261.589 | 235.856 | 25.733 | −300.458 | −345.165 | 18.030 |
| 1100 | 37.835 | 265 188 | 238.361 | 29.510 | −301.449 | −349.588 | 16.601 |
| 1200 | 37.955 | 268.486 | 240.736 | 33.300 | −399.243 | −351.479 | 15.299 |
| 1300 | 38.064 | 271.528 | 242.989 | 37.101 | −399.405 | −347 492 | 13.962 |
| 1400 | 38.165 | 274.353 | 245.130 | 40.912 | −399.568 | −343.493 | 12.816 |
| 1500 | 38.259 | 276.989 | 247.167 | 44 733 | −399.730 | −339.482 | 11.822 |
| 1600 | 38.349 | 279.461 | 249.109 | 48.564 | −399.893 | −335.460 | 10.952 |
| 1700 | 38.436 | 281.789 | 250.963 | 52.403 | −400.055 | −331.428 | 10.184 |
| 1800 | 38.519 | 283.988 | 252.737 | 56.251 | −400.216 | −327.386 | 9.500 |
| 1900 | 38.600 | 286.073 | 254.437 | 60.107 | −400.376 | −323.336 | 8.889 |
| 2000 | 38.679 | 288.055 | 256.069 | 63.971 | −400.532 | −319.277 | 8.339 |
| 2100 | 38.757 | 289.944 | 257.638 | 67.843 | −400.685 | −315.210 | 7.840 |
| 2200 | 38.834 | 291.748 | 259.147 | 71.722 | −400.833 | −311.137 | 7.387 |
| 2300 | 38.909 | 293.476 | 260.603 | 75.609 | −400.974 | −307.056 | 6.973 |
| 2400 | 38.984 | 295.134 | 262.007 | 79.504 | −401.108 | −302.970 | 6.594 |
| 2500 | 39.058 | 296.727 | 263.364 | 83.406 | −401.234 | −298.878 | 6.245 |
| 2600 | 39.131 | 298.260 | 264.677 | 87.316 | −401.350 | −294.782 | 5.922 |
| 2700 | 39.204 | 299.738 | 265.948 | 91.232 | −401.457 | −290.681 | 5.624 |
| 2800 | 39.276 | 301 165 | 267.181 | 95.156 | −401.553 | −286.576 | 5.346 |
| 2900 | 39.348 | 302.545 | 268.377 | 99.088 | −401.639 | −282.468 | 5.088 |
| 3000 | 39.419 | 303.880 | 269.538 | 103.026 | −401.715 | −278.358 | 4.847 |
| 3100 | 39.491 | 305.174 | 270.667 | 106.971 | −401.782 | −274.245 | 4.621 |
| 3200 | 39.562 | 306.429 | 271 765 | 110.924 | −401.839 | −270.130 | 4.409 |
| 3300 | 39.632 | 307.647 | 272.834 | 114.884 | −401.887 | −266.013 | 4.211 |
| 3400 | 39.703 | 308.831 | 273.875 | 118.850 | −401.929 | −261.895 | 4.024 |
| 3500 | 39.773 | 309.983 | 274.890 | 122.824 | −401.964 | −257.776 | 3.847 |
| 3600 | 39.843 | 311.105 | 275.881 | 126.805 | −401.996 | −253.656 | 3.680 |
| 3700 | 39.913 | 312.197 | 276.848 | 130.793 | −402.025 | −249.535 | 3.523 |
| 3800 | 39.983 | 313.262 | 277.792 | 134.788 | −402.054 | −245.413 | 3.373 |
| 3900 | 40.053 | 314.302 | 278.715 | 138.790 | −402.084 | −241.291 | 3.232 |
| 4000 | 40.123 | 315.317 | 279.617 | 142.798 | −402.119 | −237.167 | 3.097 |
| 4100 | 40.192 | 316.308 | 280.500 | 146.814 | −402 161 | −233.043 | 2.969 |
| 4200 | 40.262 | 317.278 | 281.364 | 150.837 | −402.211 | −228.918 | 2.847 |
| 4300 | 40.331 | 318.226 | 282.211 | 154.866 | −402.275 | −224.791 | 2.731 |
| 4400 | 40.400 | 319.154 | 283.040 | 158.903 | −402.313 | −220.666 | 2.620 |
| 4500 | 40.470 | 320.063 | 283.852 | 162.946 | −402.388 | −216.537 | 2.514 |
| 4600 | 40.539 | 320.953 | 284.649 | 166.997 | −402.491 | −212.406 | 2.412 |
| 4700 | 40.608 | 321.826 | 285.431 | 171.054 | −402.615 | −208.273 | 2.315 |
| 4800 | 40.677 | 322.681 | 286.198 | 175.118 | −402.765 | −204.136 | 2.221 |
| 4900 | 40.746 | 323.521 | 286.951 | 179.190 | −402.942 | −199.996 | 2.132 |
| 5000 | 40.815 | 324.345 | 287.691 | 183.268 | −403.143 | −195.853 | 2.046 |
| 5100 | 40.884 | 325.153 | 288.418 | 187.353 | −403.384 | −191.705 | 1.963 |
| 5200 | 40.953 | 325.948 | 289.132 | 191.445 | −403.661 | −187.552 | 1.884 |
| 5300 | 41.022 | 326.729 | 289.834 | 195.543 | −403.979 | −183.393 | 1.807 |
| 5400 | 41.091 | 327.496 | 290.524 | 199.649 | −404.340 | −179.228 | 1.734 |
| 5500 | 41.160 | 328.251 | 291.203 | 203.761 | −404.747 | −175.056 | 1.663 |
| 5600 | 41.229 | 328.993 | 291.871 | 207.881 | −405.202 | −170.875 | 1.594 |
| 5700 | 41.297 | 329.723 | 292.529 | 212.007 | −405.709 | −166.686 | 1.528 |
| 5800 | 41.366 | 330.442 | 293.177 | 216.140 | −406.269 | −162.488 | 1.463 |
| 5900 | 41.435 | 331.150 | 293.814 | 220.280 | −406.886 | −158.280 | 1.401 |
| 6000 | 41.504 | 331.847 | 294.442 | 224.427 | −407.404 | −154.079 | 1.341 |

PREVIOUS· December 1968 (1 atm)    CURRENT: December 1968 (1 bar)

$D_0^\circ = 18030 \pm 850\ \text{cm}^{-1}$
$S^\circ(298.15\ \text{K}) = 216.40 \pm 0.3\ \text{J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H^\circ(0\ \text{K}) = 108 \pm 10\ \text{kJ·mol}^{-1}$
$\Delta_f H^\circ(298.15\ \text{K}) = 109 \pm 10\ \text{kJ·mol}^{-1}$

Electronic Levels and Molecular Constants ($^{16}O^{19}F$), cm$^{-1}$

| State<br>$10^6$** | $T_e$<br>$r_e$/Å | $g_i$ | $\omega_e$ | $\omega_e x_e$* | $B_e$ | $\alpha_e$** | $D_e$ |
|---|---|---|---|---|---|---|---|
| $X^2\Pi_{3/2}$ | 0 | 2 | 1052.99376 | 9.90030 | 1.05870547 | | |
| | −0.0138015 | 4.28739 | 1.35412 | | | | |
| $X^2\Pi_{1/2}$ | 193.80 | 2 | 1052.99376 | 9.90030 | 1.05870547 | | |
| | −0.0138015 | 4.28739 | 1.35412 | | | | |

* $\omega_e y_e = -0.068456$, $\omega_e z_e = -0.0010881$, $\omega_e a_e \times 10^{-5} = -5.945$
** 3 additional higher order terms are also available

$\sigma = 1$

## Enthalpy of Formation

The dissociation energy has been calculated by many different techniques. The derived values range from 106.3 to 403.7 kJ·mol$^{-1}$. The values may be grouped into two types: (1) derived from a molecular orbital calculation and (2) extracted from reaction studies involving $F_2O$. We adopt $D_0^\circ(\text{OF}) = 18030 \pm 850\ \text{cm}^{-1}$ ($215.687 \pm 10$ kJ·mol$^{-1}$) based on the experimental studies of Clyne and Watson,[1] Czarnowski and Schumacher,[2] Berkowitz *et al.*,[3] and Zhang *et al.*[4] These four studies are all dependent on the enthalpy of formation of $OF_2(g)$ and are mass spectrometric studies except for the thermal decomposition of $OF_2$ by Czarnowski and Schumacher.[2] From the adopted value, we calculate $\Delta_f H^\circ(\text{OF,g, 298K}) = 109 \pm 10$ kJ·mol$^{-1}$ Additional data needed for the calculations presented here, e.g. thermal functions for the F(g) and $F_2$(ref), O(g) and $O_2$(ref), are taken from the JANAF Thermochemical Tables.[5]

## Heat Capacity and Entropy

The spectroscopic results tabulated above are for the $^{16}O^{19}F$ isotopomer. Isotopic relationships[6] are used to convert the above constants to those for the normally occurring, i.e. natural abundance, species. The latter values are then used in the calculation of the thermal functions. Only the X state is included in the calculation of the thermal functions; a sum–over–states technique is used.

The ground state, $X^2\Pi_{3/2}$, has been characterized by Burkholder *et al.*[7] The observations were made using a high resolution Fourier transform spectrometer and a multiple reflection absorption cell equipped to study short–lived molecules under fast flow conditions. Hammer *et al.*[8] used a high resolution Fourier transform spectrometer to study the OF infrared chemiluminescence. This latter study, the results of which we have adopted, provided values which were slightly different from the Burkholder *et al.*[7] work.

The value of A, the splitting of the ground state, has been determined experimentally by five authors: McKellar[9] ($177.3 \pm 5.6$ cm$^{-1}$), Dyke *et al.*[10] ($160 \pm 30$ cm$^{-1}$), McKellar *et al.*[11] (177.3 cm$^{-1}$), Burkholder *et al.*[7] ($198.3 \pm 6.7$ cm$^{-1}$), and Hammer *et al.*[8] ($193.80 \pm 0.97$ cm$^{-1}$). We adopt the value of Hammer *et al.* as determined by high resolution Fourier transform spectroscopy.

An $A^2\Pi$ state is assumed to exist at approximately 35,000 cm$^{-1}$ but has not been observed. This state would not contribute significantly to the thermal functions below 6000 K.

## References

[1] M.A.A. Clyne and R.T. Watson, Chem. Phys. Lett. 12 (2), 344 (1971).
[2] J.Czarnowski and H.J. Schumacher, Chem. Phys. Lett. 17 (2), 235 (1972).
[3] J.Berkowitz, P.M. Dehmer and W.A. Chupka, J. Chem. Phys. 59, 925 (1973).
[4] Z.Zhang, S.-C. Kuo, R.B. Klemm, P.S. Monk and L.J. Stieff, Chem. Phys. Lett. 229 (4-5), 377 (1994).
[5] JANAF Thermochemical Tables: F(g), June 1982; $F_2$(ref), June 1982; O(g), Sept. 1982, $O_2$(ref), Sept. 1982).
[6] G. Herzberg, Spectra of Diatomic Molecules, D. Van Nostrand Co., New York, 107 (1950).
[7] J.B. Burkholder, P.D. Hammer, C.J. Howard and A.R.W. McKellar, J. Mol. Spectrosc. 118, 471 (1986).
[8] P.D. Hammer, A. Sinha, J.B Burkholder and C.J. Howard, J. Mol. Spectrosc. 129, 199 (1988).
[9] A.R.W. McKellar, Can. J. Phys. 57, 2106 (1979).
[10] J.M. Dyke, N. Jonathan, J.D. Mills and A. Morris, Mol. Phys. 40, 1177 (1980).
[11] A.R.W. McKellar, C. Yamada and E. Hirota, J. Mol. Spectrosc. 97 (2), 425 (1983).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p^\circ$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log $K_f$ |
| 0 | 0.000 | 0 000 | INFINITE | −9.388 | 108.392 | 108.392 | INFINITE |
| 50 | 30.058 | 159.390 | 318.327 | −7.947 | 108.382 | 107.996 | −112.819 |
| 100 | 32.600 | 181.178 | 244.853 | −6.367 | 108.506 | 107.572 | −56.188 |
| 150 | 32.472 | 194.419 | 225.985 | −4.735 | 108.682 | 107.066 | −37.283 |
| 200 | 31.935 | 203.681 | 219.310 | −3.126 | 108.828 | 106.505 | −27.816 |
| 250 | 31.788 | 210.783 | 216.922 | −1.535 | 108.939 | 105.911 | −22.128 |
| 298.15 | 31.995 | 216.396 | 216.396 | 0.000 | 109.025 | 105.320 | −18.451 |
| 300 | 32.007 | 216.594 | 216.397 | 0.059 | 109.028 | 105.297 | −18.333 |
| 400 | 32.917 | 225.920 | 217.662 | 3.303 | 109.177 | 104.030 | −13.585 |
| 500 | 33.860 | 233.369 | 220.083 | 6 643 | 109.304 | 102.728 | −10.732 |
| 600 | 34.620 | 239.612 | 222.831 | 10.069 | 109.414 | 101.402 | −8.828 |
| 700 | 35.193 | 244.994 | 225.622 | 13.561 | 109.502 | 100.059 | −7.466 |
| 800 | 35.621 | 249.723 | 228.345 | 17.102 | 109.571 | 98.705 | −6.445 |
| 900 | 35.941 | 253.938 | 230.959 | 20.681 | 109.620 | 97.344 | −5.650 |
| 1000 | 36.183 | 257.738 | 233.450 | 24.288 | 109.651 | 95.978 | −5.013 |
| 1100 | 36.367 | 261.195 | 235.817 | 27.916 | 109.664 | 94.610 | −4.493 |
| 1200 | 36.509 | 264.366 | 238.066 | 31.560 | 109.661 | 93.241 | −4.059 |
| 1300 | 36.619 | 267.293 | 240.203 | 35.217 | 109.641 | 91.874 | −3.691 |
| 1400 | 36.704 | 270.010 | 242.236 | 38.883 | 109.606 | 90.509 | −3.377 |
| 1500 | 36.770 | 272.544 | 244.173 | 42.557 | 109.553 | 89.146 | −3.104 |
| 1600 | 36.821 | 274.919 | 246.021 | 46.236 | 109.485 | 87.788 | −2.866 |
| 1700 | 36.859 | 277.153 | 247.788 | 49.921 | 109.401 | 86.434 | −2.656 |
| 1800 | 36.886 | 279.260 | 249.478 | 53.608 | 109.300 | 85.086 | −2.469 |
| 1900 | 36.903 | 281.255 | 251.099 | 57.297 | 109.184 | 83.744 | −2.302 |
| 2000 | 36.910 | 283.148 | 252.654 | 60.988 | 109.053 | 82.408 | −2.152 |
| 2100 | 36.906 | 284.949 | 254.149 | 64.679 | 108.908 | 81.079 | −2.017 |
| 2200 | 36.891 | 286.666 | 255.589 | 68.369 | 108 749 | 79.758 | −1.894 |
| 2300 | 36.865 | 288.305 | 256.976 | 72.057 | 108.577 | 78.445 | −1.781 |
| 2400 | 36.826 | 289.873 | 258.314 | 75.742 | 108.394 | 77.138 | −1.679 |
| 2500 | 36.774 | 291.375 | 259.607 | 79.422 | 108.199 | 75.838 | −1.585 |
| 2600 | 36.707 | 292.816 | 260.856 | 83.096 | 107.994 | 74.549 | −1.498 |
| 2700 | 36.626 | 294.200 | 262.066 | 86.763 | 107.779 | 73.266 | −1.417 |
| 2800 | 36.530 | 295.531 | 263.238 | 90.420 | 107.554 | 71.992 | −1.343 |
| 2900 | 36.418 | 296.811 | 264.373 | 94.068 | 107.321 | 70.725 | −1.274 |
| 3000 | 36.292 | 298.043 | 265.475 | 97 704 | 107.077 | 69.469 | −1.210 |
| 3100 | 36.151 | 299.231 | 266.545 | 101.326 | 106.824 | 68.220 | −1.149 |
| 3200 | 35.996 | 300.376 | 267.584 | 104.933 | 106.561 | 66.977 | −1.093 |
| 3300 | 35.828 | 301.481 | 268.595 | 108.525 | 106.289 | 65.745 | −1.041 |
| 3400 | 35.647 | 302.548 | 269.578 | 112.098 | 106.007 | 64.521 | −0.991 |
| 3500 | 35.454 | 303.579 | 270.535 | 115.654 | 105.715 | 63.305 | −0.945 |
| 3600 | 35.251 | 304.575 | 271.467 | 119.189 | 105.411 | 62.098 | −0.901 |
| 3700 | 35.038 | 305.538 | 272.375 | 122.703 | 105.096 | 60.897 | −0.860 |
| 3800 | 34.818 | 306.469 | 273.260 | 126.196 | 104.769 | 59.710 | −0.821 |
| 3900 | 34.589 | 307.371 | 274.123 | 129.667 | 104.431 | 58.529 | −0.784 |
| 4000 | 34.355 | 308.243 | 274.965 | 133.114 | 104.079 | 57.353 | −0.749 |
| 4100 | 34.116 | 309.089 | 275.787 | 136.538 | 103.714 | 56.193 | −0.716 |
| 4200 | 33.873 | 309.908 | 276.590 | 139.937 | 103.336 | 55.036 | −0.684 |
| 4300 | 33.627 | 310.702 | 277.374 | 143.312 | 102.943 | 53.891 | −0.655 |
| 4400 | 33.379 | 311.472 | 278.140 | 146.662 | 102.536 | 52.755 | −0.626 |
| 4500 | 33 129 | 312.220 | 278.889 | 149.988 | 102.114 | 51.629 | −0.599 |
| 4600 | 32.879 | 312.945 | 279.622 | 153.288 | 101.677 | 50.510 | −0.574 |
| 4700 | 32.630 | 313.650 | 280.338 | 156.564 | 101.224 | 49.403 | −0.549 |
| 4800 | 32.381 | 314.334 | 281.039 | 159.814 | 100.755 | 48.306 | −0.526 |
| 4900 | 32.134 | 314.999 | 281.726 | 163.040 | 100.270 | 47.221 | −0.503 |
| 5000 | 31.889 | 315.646 | 282.398 | 166.241 | 99.767 | 46.142 | −0.482 |
| 5100 | 31.646 | 316.275 | 283.056 | 169.418 | 99.247 | 45.075 | −0.462 |
| 5200 | 31.407 | 316.887 | 283.700 | 172.571 | 98.711 | 44.015 | −0.442 |
| 5300 | 31.170 | 317.483 | 284.332 | 175.699 | 98.155 | 42.970 | −0.423 |
| 5400 | 30.937 | 318.064 | 284.952 | 178.805 | 97.582 | 41.935 | −0.406 |
| 5500 | 30.708 | 318.629 | 285.559 | 181.887 | 96.990 | 40.909 | −0.389 |
| 5600 | 30.483 | 319.180 | 286.154 | 184.947 | 96.379 | 39.895 | −0.372 |
| 5700 | 30.263 | 319.718 | 286.738 | 187.984 | 95.748 | 38.890 | −0.356 |
| 5800 | 30.046 | 320.242 | 287.312 | 190.999 | 95.097 | 37.900 | −0.341 |
| 5900 | 29.834 | 320.754 | 287.874 | 193.993 | 94.426 | 36.918 | −0.327 |
| 6000 | 29.627 | 321.254 | 288.426 | 196.966 | 93.734 | 35.950 | −0.313 |

PREVIOUS: December 1966 (1 bar) CURRENT: September 1995 (1 bar)

## Titanium Fluoride Oxide (OTiF) IDEAL GAS $M_r = 82.877803$

$S°(298.15\ K) = [250.667]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = [-430.918]\ kJ{\cdot}mol^{-1}$

$\Delta_f H°(298.15\ K) = [-433.211]\ kJ{\cdot}mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, $cm^{-1}$ |
|---|
| [880](1) |
| [300](1) |
| [740](1) |

Ground State Quantum Weight: [2]
Point Group: $[C_{\infty v}]$
Bond Distances: Ti–O = [1.62] Å; Ti–F = [1.74] Å
Bond Angle: O–Ti–F = [180°]
Rotational Constant: $B_0 = [0.170462]\ cm^{-1}$

$\sigma = 1$

### Enthalpy of Formation

$\Delta_f H°(0\ K)$ was estimated as −103 kcal·mol⁻¹ by Gordon.[1] $\Delta_f H°(298.15\ K)$ was then calculated.

### Heat Capacity and Entropy

Molecular constants were estimated by Gordon.[1] Principal moment was $16.419 \times 10^{-39}\ g{\cdot}cm^2$.

### Reference

[1] J. S. Gordon, Astrosystems, Inc., Caldwell Twp., N. J., personal communication, (January 10, 1963).

## Titanium Fluoride Oxide (OTiF) $F_1O_1Ti_1(g)$

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −11.291 | −430.918 | −430.918 | INFINITE |
| 100 | 33.375 | 206.489 | 289.330 | −8.284 | −431.378 | −434.017 | 226.707 |
| 200 | 42.295 | 232.558 | 254.917 | −4.472 | −432.402 | −436.255 | 113.938 |
| 250 | 45.706 | 242.373 | 251.450 | −2.269 | −432.844 | −437.166 | 91.341 |
| 298.15 | 48.472 | 250.667 | 250.667 | 0. | −433.211 | −437.964 | 76.729 |
| 300 | 48.568 | 250.967 | 250.668 | 0.090 | −433.224 | −437.993 | 76.261 |
| 350 | 50.908 | 258.636 | 251.268 | 2.579 | −433.555 | −438.761 | 65.482 |
| 400 | 52.791 | 265.561 | 252.629 | 5.173 | −433.850 | −439.484 | 57.391 |
| 450 | 54.299 | 271.870 | 254.422 | 7.852 | −434.121 | −440.172 | 51.094 |
| 500 | 55.509 | 277.656 | 256.460 | 10.598 | −434.378 | −440.831 | 46.053 |
| 600 | 57.279 | 287.944 | 260.871 | 16.243 | −434.874 | −442.075 | 38.486 |
| 700 | 58.469 | 296.868 | 265.390 | 22.035 | −435.374 | −443.235 | 33.075 |
| 800 | 59.297 | 304.733 | 269.826 | 27.925 | −435.882 | −444.324 | 29.011 |
| 900 | 59.892 | 311.753 | 274.102 | 33.886 | −436.441 | −445.347 | 25.847 |
| 1000 | 60.332 | 318.088 | 278.189 | 39.898 | −437.126 | −446.301 | 23.312 |
| 1100 | 60.666 | 323.854 | 282.082 | 45.949 | −438.005 | −447.178 | 21.235 |
| 1200 | 60.925 | 329.144 | 285.787 | 52.029 | −443.067 | −447.845 | 19.494 |
| 1300 | 61.129 | 334.029 | 289.312 | 58.132 | −443.620 | −448.222 | 18.010 |
| 1400 | 61.293 | 338.566 | 292.670 | 64.254 | −444.260 | −448.552 | 16.736 |
| 1500 | 61.427 | 342.799 | 295.873 | 70.390 | −445.000 | −448.834 | 15.630 |
| 1600 | 61.537 | 346.767 | 298.931 | 76.538 | −445.854 | −449.062 | 14.660 |
| 1700 | 61.629 | 350.501 | 301.856 | 82.697 | −446.837 | −449.233 | 13.803 |
| 1800 | 61.706 | 354.026 | 304.657 | 88.864 | −447.962 | −449.343 | 13.040 |
| 1900 | 61.772 | 357.364 | 307.344 | 95.038 | −449.241 | −449.385 | 12.354 |
| 2000 | 61.828 | 360.534 | 309.925 | 101.218 | −465.375 | −448.902 | 11.724 |
| 2100 | 61.876 | 363.551 | 312.407 | 107.403 | −467.750 | −448.020 | 11.144 |
| 2200 | 61.919 | 366.431 | 314.798 | 113.593 | −470.133 | −447.025 | 10.614 |
| 2300 | 61.956 | 369.184 | 317.103 | 119.786 | −472.522 | −445.921 | 10.127 |
| 2400 | 61.988 | 371.822 | 319.328 | 125.984 | −474.917 | −444.713 | 9.679 |
| 2500 | 62.017 | 374.353 | 321.479 | 132.184 | −477.315 | −443.406 | 9.264 |
| 2600 | 62.042 | 376.786 | 323.560 | 138.387 | −479.715 | −442.002 | 8.880 |
| 2700 | 62.065 | 379.127 | 325.575 | 144.592 | −482.115 | −440.506 | 8.522 |
| 2800 | 62.085 | 381.385 | 327.528 | 150.800 | −484.514 | −438.921 | 8.188 |
| 2900 | 62.104 | 383.564 | 329.423 | 157.009 | −486.910 | −437.250 | 7.876 |
| 3000 | 62.120 | 385.670 | 331.263 | 163.221 | −489.301 | −435.497 | 7.583 |
| 3100 | 62.135 | 387.707 | 333.051 | 169.433 | −491.687 | −433.664 | 7.307 |
| 3200 | 62.149 | 389.680 | 334.790 | 175.648 | −494.067 | −431.755 | 7.048 |
| 3300 | 62.161 | 391.592 | 336.482 | 181.863 | −496.438 | −429.771 | 6.803 |
| 3400 | 62.173 | 393.448 | 338.131 | 188.080 | −498.801 | −427.715 | 6.571 |
| 3500 | 62.183 | 395.251 | 339.737 | 194.298 | −501.155 | −425.590 | 6.352 |
| 3600 | 62.193 | 397.003 | 341.304 | 200.516 | −503.499 | −423.398 | 6.143 |
| 3700 | 62.201 | 398.707 | 342.832 | 206.736 | −914.931 | −413.352 | 5.835 |
| 3800 | 62.210 | 400.366 | 344.324 | 212.957 | −916.019 | −399.781 | 5.495 |
| 3900 | 62.217 | 401.982 | 345.782 | 219.178 | −917.152 | −386.181 | 5.172 |
| 4000 | 62.224 | 403.557 | 347.207 | 225.400 | −918.328 | −372.552 | 4.865 |
| 4100 | 62.230 | 405.093 | 348.600 | 231.623 | −919.545 | −358.893 | 4.572 |
| 4200 | 62.236 | 406.593 | 349.963 | 237.846 | −920.802 | −345.203 | 4.293 |
| 4300 | 62.242 | 408.058 | 351.297 | 244.070 | −922.097 | −331.483 | 4.027 |
| 4400 | 62.247 | 409.489 | 352.604 | 250.295 | −923.429 | −317.733 | 3.772 |
| 4500 | 62.252 | 410.888 | 353.883 | 256.519 | −924.796 | −303.951 | 3.528 |
| 4600 | 62.257 | 412.256 | 355.137 | 262.745 | −926.197 | −290.140 | 3.295 |
| 4700 | 62.261 | 413.595 | 356.367 | 268.971 | −927.630 | −276.297 | 3.071 |
| 4800 | 62.265 | 414.906 | 357.573 | 275.197 | −929.093 | −262.423 | 2.856 |
| 4900 | 62.269 | 416.190 | 358.756 | 281.424 | −930.586 | −248.519 | 2.649 |
| 5000 | 62.272 | 417.448 | 359.917 | 287.651 | −932.105 | −234.583 | 2.451 |
| 5100 | 62.275 | 418.681 | 361.058 | 293.878 | −933.652 | −220.618 | 2.260 |
| 5200 | 62.279 | 419.890 | 362.177 | 300.106 | −935.222 | −206.622 | 2.076 |
| 5300 | 62.282 | 421.076 | 363.278 | 306.334 | −936.817 | −192.594 | 1.898 |
| 5400 | 62.284 | 422.241 | 364.359 | 312.562 | −938.434 | −178.538 | 1.727 |
| 5500 | 62.287 | 423.383 | 365.422 | 318.791 | −940.072 | −164.451 | 1.562 |
| 5600 | 62.290 | 424.506 | 366.467 | 325.020 | −941.730 | −150.333 | 1.402 |
| 5700 | 62.292 | 425.608 | 367.495 | 331.249 | −943.408 | −136.187 | 1.248 |
| 5800 | 62.294 | 426.692 | 368.506 | 337.478 | −945.103 | −122.010 | 1.099 |
| 5900 | 62.296 | 427.757 | 369.501 | 343.707 | −946.816 | −107.804 | 0.954 |
| 6000 | 62.298 | 428.804 | 370.481 | 349.937 | −948.546 | −93.569 | 0.815 |

PREVIOUS: September 1963 (1 atm)    CURRENT: September 1963 (1 bar)

## Oxygen Fluoride (OFO) IDEAL GAS $M_r = 50.9972032$ Oxygen Fluoride (OFO) $F_1O_2(g)$

$\Delta_{at}H°(0\ K) = [790 \pm 20]\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = [251 \pm 1]\ J \cdot K^{-1}\ mol^{-1}$

$\Delta_f H°(0\ K) = [381.2 \pm 20]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [378.6 \pm 20]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

| State | $cm^{-1}$ | $g_i$ |
|---|---|---|
| $[^2B_2]$ | 0 | [2] |
| $[^2B_1]$ | [1049.3] | [2] |

Vibrational Frequencies and Degeneracies

| $\nu$, $cm^{-1}$ |
|---|
| [1050](1) |
| [ 600](1) |
| [1200](1) |

Point Group: $[C_{2v}]$ $\sigma = 2$
Bond Distance: F–O = [1.5591]Å
Bond Angle: O–F–O = [76.75]°
Product of the Moments of Inertia: $I_A I_B I_C = [116.8132 \times 10^{-117}]\ g^3 \cdot cm^6$

### Enthalpy of Formation

The enthalpy of formation was calculated based on the molecular geometry optimization of Gosavi *et al.*[1] This calculation yielded the result $\Delta_f H(OFO) - \Delta_f H(FOO) = 356\ kJ \cdot mol^{-1}$. It is assumed that this calculated difference referred to 0 K. In contrast, Gole and Hayes[2] earlier calculated difference of >418 $kJ \cdot mol^{-1}$.

### Heat Capacity and Entropy

The molecular geometry adopted here is that used by Gosavi *et al.*[1] in their quantum mechanical calculations (6–31G basis sets). The structure was calculated to be bent with a O–F–O angle of [76 75°] The bond length was calculated to be [1.5591]Å. The principle moments of inertia (in $g \cdot cm^2$) are: $I_A = 2.9573 \times 10^{-39}$, $I_B = 4.9779 \times 10^{-39}$, and $I_C = 7.9351 \times 10^{-39}$.

Gosavi *et al.*[1] examined the molecular geometry optimization of four electronic states of OFO at the RHF–SCF level with 6–31G and 6–31G* basis sets. In contrast, earlier calculations by Gole and Hayes[2] were based on a double–zeta sp basis set SCF total energy calculations as a function of the OFO bond angle. This latter study suggested a $^2B_1$ ground state with a bond angle of 128.22° (assuming a O–F bond distance of 1.19 Å).

The vibrational frequencies are estimated from the corresponding vibrational frequencies which describe the other OXO(g) molecules, where $X$ = Cl and Br.

### References

[1] R.K. Gosavi, P. Raghunathan and O.P. Stauz, J. Mol. Struct. 133, 25 (1985).
[2] J.L. Gole and E.F. Hayes, Intern. J. Quantum Chem. Symp. No. 5, 519 (1969).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | $J \cdot K^{-1}mol^{-1}$ | | | $kJ \cdot mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | .000 | .000 | INFINITE | −10.538 | 381.180 | 381.180 | INFINITE |
| 50 | 33.258 | 189.213 | 366.723 | −8.875 | 380.667 | 382.618 | −399.719 |
| 100 | 33.370 | 212.280 | 284.393 | −7.211 | 380.149 | 384.770 | −200.983 |
| 150 | 34.218 | 225.938 | 262.776 | −5.526 | 379.650 | 387.190 | −134.832 |
| 200 | 35.991 | 236.005 | 254.874 | −3.774 | 379.210 | 389.772 | −101.798 |
| 250 | 38.446 | 244.290 | 251.951 | −1.915 | 378.860 | 392.454 | −81.999 |
| 298.15 | 41.126 | 251.289 | 251.289 | .000 | 378.622 | 395.096 | −69.219 |
| 300 | 41.230 | 251.544 | 251.290 | .076 | 378.615 | 395.198 | −68.810 |
| 400 | 46.544 | 264.155 | 252.973 | 4.473 | 378.431 | 400.764 | −52.334 |
| 500 | 50.581 | 275.001 | 256.319 | 9.341 | 378.557 | 406.338 | −42.450 |
| 600 | 53.294 | 284.481 | 260.240 | 14.544 | 378.864 | 411.867 | −35.856 |
| 700 | 55.036 | 292.837 | 264.312 | 19.967 | 379.257 | 417.337 | −31.142 |
| 800 | 56.142 | 300.264 | 268.351 | 25.530 | 379.678 | 422.748 | −27.603 |
| 900 | 56.849 | 306.920 | 272.273 | 31.183 | 380.098 | 428.107 | −24.847 |
| 1000 | 57.306 | 312.935 | 276.043 | 36.892 | 380.501 | 433.419 | −22.640 |
| 1100 | 57.606 | 318.412 | 279.650 | 42.639 | 380.878 | 438.693 | −20.832 |
| 1200 | 57.806 | 323.434 | 283.092 | 48.410 | 381.228 | 443.933 | −19.324 |
| 1300 | 57.942 | 328.066 | 286.376 | 54.198 | 381.548 | 449.146 | −18.047 |
| 1400 | 58.034 | 332.364 | 289.509 | 59.997 | 381.838 | 454.334 | −16.951 |
| 1500 | 58.098 | 336.370 | 292.501 | 65.804 | 382.098 | 459.503 | −16.001 |
| 1600 | 58.143 | 340.121 | 295.361 | 71.616 | 382.329 | 464.656 | −15.169 |
| 1700 | 58.174 | 343.647 | 298.099 | 77.432 | 382.531 | 469.795 | −14.435 |
| 1800 | 58.196 | 346.973 | 300.723 | 83.250 | 382.703 | 474.923 | −13.782 |
| 1900 | 58.211 | 350.120 | 303.240 | 89.071 | 382.848 | 480.042 | −13.197 |
| 2000 | 58.222 | 353.106 | 305.660 | 94.892 | 382.967 | 485.154 | −12.671 |
| 2100 | 58.230 | 355.947 | 307.987 | 100.715 | 383.061 | 490.261 | −12.195 |
| 2200 | 58.235 | 358.656 | 310.229 | 106.538 | 383.131 | 495.365 | −11.761 |
| 2300 | 58.238 | 361.244 | 312.391 | 112.362 | 383.180 | 500.465 | −11.366 |
| 2400 | 58.240 | 363.723 | 314.479 | 118.186 | 383.209 | 505.563 | −11.003 |
| 2500 | 58.241 | 366.101 | 316.497 | 124.010 | 383.221 | 510.661 | −10.670 |
| 2600 | 58.242 | 368.385 | 318.449 | 129.834 | 383.218 | 515.759 | −10.362 |
| 2700 | 58.242 | 370.583 | 320.339 | 135.658 | 383.201 | 520.857 | −10.077 |
| 2800 | 58.241 | 372.701 | 322.172 | 141.482 | 383.174 | 525.956 | −9.812 |
| 2900 | 58.240 | 374.745 | 323.949 | 147.307 | 383.138 | 531.055 | −9.565 |
| 3000 | 58.240 | 376.719 | 325.676 | 153.131 | 383.094 | 536.157 | −9.335 |
| 3100 | 58.239 | 378.629 | 327.353 | 158.954 | 383.045 | 541.260 | −9.120 |
| 3200 | 58.238 | 380.478 | 328.985 | 164.778 | 382.992 | 546.364 | −8.918 |
| 3300 | 58.237 | 382.270 | 330.572 | 170.602 | 382.937 | 551.470 | −8.729 |
| 3400 | 58.235 | 384.008 | 332.119 | 176.426 | 382.881 | 556.579 | −8.551 |
| 3500 | 58.234 | 385.697 | 333.625 | 182.249 | 382.824 | 561.688 | −8.383 |
| 3600 | 58.233 | 387.337 | 335.095 | 188.072 | 382.769 | 566.799 | −8.224 |
| 3700 | 58.232 | 388.933 | 336.528 | 193.896 | 382.716 | 571.911 | −8.074 |
| 3800 | 58.231 | 390.485 | 337.928 | 199.719 | 382.665 | 577.026 | −7.932 |
| 3900 | 58.230 | 391.998 | 339.295 | 205.542 | 382.618 | 582.142 | −7.797 |
| 4000 | 58.229 | 393.472 | 340.631 | 211.365 | 382.574 | 587.258 | −7.669 |
| 4100 | 58.228 | 394.910 | 341.937 | 217.188 | 382.535 | 592.376 | −7.547 |
| 4200 | 58.227 | 396.313 | 343.216 | 223.011 | 382.499 | 597.494 | −7.431 |
| 4300 | 58.226 | 397.683 | 344.466 | 228.833 | 382.467 | 602.614 | −7.320 |
| 4400 | 58.226 | 399.022 | 345.691 | 234.656 | 382.439 | 607.733 | −7.215 |
| 4500 | 58.225 | 400.330 | 346.891 | 240.478 | 382.416 | 612.854 | −7.114 |
| 4600 | 58.224 | 401.610 | 348.066 | 246.301 | 382.395 | 617.974 | −7.017 |
| 4700 | 58.223 | 402.862 | 349.219 | 252.123 | 382.378 | 623.096 | −6.925 |
| 4800 | 58.222 | 404.088 | 350.349 | 257.945 | 382.363 | 628.218 | −6.836 |
| 4900 | 58.222 | 405.289 | 351.458 | 263.768 | 382.350 | 633.341 | −6.751 |
| 5000 | 58.221 | 406.465 | 352.547 | 269.590 | 382.339 | 638.463 | −6.670 |
| 5100 | 58.220 | 407.618 | 353.615 | 275.412 | 382.327 | 643.586 | −6.592 |
| 5200 | 58.220 | 408.748 | 354.665 | 281.234 | 382.315 | 648.708 | −6.516 |
| 5300 | 58.219 | 409.857 | 355.696 | 287.056 | 382.302 | 653.832 | −6.444 |
| 5400 | 58.219 | 410.945 | 356.709 | 292.878 | 382.286 | 658.955 | −6.374 |
| 5500 | 58.218 | 412.014 | 357.705 | 298.700 | 382.266 | 664.078 | −6.307 |
| 5600 | 58.218 | 413.063 | 358.684 | 304.521 | 382.241 | 669.203 | −6.242 |
| 5700 | 58.217 | 414.093 | 359.647 | 310.343 | 382.210 | 674.327 | −6.180 |
| 5800 | 58.217 | 415.106 | 360.594 | 316.165 | 382.172 | 679.453 | −6.119 |
| 5900 | 58.216 | 416.101 | 361.527 | 321.986 | 382.125 | 684.577 | −6.061 |
| 6000 | 58.216 | 417.079 | 362.445 | 327.808 | 382.068 | 689.705 | −6.004 |

PREVIOUS: CURRENT, September 1995 (1 bar)

## Oxygen Fluoride (FOO) IDEAL GAS $M_r = 50.9972032$ Oxygen Fluoride (FOO) $F_1O_2(g)$

$S°(298.15 K) = 259.5 \pm 0.2$ J·K⁻¹·mol⁻¹

$\Delta_f H°(0 K) = 27.2 \pm 2$ kJ·mol⁻¹
$\Delta_f H°(298.15 K) = 25.4 \pm 2$ kJ·mol⁻¹

| Electronic Level and Quantum Weights State | $\epsilon_i$, cm⁻¹ | $g_i$ |
|---|---|---|
| $X^2A''$ | 0 | 2 |
| $^2A'$ | 8630 | 2 |

| Vibrational Frequencies and Degeneracies $\nu$, cm⁻¹ |
|---|
| 1486.93(1) |
| 376 (1) |
| 579.32(1) |

Point Group: $C_s$ $\sigma = 1$
Bond Distances: F–O = 1.649Å ; O–O = 1.200Å
Bond Angle: F–O–O = 111.2°
Product of the Moments of Inertia: $I_A I_B I_C = 84.3487 \times 10^{-117}$ g³·cm⁶

### Enthalpy of Formation

The enthalpy of formation of $O_2F(g)$ at 298.15 K, 25.4 ± 2 kJ·mol⁻¹, is based on six experimental results.[1-6] Two earlier studies[7,8] are not included in this analysis. The review by Lyman[4] recommended an enthalpy of formation value based on three experimental studies.[1,7,8] These six experimental studies and their recommended values are:

| Author | $\Delta_f H°$(298 K), kJ·mol⁻¹ | T/K of study | Technique |
|---|---|---|---|
| Lyman and Holland[1] | 23.0 ± 1.7 | 298 K | Kinetic study of reaction F+$O_2$ |
| Holland *et al.*[2] | 24.1 | | Unpublished; kinetic study of reaction F+$O_2$ |
| Shamonima and Kotov[3] | 21.6 | 223–293 K | EPR measurement of rate constants |
| Lyman[4] | 22.9 | | Review |
| Pagsberg *et al.*[5] | 26.1 ± 2.1 | 295–359 K | Spectrokinetic study |
| Campuzano-Jost *et al.*[6] | 24.7 ± 4 | 100–420 K | Spectrokinetic study |

### Heat Capacity and Entropy

The structure of this molecule is bent with a F–O–O angle of 111.2° based on the diode–laser spectrum as obtained by Yamada and Hirota.[9] The bond length is F–O = 1.649Å and O–O = 1.200 Å. Supporting structural information is available from the infrared study of McKellar *et al.*,[10] a microwave study by Bogey *et al.*,[11] and a laser magnetic resonance study by Bley *et al.*[12] The principle moments of inertia (in g·cm²) are: $I_A = 1.0714 \times 10^{-39}$, $I_B = 8.3532 \times 10^{-39}$, and $I_C = 9.4246 \times 10^{-39}$.

There are numerous studies from which vibrational frequencies are derived: Yamada and Hirota,[9] Mckellar *et al.*,[10] Arkell,[13] Noble and Pimentel,[14] Spratley *et al.*,[15] Jacox,[16] and Kim and Campbell.[17] We adopt the recommendations of Jacox,[18] using gas phase values for $\nu_1$ and $\nu_3$ and the nitrogen matrix $X$ value for $\nu_2$.[15] Similar vibrational frequencies were recommended by Lyman[4] in an earlier review.

Lyman stated that the published absorption spectra of $O_2F$ Glissman and Schumacher[19] and Matchuk *et al.*[20] indicated no electronic states at energies below the dissociation energy of the molecule. Jacox[18] in her review, discussed four absorption studies in which a maximum has been observed at 205nm by Chegodaev and Tupikov,[21] 420nm by Fessenden and Schuler,[22] and 445nm Matchuk *et al.*[20] Jacox[16] observed the onset of dissociation near 490nm. Only the X and A states are used in the calculation.

### References

[1] J.L. Lyman and R. Holland, J. Phys. Chem. 92, 7232 (1988).
[2] R.Holland, G.L. Loge and J.L. Lyman, (unpublished).
[3] N.F. Shamonima and A.G. Kotov, Kinet. Katal. 20, 233 (1979).
[4] J.L. Lyman, J. Phys. Chem. Ref. Data 18 (2), 799 (1989).
[5] P.Pagsberg, E. Ratajczak, A. Sillensen and J.T. Jodkowski, Chem. Phys. Lett. 141 (1,2), 88 (1987).
[6] P.Campuzano-Jost, A.E. Crocec, H. Hippler, M. Siefke and J. Troe, J. Chem. Phys. 102 (13), 5317 (1995).
[7] H.J. Schumacher and P. Frisch, Z. physik. Chem. Abt. B27, 1 (1937).
[8] J.B. Levy and B.K.W. Copeland, J. Phys. Chem. 69, 408 (1965).
[9] C. Yamada and E. Hirota, J. Chem. Phys. 80 (10, 4694 (1984).
[10] A.R.W. McKellar, J.B. Burkholder, A. Sinha and C.J. Howard, J. Mol. Spectrosc. 125–127, 288 (1987).
[11] M. Bogey, P.B. Davies, C. Demuynck, J.L. Destombes and T.J. Sears, Mol. Phys. 67 (5), 1033 (1989).
[12] U. Bley, P.B. Davies, M. Grantz, T.J. Sears, and F. Temps, Chem. Phys. 152, 281 (1991).
[13] A. Arkell, J. Am. Chem. Soc. 87, 4057 (1965).
[14] P.N. Noble and G.C. Pimentel, J. Chem. Phys. 44, 3641 (1966).
[15] R.D. Spratley, J.J. Turner and G.C. Pimentel, J.Chem. Phys. 44 (5), 2063 (1966).

Continued on page 1214

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ (J·K⁻¹mol⁻¹) | $S°$ (J·K⁻¹mol⁻¹) | $-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹) | $H°-H°(T_r)$ (kJ·mol⁻¹) | $\Delta_f H°$ (kJ·mol⁻¹) | $\Delta_f G°$ (kJ·mol⁻¹) | log $K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | .000 | .000 | INFINITE | −11.256 | 27.240 | 27.240 | INFINITE |
| 50 | 33.278 | 193.625 | 385.481 | −9.593 | 26.728 | 28.458 | −29.730 |
| 100 | 34.495 | 216.933 | 296.015 | −7.908 | 26.230 | 30.385 | −15.872 |
| 150 | 37.360 | 231.437 | 272.202 | −6.115 | 25.839 | 32.554 | −11.336 |
| 200 | 40.260 | 242.593 | 263.455 | −4.172 | 25.590 | 34.833 | −9.098 |
| 250 | 42.627 | 251.841 | 260.233 | −2.098 | 25.455 | 37.162 | −7.765 |
| 298.15 | 44.453 | 259.511 | 259.511 | .000 | 25.400 | 39.422 | −6.907 |
| 300 | 44.516 | 259.786 | 259.511 | .082 | 25.399 | 39.509 | −6.879 |
| 400 | 47.417 | 273.011 | 261.295 | 4.687 | 25.422 | 44.213 | −5.774 |
| 500 | 49.606 | 283.838 | 264.753 | 9.542 | 25.537 | 48.899 | −5.108 |
| 600 | 51.295 | 293.038 | 268.720 | 14.591 | 25.689 | 53.557 | −4.663 |
| 700 | 52.594 | 301.047 | 272.778 | 19.788 | 25.856 | 58.189 | −4.342 |
| 800 | 53.595 | 308.138 | 276.763 | 25.100 | 26.026 | 62.796 | −4.100 |
| 900 | 54.372 | 314.498 | 280.609 | 30.500 | 26.193 | 67.382 | −3.911 |
| 1000 | 54.983 | 320.259 | 284.290 | 35.969 | 26.355 | 71.950 | −3.758 |
| 1100 | 55.472 | 325.523 | 287.803 | 41.492 | 26.510 | 76.502 | −3.633 |
| 1200 | 55.872 | 330.368 | 291.151 | 47.060 | 26.656 | 81.040 | −3.528 |
| 1300 | 56.210 | 334.854 | 294.342 | 52.665 | 26.793 | 85.567 | −3.438 |
| 1400 | 56.504 | 339.030 | 297.387 | 58.301 | 26.920 | 90.083 | −3.361 |
| 1500 | 56.769 | 342.938 | 300.295 | 63.965 | 27.037 | 94.590 | −3.294 |
| 1600 | 57.015 | 346.609 | 303.076 | 69.654 | 27.145 | 99.090 | −3.235 |
| 1700 | 57.250 | 350.073 | 305.739 | 75.367 | 27.244 | 103.584 | −3.183 |
| 1800 | 57.478 | 353.352 | 308.294 | 81.104 | 27.334 | 108.072 | −3.136 |
| 1900 | 57.702 | 356.466 | 310.748 | 86.863 | 27.418 | 112.555 | −3.094 |
| 2000 | 57.925 | 359.431 | 313.109 | 92.644 | 27.496 | 117.034 | −3.057 |
| 2100 | 58.146 | 362.262 | 315.383 | 98.448 | 27.571 | 121.509 | −3.022 |
| 2200 | 58.366 | 364.972 | 317.575 | 104.273 | 27.644 | 125.981 | −2.991 |
| 2300 | 58.585 | 367.572 | 319.693 | 110.121 | 27.716 | 130.449 | −2.963 |
| 2400 | 58.800 | 370.070 | 321.740 | 115.990 | 27.791 | 134.913 | −2.936 |
| 2500 | 59.012 | 372.474 | 323.722 | 121.881 | 27.870 | 139.375 | −2.912 |
| 2600 | 59.220 | 374.793 | 325.642 | 127.793 | 27.954 | 143.834 | −2.890 |
| 2700 | 59.421 | 377.032 | 327.504 | 133.725 | 28.046 | 148.289 | −2.869 |
| 2800 | 59.616 | 379.196 | 329.312 | 139.677 | 28.146 | 152.741 | −2.849 |
| 2900 | 59.803 | 381.292 | 331.068 | 145.648 | 28.257 | 157.189 | −2.831 |
| 3000 | 59.982 | 383.322 | 332.776 | 151.637 | 28.378 | 161.633 | −2.814 |
| 3100 | 60.152 | 385.292 | 334.439 | 157.644 | 28.512 | 166.073 | −2.798 |
| 3200 | 60.313 | 387.204 | 336.058 | 163.667 | 28.659 | 170.507 | −2.783 |
| 3300 | 60.465 | 389.062 | 337.636 | 169.706 | 28.819 | 174.937 | −2.769 |
| 3400 | 60.606 | 390.869 | 339.175 | 175.760 | 28.992 | 179.363 | −2.756 |
| 3500 | 60.738 | 392.628 | 340.678 | 181.827 | 29.180 | 183.783 | −2.743 |
| 3600 | 60.861 | 394.341 | 342.145 | 187.907 | 29.382 | 188.197 | −2.731 |
| 3700 | 60.973 | 396.010 | 343.578 | 193.999 | 29.597 | 192.606 | −2.719 |
| 3800 | 61.077 | 397.637 | 344.979 | 200.101 | 29.826 | 197.009 | −2.708 |
| 3900 | 61.171 | 399.225 | 346.350 | 206.214 | 30.068 | 201.406 | −2.698 |
| 4000 | 61.256 | 400.775 | 347.691 | 212.335 | 30.323 | 205.795 | −2.687 |
| 4100 | 61.332 | 402.289 | 349.004 | 218.465 | 30.589 | 210.179 | −2.678 |
| 4200 | 61.400 | 403.767 | 350.291 | 224 601 | 30.867 | 214.556 | −2.668 |
| 4300 | 61.461 | 405.213 | 351.551 | 230.744 | 31.156 | 218.926 | −2.659 |
| 4400 | 61.513 | 406.626 | 352.787 | 236.893 | 31.455 | 223.289 | −2.651 |
| 4500 | 61.559 | 408.009 | 353.999 | 243.047 | 31.762 | 227.645 | −2.642 |
| 4600 | 61.598 | 409.363 | 355.188 | 249.205 | 32.077 | 231.994 | −2.634 |
| 4700 | 61.631 | 410.688 | 356.355 | 255.366 | 32.399 | 236.337 | −2.627 |
| 4800 | 61.657 | 411.986 | 357.500 | 261.531 | 32.726 | 240.673 | −2.619 |
| 4900 | 61.678 | 413.257 | 358.625 | 267.698 | 33.058 | 245.002 | −2.612 |
| 5000 | 61.694 | 414.503 | 359.730 | 273.866 | 33.393 | 249.324 | −2.605 |
| 5100 | 61.705 | 415.725 | 360.816 | 280.036 | 33.729 | 253.640 | −2.598 |
| 5200 | 61.712 | 416.924 | 361.884 | 286.207 | 34.066 | 257.948 | −2.591 |
| 5300 | 61.714 | 418.099 | 362.933 | 292.379 | 34.402 | 262.251 | −2.585 |
| 5400 | 61.713 | 419.253 | 363.966 | 298.550 | 34.736 | 266.546 | −2.578 |
| 5500 | 61.708 | 420.385 | 364.981 | 304.721 | 35.065 | 270.835 | −2.572 |
| 5600 | 61.700 | 421.497 | 365.980 | 310.891 | 35.389 | 275.120 | −2.566 |
| 5700 | 61.688 | 422.589 | 366.964 | 317.061 | 35.706 | 279.398 | −2.560 |
| 5800 | 61.674 | 423.661 | 367.932 | 323.229 | 36.014 | 283.671 | −2.555 |
| 5900 | 61.658 | 424.716 | 368.886 | 329.396 | 36.312 | 287.937 | −2.549 |
| 6000 | 61.639 | 425.752 | 369.825 | 335.560 | 36.598 | 292.200 | −2.544 |

PREVIOUS: September 1966 (1 bar)    CURRENT September 1995 (1 bar)

$D_0^\circ = 443.881 \pm 19.2$ kJ·mol$^{-1}$
$S^\circ(298.15\text{ K}) = 224.968 \pm 0.04$ J·K$^{-1}$·mol$^{-1}$

$\Delta_fH^\circ(0\text{ K}) = -51.335 \pm 20.9$ kJ·mol$^{-1}$
$\Delta_fH^\circ(298.15\text{ K}) = -52.250 \pm 20.9$ kJ·mol$^{-1}$

Electronic and Molecular Constants ($\sigma = 1$)

| State | $T_0$, cm$^{-1}$ | $g_i$ | $\omega_e$, cm$^{-1}$ | $\omega_ex_e$, cm$^{-1}$ | $B_e$, cm$^{-1}$ | $\alpha_e$, cm$^{-1}$ | $r_e$, Å |
|---|---|---|---|---|---|---|---|
| $X^3\Sigma$ | 0 | 3 | 846.75 | 4.489 | 0.5665 | 0.00456 | 1.5896 |
| $a^1\Delta$ | 7090.41 | 2 | 858.79 | 4.438 | 0.5699 | 0.00467 | 1.5849 |
| $b^1\Sigma$ | 13353.9 | 1 | 866.14 | 4.51 | 0.5725 | 0.0045 | 1.5812 |
| $B^3\Pi_0$ | 29338.69 | 2 | 436 | [1.5] | 0.4632 | 0.004 | 1.752 |
| $B^3\Pi_1$ | 29481.80 | 2 | 436 | [1.5] | 0.4663 | 0.0038 | 1.752 |
| $B^3\Pi_2$ | 29623.06 | 2 | 436 | [1.5] | 0.4693 | 0.0037 | 1.752 |
| $d^1\Pi$ | 35812.29 | 2 | 413 | [1.5] | 0.4848 | 0.0062 | 1.721 |

## Enthalpy of Formation

There has been no report of a direct experimental determination of $\Delta_fH^\circ$. Sufficient information is available, however, to allow a reasonable estimate of the P–F bond energy ($D_0^\circ$) to be made.

linear Birge–Sponer extrapolation of the ground state vibrational constants leads to $D''(\text{LBX}) = 4.90$ eV. This value can be refined by taking into account the ionic character of the P–F bond. Using relationships developed by Hildenbrand,[1] we adjust the value of $D''(\text{LBX})$ to obtain $D'' = 4.25$ eV. A similar treatment of spectroscopic data[5] for related molecules (AlF, SiF, and ClF) which have well established bond energies indicates that the true $D_0^\circ$ value could be higher than $D''$ by roughly 0.3 eV. Additional support for this is provided by the results of two molecular orbital studies[2,3] which have led to estimates of $D_0^\circ$ of 4.5 eV and 4.65 ± 0.2 eV. The latter value, obtained from Hartree–Fock energies and estimated corrections for correlation effects, is believed to be reliable within the quoted uncertainty. A CNDO/2 MO study,[4] employing energy partitioning concepts, has led to a much higher estimate of $D_0^\circ$ equal to 5.17 eV.

We adopt $D_0^\circ(\text{PF}) = 4.60 \pm 0.2$ eV (106.08 kcal·mol$^{-1}$) which gives $\Delta_fH^\circ(\text{PF}) = -8.546 \pm 5.0$ kcal·mol$^{-1}$ when combined with JANAF auxiliary data[5] for P and F. The adopted $D_0^\circ$ value lies midway between the well established bond energies[5] for SiF (130.3 kcal·mol$^{-1}$) and SF (81.2 kcal·mol$^{-1}$) and is near the mean bond energy ($D = 109.1$ kcal·mol$^{-1}$) in $PF_5$.[5] $\Delta_fH^\circ$ at 298.15 K is −8.345 kcal·mol$^{-1}$.

## Heat Capacity and Entropy

The thermal functions are calculated from the partition function $Q = Q_t \sum g_i Q_r^i Q_v^i \exp(-c_2\epsilon_i/T)$ in which $Q_r^i$ and $Q_v^i$ contain first order corrections for anharmonicity. The electronic and molecular constants are taken from the compilation of Suchard.[6] Values of $\omega_ex_e$ placed in brackets are estimates obtained from data on isoconfigurational states of SO ($A^3\Pi^6$) and PF($B^3\Pi$). Our entropies may contain significant errors, amounting to several tenths of a cal K$^{-1}$·mol$^{-1}$, above 3500 K due to the omission of many unobserved electronic levels which have been predicted[7] to lie above the $b^1\Sigma$ state at 13353.91 cm$^{-1}$. In addition, Skolnik and Goodfriend[8] recently observed in emission a triple headed band system near 5600Å which was tentatively assigned to a $^3\Delta_{inv} - {}^3\Pi_{inv}$ transition of PF. These inverted triplet levels are also omitted since we are unable to estimate their term values with respect to the $X^3\Sigma^-$ ground state.

Our calculations essentially update and extend those previously made on PF by O'Hare.[9] The most significant difference is that our calculations are based on solid phosphorus (Red, V) as the reference state below 704 K rather than the ideal diatomic gas selected by O'Hare.[9]

## References

[1] D. L. Hildenbrand in "Advances in High Temperature Chemistry," Leroy Eyring, ed., Vol. 1, Academic Press, New York, p. 163, (1967).
[2] P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. 54, 4563 (1971).
[3] P. A. G. O'Hare, J. Chem. Phys. 59, 3842 (1973).
[4] A. L. Companion and Y. P. Hsia, J. Mol. Struct. 14, 117 (1972).
[5] JANAF Thermochemical Tables: AlF(g), 12–31–75, SiF(g), 12–31–76; ClF(g) and F(g), 9–30–65, P(g), 6–30–62; SF(g), 6–30–76; $PF_5$(g), 12–31–69.
[6] S. N. Suchard, The Aerospace Corporation, Aerospace Report No. TR–0074 (4641)–6, (March 1974).
[7] A. E. Douglas and M. Frackowiak, Can. J. Phys. 40, 832 (1962).
[8] E. G. Skolnik and P. L. Goodfriend, J. Mol. Spectrosc. 50, 202 (1974).
[9] P. A. G. O'Hare, Argonne National Labortory, ANL 7459, (December 1968).

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p^\circ$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_fH^\circ$ | $\Delta_fG^\circ$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −8.858 | −51.335 | −51.335 | INFINITE |
| 100 | 29.115 | 192.409 | 251.908 | −5.950 | −50.768 | −59.722 | 31.195 |
| 200 | 29.854 | 212.729 | 227.801 | −3.014 | −51.560 | −68.616 | 17.921 |
| 250 | 30.716 | 219.480 | 225.484 | −1.501 | −51.890 | −72.843 | 15.220 |
| 298.15 | 31.620 | 224.968 | 224.968 | 0. | −52.250 | −76.846 | 13.463 |
| 300 | 31.654 | 225.164 | 224.969 | 0.059 | −52.264 | −76.999 | 13.407 |
| 350 | 32.528 | 230.110 | 225.357 | 1.663 | −53.390 | −81.018 | 12.091 |
| 400 | 33.289 | 234.505 | 226.231 | 3.309 | −53.875 | −84.932 | 11.091 |
| 450 | 33.928 | 238.464 | 227.374 | 4.990 | −54.344 | −88.785 | 10.306 |
| 500 | 34.461 | 242.067 | 228.666 | 6.700 | −54.799 | −92.588 | 9.673 |
| 600 | 35.270 | 248.426 | 231.443 | 10.189 | −55.680 | −100.062 | 8.711 |
| 700 | 35.838 | 253.908 | 234.270 | 13.746 | −56.531 | −107.391 | 8.014 |
| 800 | 36.250 | 258.721 | 237.032 | 17.352 | −57.363 | −114 600 | 7.483 |
| 900 | 36.563 | 263.010 | 239.684 | 20.993 | −58.181 | −121.706 | 7.064 |
| 1000 | 36.813 | 266.876 | 242.213 | 24.662 | −58.990 | −128.720 | 6.724 |
| 1100 | 37.025 | 270.394 | 244.617 | 28.355 | −59.790 | −135.655 | 6.442 |
| 1200 | 37.215 | 273.624 | 246.902 | 32.067 | −124.156 | −141.438 | 6.157 |
| 1300 | 37.395 | 276.610 | 249.074 | 35.797 | −124.168 | −142.878 | 5.741 |
| 1400 | 37.573 | 279.388 | 251.141 | 39.546 | −124.177 | −144.317 | 5.385 |
| 1500 | 37.751 | 281.986 | 253.112 | 43.312 | −124.183 | −145.755 | 5.076 |
| 1600 | 37.933 | 284.429 | 254.993 | 47.096 | −124.183 | −147.193 | 4.805 |
| 1700 | 38.120 | 286.734 | 256.793 | 50.899 | −124.177 | −148.631 | 4.567 |
| 1800 | 38.310 | 288.918 | 258.518 | 54.720 | −124.162 | −150.070 | 4.355 |
| 1900 | 38.503 | 290.994 | 260.173 | 58.561 | −124.136 | −151.510 | 4.165 |
| 2000 | 38.697 | 292.974 | 261.764 | 62.421 | −124.098 | −152.952 | 3 995 |
| 2100 | 38.892 | 294.867 | 263.296 | 66.300 | −124.045 | −154.396 | 3.840 |
| 2200 | 39.085 | 296.681 | 264.772 | 70.199 | −123.977 | −155.843 | 3.700 |
| 2300 | 39.276 | 298.422 | 266.198 | 74.117 | −123.890 | −157.293 | 3.572 |
| 2400 | 39 464 | 300.098 | 267.575 | 78.054 | −123 784 | −158.747 | 3.455 |
| 2500 | 39 647 | 301 713 | 268 909 | 82.010 | −123.656 | −160.207 | 3.347 |
| 2600 | 39.825 | 303.271 | 270.201 | 85.983 | −123.506 | −161.672 | 3.248 |
| 2700 | 39.998 | 304.777 | 271.454 | 89.975 | −123.333 | −163.143 | 3.156 |
| 2800 | 40.164 | 306.235 | 272.670 | 93.983 | −123.134 | −164.621 | 3.071 |
| 2900 | 40.324 | 307.647 | 273.852 | 98.007 | −122.910 | −166.106 | 2.992 |
| 3000 | 40.478 | 309.017 | 275.001 | 102.047 | −122.659 | −167.600 | 2.918 |
| 3100 | 40.626 | 310.347 | 276.120 | 106.103 | −122.381 | −169.103 | 2.849 |
| 3200 | 40.767 | 311.639 | 277.210 | 110.172 | −122.076 | −170.614 | 2.785 |
| 3300 | 40.902 | 312.895 | 278.272 | 114.256 | −121.743 | −172.136 | 2.725 |
| 3400 | 41.032 | 314.118 | 279.309 | 118.353 | −121.383 | −173.669 | 2.668 |
| 3500 | 41.157 | 315.310 | 280.320 | 122.462 | −120.995 | −175.212 | 2.615 |
| 3600 | 41.277 | 316.471 | 281.308 | 126.584 | −120.579 | −176.767 | 2.565 |
| 3700 | 41.393 | 317.603 | 282.274 | 130.717 | −120.136 | −178.334 | 2.518 |
| 3800 | 41.506 | 318.709 | 283.218 | 134.862 | −119.666 | −179.913 | 2.473 |
| 3900 | 41.615 | 319.788 | 284.142 | 139.019 | −119.169 | −181.505 | 2.431 |
| 4000 | 41.723 | 320 843 | 285.047 | 143.185 | −118.645 | −183.110 | 2.391 |
| 4100 | 41.828 | 321.875 | 285.932 | 147.363 | −118.095 | −184.728 | 2.353 |
| 4200 | 41.933 | 322.884 | 286.800 | 151.551 | −117.519 | −186.360 | 2.318 |
| 4300 | 42.037 | 323.872 | 287.651 | 155.750 | −116.917 | −188.006 | 2.284 |
| 4400 | 42.141 | 324.839 | 288.485 | 159.958 | −116.290 | −189.667 | 2.252 |
| 4500 | 42.245 | 325.788 | 289.304 | 164.178 | −115.637 | −191.342 | 2.221 |
| 4600 | 42.351 | 326.717 | 290.107 | 168.408 | −114.959 | −193.032 | 2.192 |
| 4700 | 42.459 | 327.629 | 290.896 | 172.648 | −114.256 | −194.736 | 2.164 |
| 4800 | 42.569 | 328.524 | 291.670 | 176.899 | −113.529 | −196.456 | 2.138 |
| 4900 | 42.682 | 329.403 | 292.431 | 181.162 | −112.777 | −198.192 | 2.113 |
| 5000 | 42.798 | 330.267 | 293.179 | 185.436 | −112.000 | −199.943 | 2.089 |
| 5100 | 42.917 | 331.115 | 293.915 | 189.722 | −111.199 | −201.709 | 2.066 |
| 5200 | 43.040 | 331.950 | 294.638 | 194.019 | −110.374 | −203.492 | 2.044 |
| 5300 | 43.167 | 332.771 | 295.350 | 198.330 | −109.523 | −205.291 | 2.023 |
| 5400 | 43.298 | 333.579 | 296.051 | 202.653 | −108.649 | −207.106 | 2.003 |
| 5500 | 43.434 | 334.375 | 296.740 | 206.989 | −107.750 | −208.938 | 1.984 |
| 5600 | 43.575 | 335.159 | 297.419 | 211.340 | −106.826 | −210.785 | 1.966 |
| 5700 | 43.720 | 335.931 | 298.088 | 215.705 | −105.877 | −212.651 | 1.949 |
| 5800 | 43.870 | 336.693 | 298.747 | 220.084 | −104.904 | −214.532 | 1.932 |
| 5900 | 44.025 | 337.444 | 299.397 | 224.479 | −103.905 | −216.431 | 1.916 |
| 6000 | 44.185 | 338.185 | 300.037 | 228.889 | −102.881 | −218.347 | 1 901 |

PREVIOUS: June 1977 (1 atm)    CURRENT· June 1977 (1 bar)

## Phosphorus Fluoride, Ion (PF$^+$) IDEAL GAS $M_r = 49.971614$ Phosphorus Fluoride, Ion (PF$^+$) $F_1P_1^+(g)$

$D_0^\circ = 508.356 \pm 41.8$ kJ·mol$^{-1}$
$S^\circ(298.15\ K) = 224.035 \pm 0.21$ J·K$^{-1}$·mol$^{-1}$

$\Delta_f H^\circ(0\ K) = 895.664 \pm 37.7$ kJ·mol$^{-1}$
$\Delta_f H^\circ(298\ 15\ K) = 901.518 \pm 37.7$ kJ·mol$^{-1}$

Electronic States and Molecular Constants ($\sigma = 1$)

| State | $T_0$, cm$^1$ | $g_i$ | $\omega_e$, cm$^{-1}$ | $\omega_e x_e$, cm$^{-1}$ | $B_e$, cm$^{-1}$ | $\alpha_e$, cm$^{-1}$ | $r_e$, Å |
|---|---|---|---|---|---|---|---|
| $X^2\Pi_{1/2}$ | 0 | 2 | 1053.25 | 5.047 | 0.6360 | 0.0048 | 1.5003 |
| $X^2\Pi_{3/2}$ | 323 95 | 2 | 1053.25 | 5.047 | 0.6360 | 0.0048 | 1.5003 |
| $^2\Sigma$ | 35434.64 | 2 | 619.0 | 4.615 | 0.5593 | 0.0079 | 1.5998 |

### Enthalpy of Formation

Harland *et al* [1] and Torgerson and Westmore[2] reported the appearance potential of PF$^+$ from PF$_3$ as 21.0 ± 0.3 eV and 20.5 ± 0.2 eV, respectively. We use the mean value of AP(PF$^+$/PF$_3$) = 20.75 ± 0.3 eV (478.50 kcal·mol$^{-1}$) in the expression $\Delta_r H^\circ(0\ K) = AP-E^*$ for the process $PF_3(g) + e^- = PF^+(g) + 2\ F(g) + 2e^-$. With the assumption $E^* = 0$, the value of $\Delta_r H^\circ(0\ K)$ gives $\Delta_f H^\circ(PF^+, g, 0\ K) = 217.823 \pm 9.0$ kcal mol$^{-1}$ with $\Delta_f H^\circ(PF_3, g, 0\ K) = -223.97 \pm 0.9$ kcal·mol$^{-1}$ and $\Delta_f H^\circ(F, g, 0\ K) = 18.36 \pm 0.4$ kcal·mol$^{-1}$.[3] We adopted this value. In the same paper, Harland *et al.*[1] also reported AP(PF$^+$/PF$_2$CN) = 19.1 ± 0.2 eV which leads to $\Delta_f H^\circ(PF^+, g, 0\ K) = 233.56 \pm 21\ 3$ kcal·mol$^{-1}$, in reasonable accord with the adopted result.

$\Delta_f H^\circ$ at 298.15 K is 219.641 ± 9.0 kcal·mol$^{-1}$, and the adopted ionization potential (IP) is 9.82 ± 0.61 eV. This IP compares favorably with values predicted from quantum mechanical calculations. These have included (all in eV) 9.5 ± 0.2,[4] 9.6,[5] and 10.35.[6] The latter value is based on IP(P) = 10 98 eV which is 0.5 eV higher than the current best value of 10.486 eV.[7] Recalculation of the results of Companion and Hsia[6] gives IP(PF) = 9.85 eV.

The primary bond dissociation energy $D_0^\circ(PF^+)$ is calculated to be 121.5 kcal·mol$^{-1}$ which can be compared with 106.1 kcal·mol$^{-1}$.[3] in the neutral molecule. The stronger P–F bond in the ion is consistent with theoretical predictions[4-6] that the electron lost from PF occupies an antibonding orbital.

### Heat Capacity and Entropy

The thermal functions are calculated from the partition function $Q = Q_t \Sigma g_i Q_r^i Q_v^i \exp(-c_2\epsilon_i/T)$ in which $Q_r^i$ and $Q_v^i$ contain first order corrections for anharmonicity The electronic and molecular constants are taken from Douglas and Frackowiak[8] who observed one band system in the emission spectrum of PF$^+$ formed by passing a discharge through a mixture of PF$_3$ and He. We treat the ground state as two distinct electronic levels with a splitting of 323 95 cm$^{-1}$. This procedure gives functions which are slightly biased below 400 K. The uncertainty in the value of $S^\circ(298.15\ K)$ includes this error. By analogy with the isoelectronic molecules SiF and PO,[3] other excited states are predicted to lie in the range 20000–30000 cm$^{-1}$. We prefer to omit these levels, but if they do exist our entropies could be slightly low above 4500 K.

### References

[1] P. W.Harland, D. W.H. Rankin and J. C. J. Thynne, Int. J. Mass Spectr. Ion Phys. **13**, 395 (1974).
[2] D. F. Torgerson and J. B. Westmore, Can. J. Chem. 53, 933 (1975).
[3] JANAF Thermochemical Tables: PF$_3$(g), 12–31–69; F(g), 9–30–65; SiF(g), 12–31–76, PO(g), 6–30–71; PF(g), 6–30–77.
[4] P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. 54, 4563 (1971).
[5] P. A. G. O'Hare, J. Chem. Phys. 59, 3842 (1973).
[6] A. L. Companion and Y. P.Hsia, J. Mol. Struct. 14, 117 (1972).
[7] H. M. Rosenstock, K. Draxl, et al, J. Phys. Chem. Ref. Data 6, Suppl. 1 (1977).
[8] A. E. Douglas and M. Frackowiak, Can. J. Phys. 40, 832 (1962).

Enthalpy Reference Temperature = $T_r$ = 298.15 K
Standard State Pressure = $p^\circ$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −9 430 | 895.664 | | |
| 100 | 30.783 | 188.512 | 253.369 | −6.486 | | | |
| 200 | 33.019 | 210.776 | 227.079 | −3.261 | | | |
| 250 | 33.221 | 218.167 | 224.584 | −1.604 | | | |
| 298.15 | 33.428 | 224.035 | 224.035 | 0. | 901.518 | 870.945 | −152.586 |
| 300 | 33.438 | 224.242 | 224.036 | 0.062 | 901.545 | 870.755 | −151.612 |
| 350 | 33.734 | 229.418 | 224.444 | 1 741 | 901.533 | 865.638 | −129.189 |
| 400 | 34.078 | 233.945 | 225.354 | 3.436 | 902.136 | 860.469 | −112.366 |
| 450 | 34.431 | 237.979 | 226.537 | 5.149 | 902.739 | 855.225 | −99.272 |
| 500 | 34.767 | 241.624 | 227.866 | 6.879 | 903.343 | 849.913 | −88 790 |
| 600 | 35.352 | 248.017 | 230.707 | 10.386 | 904.559 | 839.113 | −73.051 |
| 700 | 35.812 | 253.502 | 233.581 | 13.945 | 905.788 | 828.108 | −61 794 |
| 800 | 36.168 | 258.308 | 236.377 | 17.545 | 907.029 | 816.927 | −53.340 |
| 900 | 36.446 | 262.585 | 239.056 | 21.176 | 908.279 | 805.589 | −46.755 |
| 1000 | 36.666 | 266.437 | 241.605 | 24.832 | 909.536 | 794.112 | −41.480 |
| 1100 | 36.843 | 269.940 | 244.024 | 28.508 | 910.798 | 782.508 | −37.158 |
| 1200 | 36.989 | 273.152 | 246.319 | 32.200 | 848.491 | 771.868 | −33.599 |
| 1300 | 37.111 | 276.118 | 248.499 | 35.905 | 850.533 | 765.400 | −30.754 |
| 1400 | 37.215 | 278.872 | 250.571 | 39.621 | 852.570 | 758.775 | −28.310 |
| 1500 | 37.305 | 281.443 | 252.545 | 43.347 | 854.602 | 752.004 | −26.187 |
| 1600 | 37.383 | 283.853 | 254.427 | 47.082 | 856.631 | 745.098 | −24.325 |
| 1700 | 37.454 | 286.121 | 256.225 | 50.824 | 858.655 | 738.065 | −22.678 |
| 1800 | 37.517 | 288.264 | 257.946 | 54.572 | 860.676 | 730.913 | −21.211 |
| 1900 | 37.574 | 290.294 | 259.596 | 58.327 | 862.694 | 723.649 | −19.895 |
| 2000 | 37.627 | 292.223 | 261.179 | 62.087 | 864.711 | 716.279 | −18.707 |
| 2100 | 37.676 | 294.060 | 262.702 | 65.852 | 866.728 | 708.808 | −17.631 |
| 2200 | 37.722 | 295.814 | 264.167 | 69.622 | 868 746 | 701.240 | −16.650 |
| 2300 | 37.765 | 297.491 | 265.580 | 73.397 | 870.768 | 693.581 | −15 752 |
| 2400 | 37.806 | 299.099 | 266.943 | 77.175 | 872.794 | 685.834 | −14.927 |
| 2500 | 37.845 | 300.644 | 268.260 | 80.958 | 874.827 | 678.002 | −14.166 |
| 2600 | 37.883 | 302.129 | 269.535 | 84.744 | 876.868 | 670.089 | −13.462 |
| 2700 | 37.919 | 303.559 | 270.769 | 88.534 | 878.920 | 662.097 | −12.809 |
| 2800 | 37.954 | 304.939 | 271.964 | 92.328 | 880.982 | 654.029 | −12.201 |
| 2900 | 37.987 | 306.271 | 273.125 | 96.125 | 883.058 | 645.887 | −11.634 |
| 3000 | 38.020 | 307.559 | 274.251 | 99.925 | 885.148 | 637.673 | −11.103 |
| 3100 | 38.053 | 308.807 | 275.346 | 103.729 | 887.252 | 629.389 | −10.605 |
| 3200 | 38.084 | 310.015 | 276.410 | 107.536 | 889.373 | 621.037 | −10.137 |
| 3300 | 38.115 | 311.188 | 277.447 | 111.346 | 891.511 | 612.619 | −9.697 |
| 3400 | 38.145 | 312.326 | 278.456 | 115.159 | 893.666 | 604.135 | −9.281 |
| 3500 | 38.176 | 313.432 | 279.439 | 118.975 | 895.839 | 595.588 | −8.889 |
| 3600 | 38.205 | 314.508 | 280.399 | 122.794 | 898.031 | 586.978 | −8.517 |
| 3700 | 38.235 | 315.555 | 281.335 | 126.616 | 900.241 | 578.308 | −8.164 |
| 3800 | 38.264 | 316.575 | 282.249 | 130.441 | 902.470 | 569.577 | −7.829 |
| 3900 | 38.293 | 317.570 | 283.142 | 134.269 | 904.717 | 560.787 | −7.511 |
| 4000 | 38.322 | 318.539 | 284.015 | 138.099 | 906.983 | 551.940 | −7.208 |
| 4100 | 38.351 | 319.486 | 284.868 | 141.933 | 909.268 | 543.035 | −6.918 |
| 4200 | 38.380 | 320.411 | 285.703 | 145.769 | 911.571 | 534.075 | −6.642 |
| 4300 | 38.409 | 321.314 | 286.521 | 149.609 | 913.893 | 525.059 | −6.378 |
| 4400 | 38.438 | 322.197 | 287.322 | 153.451 | 916.232 | 515.990 | −6.126 |
| 4500 | 38.468 | 323.061 | 288.107 | 157.297 | 918.590 | 506.867 | −5.884 |
| 4600 | 38.498 | 323.907 | 288.876 | 161.145 | 920.965 | 497.691 | −5.651 |
| 4700 | 38.528 | 324.736 | 289.630 | 164.996 | 923.357 | 488.464 | −5.429 |
| 4800 | 38.559 | 325.547 | 290.370 | 168.851 | 925.766 | 479.186 | −5.215 |
| 4900 | 38.591 | 326.342 | 291.096 | 172.708 | 928.191 | 469.857 | −5.009 |
| 5000 | 38.622 | 327.122 | 291.809 | 176.569 | 930.633 | 460.478 | −4.811 |
| 5100 | 38.655 | 327.887 | 292.509 | 180.433 | 933.091 | 451.051 | −4.620 |
| 5200 | 38.688 | 328.638 | 293.196 | 184.300 | 935.565 | 441.575 | −4.436 |
| 5300 | 38.722 | 329.376 | 293.872 | 188.170 | 938.054 | 432.051 | −4.258 |
| 5400 | 38.757 | 330.100 | 294.536 | 192.044 | 940.558 | 422.481 | −4.087 |
| 5500 | 38.793 | 330.811 | 295.189 | 195.922 | 943.076 | 412.863 | −3.921 |
| 5600 | 38.830 | 331.511 | 295.832 | 199.803 | 945.609 | 403.201 | −3.761 |
| 5700 | 38.867 | 332.198 | 296.464 | 203.688 | 948.157 | 393.492 | −3.606 |
| 5800 | 38.906 | 332.875 | 297.085 | 207.576 | 950.718 | 383.739 | −3.456 |
| 5900 | 38.946 | 333.540 | 297.698 | 211.469 | 953.293 | 373.941 | −3.311 |
| 6000 | 38.987 | 334.195 | 298.301 | 215.366 | 955.882 | 364.100 | −3.170 |

PREVIOUS June 1977 (1 atm)
*CURRENT. June 1977 (1 bar)*

## Phosphorus Fluoride, Ion ($PF^-$) IDEAL GAS $M_r = 49.972712$ Phosphorus Fluoride, Ion ($PF^-$) $F_1P_1^-(g)$

$D_0^\circ = 222.170 \pm 71.1\ \text{kJ·mol}^{-1}$
$S^\circ(298.15\ \text{K}) = [225.218 \pm 2.1]\ \text{J·K}^{-1}\text{·mol}^{1}$

$\Delta_f H^\circ(0\ \text{K}) = -157.592 \pm 69.0\ \text{kJ·mol}^{-1}$
$\Delta_f H^\circ(298.15\ \text{K}) = [-164.046 \pm 69.0]\ \text{kJ·mol}^{-1}$

Electronic Levels and Quantum Weights

| State | $\epsilon_i$, $\text{cm}^{1}$ | $g_i$ |
|---|---|---|
| $[^2\Pi_{3/2}]$ | 0 | [2] |
|  | [350] | [2] |
|  | [25000] | [4] |

$\omega_e = [840]\ \text{cm}^{-1}$ $\omega_e x_e = [4.6]\ \text{cm}^{-1}$ $\sigma = 1$
$B_e = [0.56626]\ \text{cm}^{-1}$ $\alpha_e = [0.00424]\ \text{cm}^{-1}$ $r_e = [1.59]$ Å

### Enthalpy of Formation

We calculate the enthalpy of formation at 0 K as the difference between $\Delta_f H^\circ(\text{PF, g, 0 K}) = -8.55 \pm 5.0\ \text{kcal mol}^{-1}$,[1] and the selected value of $1.1 \pm 0.5$ eV ($25.366\ \text{kcal·mol}^{-1}$) for the electron affinity (EA) of PF. The value of EA refers to the vertical electron detachment process $PF^-(g) = PF(g) + e^-$ and is taken from the molecular orbital study of O'Hare.[2] This value was obtained from Hartree Fock energies and estimated corrections for correlation effects The estimated uncertainty in EA is 0.5 eV which should be adequate to cover the possibility that the adiabatic value is lower than the vertical EA. Other theoretical predictions of EA include 2.55 eV[3] and 1.4 eV.[4]

$\Delta_f H^\circ$ at 298.15 K is $-35.035\ \text{kcal mol}^{-1}$, and the primary bond dissociation energy (Products $P(g) + F^-(g)$) is $53.1\ \text{kcal·mol}^{-1}$ The latter value can be compared with $D_0^\circ(\text{PF}) = 106.1\ \text{kcal·mol}^{-1}$,[1] indicating that the P–F bond is much weaker in the anion relative to the neutral molecule. This is consistent with MO predictions[2,4] which indicate that the electron captured by PF occupies an antibonding orbital located primarily on the phosphorus atom.

Our thermal functions indicate that $PF^-$ is thermodynamically stable with respect to dissociation ($P + F^-$) below 2500 K. These predictions agree qualitatively with the results of MacNeil and Thynne[5] who observed $PF^-$ in the negative ion mass spectrum of $PF_3$. Their reported appearance potential, $\text{AP}(PF^-/PF_3) = 11.4 \pm 0.1$ eV, gives $\text{EA(PF)} = -0.47$ eV assuming that the dissociative electron capture process is $PF_3(g) + e^- = PF^-(g) + 2F(g)$. We believe this value is too low probably because of excess kinetic and/or excitation energies amounting to roughly 1.5 eV.

### Heat Capacity and Entropy

The bond length and vibrational constants are assumed to lie between those for PF and SF.[1] The value of $B_e$ is obtained from $r_e$. We calculate $\alpha_e$ from the other constants assuming a Morse potential function.

The ground state electronic configuration ($^2\Pi_{3/2}$), ground state splitting ($A = 350\ \text{cm}^{-1}$), and excited state ($^2\Pi$) at $25000\ \text{cm}^{-1}$ are estimated by analogy with those for the isoelectronic molecule SF.[1] The major source of error in our calculations below 500 K arises from the uncertainty in the ground state splitting. With $A = 0\ \text{cm}^{-1}$, the value of $S^\circ(298.15\ \text{K})$ increases by $0.5\ \text{cal K}^{-1}\text{·mol}^{-1}$. At higher temperatures the differences in S become smaller, indicating that the uncertainty in the adopted entropies above 1000 K is less than $0.2\ \text{cal K}^{-1}\text{·mol}^{-1}$.

### References

[1] JANAF Thermochemical Tables: PF(g), 6–30–77, SF(g), 6–30–76.
[2] P. A. G. O'Hare, J. Chem. Phys. 59, 3842 (1973).
[3] A. L. Companion and Y P. Hsia, J. Mol. Struct. 14, 117 (1972).
[4] P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. 54, 4563 (1971).
[5] K. A. G. MacNeil and J C. J Thynne, J. Phys. Chem. 74, 2257 (1970).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p^\circ$ = 0.1 MPa

|  | $\text{J·K}^{-1}\text{mol}^{-1}$ |  |  | $\text{kJ·mol}^{-1}$ |  |  |  |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ - H^\circ(T_r)]/T$ | $H^\circ - H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −9.516 | −157.592 |  |  |
| 100 | 30.469 | 189.364 | 255.166 | −6.580 |  |  |  |
| 200 | 33.518 | 211.573 | 228.364 | −3.358 |  |  |  |
| 250 | 34.258 | 219.137 | 225.788 | −1.663 |  |  |  |
| 298.15 | 34.786 | 225.218 | 225.218 | 0. | −164.046 | −182.462 | 31.967 |
| 300 | 34.804 | 225.433 | 225.218 | 0.064 | −164.093 | −182.576 | 31.789 |
| 350 | 35.242 | 230.832 | 225.644 | 1.816 | −166.111 | −185.484 | 27.682 |
| 400 | 35.603 | 235.562 | 226.594 | 3.587 | −167.511 | −188.156 | 24.571 |
| 450 | 35.903 | 239.774 | 227.829 | 5.375 | −168.912 | −190.652 | 22.130 |
| 500 | 36.152 | 243.570 | 229.216 | 7.177 | −170.315 | −192.992 | 20.162 |
| 600 | 36.535 | 250.197 | 232.177 | 10.812 | −173 128 | −197.264 | 17.173 |
| 700 | 36.810 | 255.850 | 235.165 | 14.480 | −175 947 | −201.064 | 15.004 |
| 800 | 37.016 | 260.780 | 238.065 | 18.172 | −178.771 | −204.459 | 13.350 |
| 900 | 37.175 | 265.149 | 240.836 | 21.882 | −181.599 | −207.500 | 12.043 |
| 1000 | 37.302 | 269.073 | 243.467 | 25.606 | −184.432 | −210.226 | 10.981 |
| 1100 | 37.407 | 272.633 | 245.959 | 29.341 | −187.267 | −212.669 | 10.099 |
| 1200 | 37.496 | 275.892 | 248.320 | 33.087 | −253.678 | −213 774 | 9.305 |
| 1300 | 37.574 | 278.896 | 250.558 | 36.840 | −255.746 | −210.365 | 8.453 |
| 1400 | 37.643 | 281.683 | 252.683 | 40.601 | −257.821 | −206.797 | 7.716 |
| 1500 | 37.705 | 284.283 | 254.704 | 44.369 | −259.904 | −203.079 | 7.072 |
| 1600 | 37.763 | 286.718 | 256.629 | 48.142 | −261 994 | −199.223 | 6.504 |
| 1700 | 37.816 | 289.009 | 258.467 | 51.921 | −264.090 | −195.235 | 5.999 |
| 1800 | 37.866 | 291.172 | 260.224 | 55.705 | −266.191 | −191.124 | 5.546 |
| 1900 | 37.914 | 293.220 | 261.908 | 59.494 | −268.295 | −186.897 | 5.138 |
| 2000 | 37 960 | 295.166 | 263.522 | 63.288 | −270.402 | −182.558 | 4.768 |
| 2100 | 38.004 | 297.019 | 265.074 | 67.086 | −272.509 | −178.114 | 4.430 |
| 2200 | 38.046 | 298.788 | 266.566 | 70.889 | −274.615 | −173.570 | 4.121 |
| 2300 | 38.088 | 300.481 | 268.004 | 74.695 | −276 719 | −168.930 | 3.837 |
| 2400 | 38.128 | 302.102 | 269.391 | 78.506 | −278.817 | −164.198 | 3.574 |
| 2500 | 38.168 | 303.660 | 270.731 | 82.321 | −280.909 | −159.379 | 3.330 |
| 2600 | 38.208 | 305.157 | 272.027 | 86.140 | −282.993 | −154 477 | 3.103 |
| 2700 | 38.247 | 306.600 | 273.281 | 89.963 | −285.066 | −149.495 | 2.892 |
| 2800 | 38.286 | 307.992 | 274.496 | 93.789 | −287.128 | −144.436 | 2.694 |
| 2900 | 38.325 | 309.336 | 275.674 | 97.620 | −289.176 | −139.303 | 2.509 |
| 3000 | 38.364 | 310.636 | 276.818 | 101.454 | −291.209 | −134.101 | 2.335 |
| 3100 | 38.404 | 311.895 | 277.929 | 105.293 | −293.227 | −128.831 | 2.171 |
| 3200 | 38.444 | 313.114 | 279.010 | 109.135 | −295.228 | −123.495 | 2.016 |
| 3300 | 38.484 | 314.298 | 280.061 | 112.981 | −297.211 | −118.098 | 1.869 |
| 3400 | 38.526 | 315.448 | 281.085 | 116.832 | −299.175 | −112.641 | 1.731 |
| 3500 | 38.568 | 316.565 | 282.083 | 120.687 | −301.121 | −107.126 | 1.599 |
| 3600 | 38.611 | 317.652 | 283.056 | 124.545 | −303.046 | −101.556 | 1 474 |
| 3700 | 38.656 | 318.710 | 284.005 | 128.409 | −304.952 | −95.933 | 1.354 |
| 3800 | 38.702 | 319.742 | 284.932 | 132.277 | −306.838 | −90.259 | 1.241 |
| 3900 | 38.750 | 320.748 | 285.838 | 136.149 | −308.703 | −84.535 | 1.132 |
| 4000 | 38.799 | 321.730 | 286.723 | 140.027 | −310.547 | −78.763 | 1.029 |
| 4100 | 38.849 | 322.688 | 287.588 | 143.909 | −312.371 | −72.946 | 0.929 |
| 4200 | 38.902 | 323.625 | 288.435 | 147.797 | −314.174 | −67.084 | 0.834 |
| 4300 | 38.956 | 324.541 | 289.264 | 151.689 | −315.956 | −61.180 | 0.743 |
| 4400 | 39.012 | 325.437 | 290.076 | 155.588 | −317.718 | −55.235 | 0.656 |
| 4500 | 39.070 | 326.315 | 290.872 | 159.492 | −319.459 | −49.250 | 0.572 |
| 4600 | 39.130 | 327.174 | 291.652 | 163.402 | −321.180 | −43.226 | 0.491 |
| 4700 | 39.191 | 328.016 | 292.417 | 167.318 | −322.880 | −37.165 | 0.413 |
| 4800 | 39.255 | 328.842 | 293.167 | 171.240 | −324.560 | −31.068 | 0.338 |
| 4900 | 39.320 | 329.652 | 293.903 | 175.169 | −326.220 | −24.937 | 0.266 |
| 5000 | 39.388 | 330.447 | 294.626 | 179.104 | −327.861 | −18.771 | 0.196 |
| 5100 | 39.457 | 331.228 | 295.336 | 183.047 | −329.482 | −12.574 | 0.129 |
| 5200 | 39.528 | 331.995 | 296.034 | 186.996 | −331.084 | −6.344 | 0.064 |
| 5300 | 39.601 | 332.748 | 296.719 | 190.952 | −332.666 | −0.084 | 0.001 |
| 5400 | 39.675 | 333.489 | 297.394 | 194.916 | −334.229 | 6.206 | −0.060 |
| 5500 | 39.751 | 334.218 | 298.057 | 198.887 | −335.774 | 12.524 | −0.119 |
| 5600 | 39.828 | 334.935 | 298.709 | 202.866 | −337.300 | 18.871 | −0.176 |
| 5700 | 39.907 | 335.640 | 299.350 | 206.853 | −338.808 | 25.245 | −0.231 |
| 5800 | 39.988 | 336.335 | 299.982 | 210.848 | −340.298 | 31.644 | −0.285 |
| 5900 | 40.069 | 337.019 | 300.604 | 214.850 | −341.770 | 38.070 | −0.337 |
| 6000 | 40.152 | 337.694 | 301.217 | 218.862 | −343.224 | 44.520 | −0 388 |

PREVIOUS. June 1977 (1 atm) CURRENT June 1977 (1 bar)

## Thiophosphoryl Fluoride (PSF) IDEAL GAS $M_r = 82.032163$ Thiophosphoryl Fluoride (PSF) $F_1P_1S_1(g)$

$S°(298.15\ K) = [277.717 \pm 12.6]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = [-169.189 \pm 62.8]\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [-172.268 \pm 62.8]\ kJ{\cdot}mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, cm$^{-1}$ |
|---|
| [940](1) |
| [740](1) |
| [400](1) |

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: $C_s$
Product of the Moments of Inertia: $I_A I_B I_C = [7.999 \times 10^{-114}]\ g^3{\cdot}cm^6$

### Enthalpy of Formation

The $\Delta_f H°(298.15\ K)$ was estimated by Henderson and Scheffee.[1]

### Heat Capacity and Entropy

The vibrational frequencies were estimated by comparison with the corresponding frequencies of PF(g), PS(g), and $PF_2(g)$. The vibrational levels of $PF_2(g)$ in turn were estimated by Gordon.[2] The entropy was estimated by Henderson and Scheffee.[1] The product of the moment of inertia was derived from the estimated entropy.

### References

[1] C. B. Henderson and R. S. Scheffee, "Survey of Thermochemical Data," Atlantic Research Corp., Alexandria, Virginia, (January 1960).
[2] J. S. Gordon, "Thermodynamic Data for Combustion Products," Thiokol Corp., Reaction Motors Division, Denville, New Jersey, (January 1960).

Enthalpy Reference Temperature = $T_r$ = 298.15 K; Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −11.106 | −169.189 | −169.189 | INFINITE |
| 100 | 34.160 | 235.944 | 313.591 | −7.765 | −168.879 | −180.934 | 94.510 |
| 200 | 39.208 | 261.056 | 281.619 | −4.113 | −170.596 | −192.590 | 50.299 |
| 250 | 41.993 | 270.107 | 278.435 | −2.082 | −171.428 | −197.993 | 41.368 |
| 298.15 | 44.439 | 277.717 | 277.717 | 0. | −172.268 | −203.034 | 35.571 |
| 300 | 44.526 | 277.992 | 277.718 | 0.082 | −172.301 | −203.224 | 35.385 |
| 350 | 46.695 | 285.023 | 278.268 | 2.364 | −173.915 | −208.237 | 31.078 |
| 400 | 48.493 | 291.380 | 279.516 | 4.746 | −177.096 | −212.986 | 27.813 |
| 450 | 49.962 | 297.179 | 281.161 | 7.208 | −178.709 | −217.384 | 25.233 |
| 500 | 51.159 | 302.508 | 283.033 | 9.737 | −180.348 | −221.590 | 23.149 |
| 600 | 52.936 | 312.003 | 287.090 | 14.948 | −183.091 | −229.573 | 19.986 |
| 700 | 54.148 | 320.259 | 291.251 | 20.306 | −185.489 | −237.127 | 17.695 |
| 800 | 54.999 | 327.549 | 295.342 | 25.765 | −187.677 | −244.352 | 15.955 |
| 900 | 55.615 | 334.064 | 299.289 | 31.298 | −242.862 | −250.231 | 14.523 |
| 1000 | 56.073 | 339.949 | 303.065 | 36.883 | −243.610 | −251.010 | 13.111 |
| 1100 | 56.421 | 345.310 | 306.666 | 42.509 | −244.348 | −251.714 | 11.953 |
| 1200 | 56.692 | 350.231 | 310.094 | 48.165 | −308.657 | −251.273 | 10.938 |
| 1300 | 56.906 | 354.778 | 313.358 | 53.845 | −308.621 | −246.492 | 9.904 |
| 1400 | 57.078 | 359.002 | 316.470 | 59.545 | −308.598 | −241.714 | 9.018 |
| 1500 | 57.218 | 362.944 | 319.438 | 65.260 | −308.588 | −236.937 | 8.251 |
| 1600 | 57.334 | 366.641 | 322.274 | 70.988 | −308.593 | −232.160 | 7.579 |
| 1700 | 57.430 | 370.120 | 324.987 | 76.726 | −308.614 | −227.383 | 6.987 |
| 1800 | 57.512 | 373.405 | 327.586 | 82.473 | −308.649 | −222.604 | 6.460 |
| 1900 | 57.581 | 376.516 | 330.081 | 88.228 | −308.699 | −217.822 | 5.988 |
| 2000 | 57.640 | 379.471 | 332.477 | 93.989 | −308.761 | −213.037 | 5.564 |
| 2100 | 57.692 | 382.285 | 334.782 | 99.756 | −308.834 | −208.250 | 5.180 |
| 2200 | 57.736 | 384.970 | 337.003 | 105.527 | −308.915 | −203.458 | 4.831 |
| 2300 | 57.775 | 387.537 | 339.145 | 111.303 | −309.003 | −198.662 | 4.512 |
| 2400 | 57.810 | 389.997 | 341.213 | 117.082 | −309.095 | −193.863 | 4.219 |
| 2500 | 57.840 | 392.357 | 343.211 | 122.864 | −309.189 | −189.060 | 3.950 |
| 2600 | 57.867 | 394.626 | 345.146 | 128.650 | −309.284 | −184.253 | 3.702 |
| 2700 | 57.891 | 396.811 | 347.019 | 134.438 | −309.375 | −179.442 | 3.472 |
| 2800 | 57.912 | 398.916 | 348.835 | 140.228 | −309.462 | −174.628 | 3.258 |
| 2900 | 57.932 | 400.949 | 350.597 | 146.020 | −309.544 | −169.811 | 3.059 |
| 3000 | 57.949 | 402.913 | 352.309 | 151.814 | −309.618 | −164.992 | 2.873 |
| 3100 | 57.965 | 404.814 | 353.972 | 157.610 | −309.683 | −160.170 | 2.699 |
| 3200 | 57.980 | 406.654 | 355.589 | 163.407 | −309.738 | −155.346 | 2.536 |
| 3300 | 57.993 | 408.439 | 357.164 | 169.206 | −309.782 | −150.520 | 2.383 |
| 3400 | 58.005 | 410.170 | 358.698 | 175.006 | −309.815 | −145.694 | 2.238 |
| 3500 | 58.016 | 411.852 | 360.193 | 180.807 | −309.835 | −140.866 | 2.102 |
| 3600 | 58.026 | 413.486 | 361.650 | 186.609 | −309.844 | −136.038 | 1.974 |
| 3700 | 58.035 | 415.076 | 363.073 | 192.412 | −309.840 | −131.210 | 1.852 |
| 3800 | 58.044 | 416.624 | 364.462 | 198.216 | −309.824 | −126.383 | 1.737 |
| 3900 | 58.052 | 418.132 | 365.819 | 204.021 | −309.795 | −121.556 | 1.628 |
| 4000 | 58.059 | 419.601 | 367.145 | 209.826 | −309.755 | −116.730 | 1.524 |
| 4100 | 58.066 | 421.035 | 368.442 | 215.632 | −309.702 | −111.905 | 1.426 |
| 4200 | 58.072 | 422.435 | 369.711 | 221.439 | −309.638 | −107.081 | 1.332 |
| 4300 | 58.078 | 423.801 | 370.953 | 227.247 | −309.564 | −102.259 | 1.242 |
| 4400 | 58.083 | 425.136 | 372.169 | 233.055 | −309.479 | −97.439 | 1.157 |
| 4500 | 58.089 | 426.442 | 373.361 | 238.863 | −309.384 | −92.621 | 1.075 |
| 4600 | 58.093 | 427.718 | 374.529 | 244.672 | −309.279 | −87.805 | 0.997 |
| 4700 | 58.098 | 428.968 | 375.674 | 250.482 | −309.166 | −82.992 | 0.922 |
| 4800 | 58.102 | 430.191 | 376.797 | 256.292 | −309.045 | −78.181 | 0.851 |
| 4900 | 58.106 | 431.389 | 377.899 | 262.102 | −308.916 | −73.372 | 0.782 |
| 5000 | 58.110 | 432.563 | 378.980 | 267.913 | −308.781 | −68.567 | 0.716 |
| 5100 | 58.113 | 433.714 | 380.042 | 273.724 | −308.638 | −63.764 | 0.653 |
| 5200 | 58.117 | 434.842 | 381.085 | 279.536 | −308.490 | −58.964 | 0.592 |
| 5300 | 58.120 | 435.949 | 382.110 | 285.348 | −308.337 | −54.167 | 0.534 |
| 5400 | 58.123 | 437.036 | 383.117 | 291.160 | −308.179 | −49.372 | 0.478 |
| 5500 | 58.126 | 438.102 | 384.107 | 296.972 | −308.017 | −44.581 | 0.423 |
| 5600 | 58.128 | 439.150 | 385 081 | 302.785 | −307.851 | −39.793 | 0.371 |
| 5700 | 58.131 | 440.179 | 386.039 | 308.598 | −307.681 | −35.008 | 0.321 |
| 5800 | 58.133 | 441.190 | 386.981 | 314.411 | −307.508 | −30.226 | 0.272 |
| 5900 | 58.135 | 442.183 | 387.908 | 320.225 | −307.333 | −25.446 | 0.225 |
| 6000 | 58.138 | 443.160 | 388.821 | 326.038 | −307.156 | −20.670 | 0.180 |

PREVIOUS: *September 1962 (1 atm)* CURRENT: *September 1962 (1 bar)*

## Lead Fluoride (PbF) IDEAL GAS $M_r = 226.198403$ Lead Fluoride (PbF) $F_1Pb_1(g)$

$\Delta_f H^\circ(0\ K) = -78.243 \pm 10.5\ kJ \cdot mol^{-1}$

$S^\circ(298.15\ K) = 249.957 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H^\circ(298.15\ K) = -80.266 \pm 10.5\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

| State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|
| $X^2\Pi_{1/2}$ | 0 | 2 |
| $^2\Pi_{3/2}$ | 8264.7 | 2 |
| $A[^2\Sigma]$ | 22566.6 | [2] |
| $B^2\Sigma^+$ | 35643 | 2 |

$\omega_e = 507.2\ cm^{-1}$ $\omega_e x_e = 2.30\ cm^{-1}$ $\sigma = 1$

$B_e = 0.2288\ cm^{-1}$ $\alpha_e = [0\ 0013]\ cm^{-1}$ $r_e = 2.058$ Å

### Enthalpy of Formation

Rosen[1] lists $D^\circ = 84.0 \pm 2$ kcal·mol$^{-1}$ derived from the mass spectrometric work of Zmbov *et al.*[2] The partial pressures and log K for the $PbF_2(g) + Pb(g) = 2PbF(g)$ reaction in the latter reference are inconsistent. 3rd law calculations show that the log K value corresponds to the heat of reaction given. The dissociation energy calculated by the linear Birge–Sponer extrapolation of the adopted ground state vibrational constants, as derived from emission and absorption spectra ($\nu$, 0–13),[3] [4] is 3.44 eV. Correcting this value for the ionic character of PbF as suggested by Hildenbrand[5] gives $D_0^\circ = 3.64$ eV (83.9 kcal·mol$^{-1}$). The upper limit of the value recommended by Gaydon[6] (3 ± 0.5 eV) falls at 80.7 kcal·mol$^{-1}$. An intercomparison of the dissociation energies of the lead,[7] mercury,[1] and potassium[7] monohalides indicates that $D_0^\circ = 84.0 \pm 2$ kcal·mol$^{-1}$ is reasonable. Combining this with $\Delta_f H^\circ$(Pb, g, 0 K) = 46.91 ± 0.13 kcal·mol$^{-1}$,[7] and $\Delta_f H^\circ$(F, g, 0 K) = 18.36 ± 0.40 kcal·mol$^{-1}$,[7] gives $\Delta_f H^\circ$(PbF, g, 0 K) = −18.73 ± 2.5 kcal·mol$^{-1}$. We adopt $\Delta_f H^\circ$(PbF, g, 0 K) = −18.70 ± 2.5 kcal·mol$^{-1}$ which is consistent with the above $\Delta_f H^\circ$(PbF, g, 298.15 K) = −19.18 ± 2.5 kcal·mol$^{-1}$ is calculated from $\Delta_f H^\circ$(0 K).

### Heat Capacity and Entropy

The vibrational constants, the electronic states and levels, and the rotational constant are those recommended in Rosen[1] with the following modifications. The first excited state, unassigned in Rosen,[1] is tentatively classed as a $^2\Sigma$ state in accordance with the preference for $^2\Sigma$ over $^2\Delta$ expressed by Barrow *et al.*[8] If the state is $^2\Delta$ rather than $^2\Sigma$, the entropy is increased by 0.005 cal K$^{-1}$·mol$^{-1}$ at 4000 K and 0.05 cal K$^{-1}$·mol$^{-1}$ at 6000 K. The *C* and higher electronic states[1] have been omitted; inclusion increases the entropy only by approximately 0.005 cal K$^{-1}$·mol$^{-1}$ at 6000 K. The adopted $B_e = 0.2288$ cm$^{-1}$ is obtained by an approximate correction to $B_0 = 0.2281$ cm$^{-1}$ given in Rosen,[1] and $r_e = 2.058$ Å calculated from $B_e$ compares with $r_0 = 2.061$ Å given in Rosen.[1] The value for $\alpha_e$ is calculated assuming a Morse potential function.

### References

[1] B. Rosen, Ed., "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, (1970).

[2] K. Zmbov, J. W. Hastie, and J. L. Margrave, Trans. Faraday Soc. **64**, 861 (1968).

[3] G. D. Rochester, Proc. Roy. Soc. (London) A **153**, 407 (1936).

[4] G. D. Rochester, proc. Roy Soc. (London) A **167**, 569 (1938).

[5] D. L. Hildenbrand in "Advances in High Temperature Chemistry," Vol. 1, L. Eyring, editor, Academic Press, New York, pp. 193–215, (1967).

[6] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed., Chapman and Hall, London, (1968).

[7] JANAF Thermochemical Tables: Pb(g), 3–31–62; F(g), 9–30–65; PbCl(g), 6–30–73; PbBr(g), 12–31–73; PbI(g), 12–31–73; KF(g), 6–30–69, KCl(g), 3–31–66; KBr(g), 3–31–67; KI(g), 6–30–67.

[8] R. F. Barrow, D. Butler, J. W. C. Johns, and J. L. Powell, Proc. Phys. Soc. (London) **73**, 317 (1959).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p^\circ$ = 0.1 MPa

|  | J·K$^{-1}$mol$^{-1}$ |  |  | kJ·mol$^{-1}$ |  |  |  |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −9.268 | −78.243 | −78.243 | INFINITE |
| 100 | 29.426 | 215.448 | 278.991 | −6.354 | −78.549 | −87.893 | 45.910 |
| 200 | 32.232 | 236.643 | 253.043 | −3.280 | −79.464 | −96.873 | 25.301 |
| 250 | 33.491 | 243.976 | 250.519 | −1.636 | −79.876 | −101.177 | 21.140 |
| 298.15 | 34.399 | 249.957 | 249.957 | 0. | −80.266 | −105.244 | 18.438 |
| 300 | 34.429 | 250.170 | 249.958 | 0.064 | −80.281 | −105.399 | 18.352 |
| 350 | 35.115 | 255.531 | 250.380 | 1.803 | −80.689 | −109.553 | 16.350 |
| 400 | 35.622 | 260.255 | 251.325 | 3.572 | −81.111 | −113.648 | 14.841 |
| 450 | 36.004 | 264.474 | 252.555 | 5.363 | −81.550 | −117.689 | 13.661 |
| 500 | 36.298 | 268.283 | 253.941 | 7.171 | −82.009 | −121.680 | 12.712 |
| 600 | 36.717 | 274.941 | 256.902 | 10.823 | −82.982 | −129.524 | 11.276 |
| 700 | 36.998 | 280.623 | 259.895 | 14.510 | −88.893 | −136.401 | 10.178 |
| 800 | 37.201 | 285.578 | 262.802 | 18.220 | −90.005 | −143.112 | 9.344 |
| 900 | 37.357 | 289.969 | 265.581 | 21.949 | −91.089 | −149.685 | 8.687 |
| 1000 | 37.486 | 293.911 | 268.220 | 25.691 | −92.146 | −156.138 | 8.156 |
| 1100 | 37.601 | 297.490 | 270.721 | 29.445 | −93.176 | −162.488 | 7.716 |
| 1200 | 37.711 | 300.766 | 273.090 | 33.211 | −94.178 | −168.744 | 7.345 |
| 1300 | 37.823 | 303.789 | 275.337 | 36.988 | −95.156 | −174.918 | 7.028 |
| 1400 | 37.943 | 306.596 | 277.471 | 40.776 | −96.126 | −181.017 | 6.754 |
| 1500 | 38.075 | 309.219 | 279.501 | 44.577 | −97.095 | −187.047 | 6.514 |
| 1600 | 38.219 | 311.680 | 281.436 | 48.391 | −98.067 | −193.012 | 6.301 |
| 1700 | 38.378 | 314.002 | 283.284 | 52.221 | −99.045 | −198.917 | 6.112 |
| 1800 | 38.551 | 316.201 | 285.052 | 56.067 | −100.030 | −204.763 | 5.942 |
| 1900 | 38.737 | 318.290 | 286.747 | 59.932 | −101.022 | −210.555 | 5.789 |
| 2000 | 38.933 | 320.282 | 288.374 | 63.815 | −102.019 | −216.294 | 5.649 |
| 2100 | 39.138 | 322.186 | 289.939 | 67.719 | −280.241 | −214.868 | 5.345 |
| 2200 | 39.350 | 324.012 | 291.447 | 71.643 | −280.854 | −211.741 | 5.027 |
| 2300 | 39.567 | 325.766 | 292.901 | 75.589 | −281.533 | −208.584 | 4 737 |
| 2400 | 39.785 | 327.454 | 294.306 | 79.557 | −282.279 | −205.397 | 4.470 |
| 2500 | 40.004 | 329.083 | 295.664 | 83.546 | −283.090 | −202.177 | 4.224 |
| 2600 | 40.222 | 330.656 | 296.980 | 87.557 | −283.963 | −198.923 | 3.996 |
| 2700 | 40.436 | 332.178 | 298.256 | 91.590 | −284.895 | −195.635 | 3.785 |
| 2800 | 40.646 | 333.652 | 299.494 | 95.644 | −285.880 | −192.311 | 3.588 |
| 2900 | 40.850 | 335.082 | 300.696 | 99.719 | −286.915 | −188.951 | 3.403 |
| 3000 | 41 049 | 336.471 | 301.866 | 103.814 | −287.991 | −185.555 | 3.231 |
| 3100 | 41.240 | 337.820 | 303.004 | 107.929 | −289.103 | −182.122 | 3.069 |
| 3200 | 41.425 | 339.132 | 304.113 | 112.062 | −290.244 | −178.653 | 2.916 |
| 3300 | 41.602 | 340.409 | 305.193 | 116.213 | −291.406 | −175.148 | 2.772 |
| 3400 | 41.771 | 341.654 | 306.247 | 120.382 | −292.584 | −171.607 | 2.636 |
| 3500 | 41.933 | 342.867 | 307.276 | 124.567 | −293.770 | −168.032 | 2.508 |
| 3600 | 42.087 | 344.051 | 308.282 | 128.768 | −294.958 | −164.422 | 2.386 |
| 3700 | 42.234 | 345.206 | 309.264 | 132.985 | −296.142 | −160.780 | 2.270 |
| 3800 | 42.374 | 346.334 | 310.225 | 137.215 | −297.316 | −157.106 | 2.160 |
| 3900 | 42.508 | 347.436 | 311.165 | 141.459 | −298.476 | −153.401 | 2.055 |
| 4000 | 42.635 | 348.514 | 312.085 | 145.716 | −299.616 | −149.667 | 1.954 |
| 4100 | 42.756 | 349.568 | 312.986 | 149.986 | −300.733 | −145.904 | 1.859 |
| 4200 | 42.872 | 350.600 | 313.870 | 154.268 | −301.823 | −142.114 | 1.767 |
| 4300 | 42.983 | 351.610 | 314.736 | 158.560 | −302.882 | −138.299 | 1.680 |
| 4400 | 43.088 | 352.600 | 315.585 | 162.864 | −303.909 | −134.460 | 1.596 |
| 4500 | 43.189 | 353.569 | 316.418 | 167.178 | −304.900 | −130.597 | 1.516 |
| 4600 | 43.286 | 354.519 | 317.236 | 171.502 | −305.855 | −126.714 | 1.439 |
| 4700 | 43.379 | 355.451 | 318.040 | 175.835 | −306.771 | −122.809 | 1.365 |
| 4800 | 43.469 | 356.366 | 318.829 | 180.177 | −307.648 | −118.886 | 1.294 |
| 4900 | 43.555 | 357.263 | 319.604 | 184.529 | −308.485 | −114.944 | 1.225 |
| 5000 | 43.639 | 358.144 | 320.366 | 188.888 | −309.281 | −110.987 | 1.159 |
| 5100 | 43.720 | 359.009 | 321.115 | 193.256 | −310.038 | −107.013 | 1.096 |
| 5200 | 43 798 | 359.858 | 321.852 | 197.632 | −310.753 | −103.025 | 1.035 |
| 5300 | 43.874 | 360.693 | 322.577 | 202.016 | −311.429 | −99.024 | 0.976 |
| 5400 | 43.949 | 361.514 | 323.291 | 206.407 | −312.066 | −95.010 | 0.919 |
| 5500 | 44.021 | 362.321 | 323.993 | 210.805 | −312.663 | −90.985 | 0.864 |
| 5600 | 44.092 | 363.115 | 324.684 | 215.211 | −313.223 | −86.949 | 0.811 |
| 5700 | 44.162 | 363.896 | 325.365 | 219.624 | −313.746 | −82.904 | 0.760 |
| 5800 | 44.230 | 364.665 | 326.036 | 224.043 | −314.234 | −78.850 | 0.710 |
| 5900 | 44.297 | 365.421 | 326.698 | 228.470 | −314.686 | −74.788 | 0.662 |
| 6000 | 44.363 | 366.166 | 327.349 | 232.903 | −315.105 | −70.718 | 0.616 |

PREVIOUS December 1973 (1 atm) CURRENT: December 1973 (1 bar)

**Sulfur Fluoride (SF)** **IDEAL GAS** $M_r = 51.058403$ **Sulfur Fluoride (SF)** $F_1S_1(g)$

$\Delta_f H°(0\ K) = 12.316 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298\ 15\ K) = 12.970 \pm 6.3\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = [225.275 \pm 0.8]\ J \cdot K^{-1} \cdot mol^{-1}$

| Electronic Levels and Quantum Weights | | |
|---|---|---|
| State | $\epsilon_i$, cm$^{1}$ | $g_i$ |
| $X^2\Pi_{3/2}$ | 0 | 2 |
| $^2\Pi_{1/2}$ | 398 | 2 |
| $A^2\Pi_{3/2}$ | 24991 | 2 |
| $^2\Pi_{1/2}$ | 25601 | 2 |

$\omega_e = [830 \pm 20]\ cm^{1}$ $\omega_e x_e = [4.7 \pm 0.4]\ cm^{-1}$ $\sigma = 1$
$B = 0.55427 \pm 0\ 0005\ cm^{-1}$ $\alpha = [0\ 0042]\ cm^{-1}$ $r_e = 1.5967 \pm 0.001$

## Enthalpy of Formation

Hildenbrand[1] has investigated the isomolecular reaction $CS_2(g) + 2SF(g) = CF_2(g) + 2S_2(g)$ by mass spectrometry. The various molecular species were found to be formed as products of the reaction of gaseous $SF_6$ with graphite at temperatures in the range 1436–1611 K. This study employed three different effusion cell configurations which were used to optimize the reaction conditions, and ion abundances for each species were measured at 2 eV above their appearance potentials in order to eliminate fragmentation effects. We analyze the reported equilibrium data by the 2nd and 3rd law methods with the results being presented below.

| Series | Cell Configuration | Data Points | T/K | $\Delta_r H°$(298 15 K), kcal·mol$^{-1}$ 2nd law | 3rd law | Drift cal K$^{-1}$·mol$^{-1}$ | $\Delta_f H°$(298.15 K) kcal mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 1 | Mo cell/C liner/packed with C cloth | 2 | 1529–1611 | −11.6 | −16.2<br>±0.3 | 2.9 | 3.2<br>±1.2 |
| 3 | C cell/wound Pt wire | 4 | 1436–1564 | 6.8 | −16.0<br>±1.8 | −15.1<br>±5.0 | 3.1<br>±2.0 |
| 3 | C cell/Pt partition/packed with C cloth and Pt wire | 7 | 1478 1588 | −37.2 | −15.8<br>±1.4 | 13.9<br>±5.0 | 3 0<br>±1.8 |

The three cell configurations used by Hildenbrand[1] yield almost identical 3rd law $\Delta_f H°$ values. We adopt the mean value of $3.1 \pm 1.5$ kcal·mol$^{-1}$. This value corresponds to a $D_0°$ of $81.2 \pm 2\ 0$ kcal mol$^{-1}$ which is close to the average bond energies (80 0 kcal·mol$^{-1}$) for $SF_4$ and $SF_3$[2]. Other reported $D_0°$ values include 96.9 kcal·mol$^{-1}$ [3] and <76.1 kcal·mol$^{-1}$ [4] The former value is based on Hartree Foch binding energies[3] which were combined with an estimate of the extra molecular correlation energy. This estimate now appears to be about 20% too high. The upper limit value for $D_0°$ was obtained from predissociation observed in the $A^2\Pi$ state by Di Lonardo and Trombetti.[4]

## Heat Capacity and Entropy

The electronic states and levels ($T_o$) are taken from the recent compilation of Barrow.[5] His results were derived from the spectral measurements of Di Lonardo and Trombetti.[4] Further confirmation that the ground state is inverted $^2\Pi$ is provided by the results of an analysis of the gas phase electron resonance spectra by Carrington *et al.*[6] The rotational constant ($B_e$) is calculated from the microwave data ($B_{eff}$) of Amano and Hirota.[7] Other values for $B_e$ determined from EPR[6] measurements and from a rotational analysis[4] of the $A^2\Pi$ $X^2\Pi$ band system agree with the microwave results but are less precise. The value of $r_e$ is calculated from $B_e$.

The ground state vibrational constants have not been determined experimentally. O'Hare[8] computed Hartree Fock total energies for the ground states of NF, SiF, PF, and SF and derived spectroscopic constants for each monofluoride by a Dunham analysis. He adjusted the computed values for SF for differences found between calculated and experimental data for the other three monofluorides. We adopt his predicted vibrational constants along with his computed value for $\alpha_e$. We do not include the rotational and vibrational constants[4, 5] for the $A^2\Pi$ state since they have a negligible effect.

Thermal functions have been previously reported for SF by Wilkins[9] and O'Hare.[10] These two sets of functions agree reasonably well, and presumably they are both based on a ground state quantum weight of 2. Our entropies are consistently higher than the literature data[9, 10] at all temperatures by roughly 1.0 1.5 cal K$^{-1}$ mol$^{-1}$. This increase can be attributed primarily to the entropy contribution from the $X\ ^2\Pi_{1/2}$ state which lies at 398 cm$^{-1}$.

## References

[1] D. L. Hildenbrand, J. Phys. Chem. 77, 897 (1973).
[2] JANAF Thermochemical Tables: $CS_2(g)$, 6–30–61; $CF_2(g)$, 6–30–70; $S_2(g)$, 12–31–65; $SF_4(g)$ and $SF_3(g)$, 6–30–76.
[3] P. A. G. O'Hare and A. C. Wahl, J. Chem Phys. 53, 2834 (1970).
[4] G. Di Lonardo and A Trombetti, Trans. Faraday Soc 66, 2694 (1970).
[5] R. F. Barrow, "Diatomic Molecules: A Critical Bibliography of Spectroscopic Data," Centre National De La Recherche Scientifique, Paris, (1973).
[6] A Carrington, G. N. Currie, T. A. Miller, and D. H. Levy, J. Chem. Phys. 50, 2726 (1969).
[7] T. Amano and E. Hirota, J Mol. Spectrosc. 45, 417 (1973).
[8] P. A. G. O'Hare, J. Chem. Phys. 59, 3842 (1973).
[9] R. L. Wilkins, Aerospace Corporation, Report No. TR–0158 (3240 20) 19, (July 1968).
[10] P. A. G. O'Hare, Argonne National Laboratory, ANL 7315, (July 1968).

Enthalpy Reference Temperature = $T_r$ = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
|---|---|---|---|---|---|---|---|
| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
| 0 | 0. | 0 | INFINITE | −9.478 | 12.316 | 12.316 | INFINITE |
| 100 | 29.999 | 189.668 | 255.214 | −6.555 | 13.097 | 3.901 | −2.038 |
| 200 | 33.400 | 211.569 | 228.443 | −3.375 | 13.170 | −5.351 | 1.398 |
| 250 | 34 454 | 219.143 | 225.850 | −1.677 | 13.098 | −9.974 | 2.084 |
| 298.15 | 35.152 | 225.275 | 225.275 | 0. | 12.970 | −14.407 | 2.524 |
| 300 | 35.174 | 225.493 | 225.276 | 0.065 | 12.964 | −14.577 | 2.538 |
| 350 | 35.683 | 230.955 | 225.706 | 1.837 | 12.776 | −19.153 | 2.858 |
| 400 | 36.055 | 235.745 | 226.668 | 3.631 | 10.324 | −23 611 | 3.083 |
| 450 | 36.337 | 240.009 | 227.917 | 5.441 | 9.375 | −27.805 | 3.227 |
| 500 | 36.556 | 243.849 | 229.322 | 7.264 | 8.346 | −31.878 | 3.330 |
| 600 | 36.872 | 250.544 | 232.317 | 10.936 | 6.697 | −39.763 | 3.462 |
| 700 | 37.088 | 256.245 | 235.338 | 14.635 | 5.273 | −47.391 | 3.536 |
| 800 | 37.246 | 261.209 | 238.269 | 18.352 | 3.974 | −54.825 | 3.580 |
| 900 | 37.368 | 265.603 | 241.066 | 22.083 | −50.379 | −61.019 | 3.541 |
| 1000 | 37.466 | 269.545 | 243.720 | 25.825 | −50.338 | −62.204 | 3.249 |
| 1100 | 37.549 | 273.120 | 246.233 | 29.576 | −50.319 | −63.392 | 3.010 |
| 1200 | 37.620 | 276.390 | 248.612 | 33.334 | −50.320 | −64.580 | 2.811 |
| 1300 | 37.684 | 279 404 | 250.866 | 37.099 | −50.342 | −65 768 | 2.643 |
| 1400 | 37.741 | 282.199 | 253.006 | 40.871 | −50.384 | −66.953 | 2.498 |
| 1500 | 37.795 | 284.805 | 255.040 | 44.648 | −50.446 | −68.135 | 2.373 |
| 1600 | 37.844 | 287.245 | 256 977 | 48.430 | −50.527 | −69.311 | 2.263 |
| 1700 | 37.892 | 289.541 | 258.826 | 52.216 | −50.625 | −70.482 | 2.166 |
| 1800 | 37.937 | 291.708 | 260.593 | 56.008 | −50.740 | −71 647 | 2.079 |
| 1900 | 37 980 | 293.761 | 262.285 | 59.804 | −50.870 | −72.805 | 2.002 |
| 2000 | 38.023 | 295.710 | 263.908 | 63.604 | −51.011 | −73.956 | 1.932 |
| 2100 | 38.064 | 297.566 | 265.467 | 67.408 | −51.163 | −75.100 | 1.868 |
| 2200 | 38 104 | 299.338 | 266.966 | 71.217 | −51.322 | −76.236 | 1.810 |
| 2300 | 38.143 | 301.032 | 268 411 | 75.029 | −51.486 | −77.365 | 1.757 |
| 2400 | 38.182 | 302.657 | 269.804 | 78.845 | −51.652 | −78.486 | 1.708 |
| 2500 | 38.221 | 304.216 | 271.150 | 82.665 | −51.818 | −79.601 | 1.663 |
| 2600 | 38.259 | 305.716 | 272 451 | 86.489 | −51.981 | −80 709 | 1.621 |
| 2700 | 38.298 | 307.160 | 273.710 | 90.317 | −52.138 | −81.811 | 1.583 |
| 2800 | 38.336 | 308.554 | 274.929 | 94.149 | −52.288 | −82.907 | 1.547 |
| 2900 | 38.374 | 309.900 | 276.112 | 97 984 | −52.429 | −83 998 | 1.513 |
| 3000 | 38.413 | 311.201 | 277.260 | 101.824 | −52.559 | −85.085 | 1.481 |
| 3100 | 38.452 | 312.462 | 278.375 | 105.667 | −52.676 | −86.167 | 1.452 |
| 3200 | 38.491 | 313.683 | 279.460 | 109.514 | −52.780 | −87.246 | 1 424 |
| 3300 | 38.531 | 314.868 | 280.515 | 113.365 | −52.868 | −88.321 | 1.398 |
| 3400 | 38.573 | 316.019 | 281.542 | 117.220 | −52.941 | −89.394 | 1.373 |
| 3500 | 38.615 | 317.138 | 282.543 | 121.080 | −52.998 | −90 466 | 1.350 |
| 3600 | 38.658 | 318.226 | 283.520 | 124.943 | −53.039 | −91.535 | 1.328 |
| 3700 | 38.702 | 319.286 | 284.472 | 128.811 | −53.061 | −92.604 | 1.307 |
| 3800 | 38.748 | 320.319 | 285.402 | 132.684 | −53.067 | −93.673 | 1.288 |
| 3900 | 38.795 | 321.326 | 286.310 | 136.561 | −53.055 | −94.742 | 1.269 |
| 4000 | 38.843 | 322.308 | 287.198 | 140.443 | −53.026 | −95.811 | 1.251 |
| 4100 | 38.893 | 323.268 | 288.066 | 144.330 | −52.980 | −96.881 | 1.234 |
| 4200 | 38.945 | 324.206 | 288.915 | 148.222 | −52.917 | −97.953 | 1.218 |
| 4300 | 38.999 | 325.123 | 289.747 | 152.119 | −52.836 | −99.026 | 1.203 |
| 4400 | 39.055 | 326.020 | 290.561 | 156.021 | −52.740 | −100.101 | 1.188 |
| 4500 | 39.112 | 326.899 | 291.359 | 159.930 | −52.627 | −101.179 | 1.174 |
| 4600 | 39.171 | 327.759 | 292.141 | 163.844 | −52.498 | −102.259 | 1.161 |
| 4700 | 39.232 | 328.602 | 292.907 | 167.764 | −52.354 | −103.342 | 1.149 |
| 4800 | 39.295 | 329.429 | 293.660 | 171.690 | −52.194 | −104.429 | 1.136 |
| 4900 | 39.360 | 330.239 | 294.398 | 175.623 | −52.020 | −105.519 | 1.125 |
| 5000 | 39 427 | 331.035 | 295.123 | 179.562 | −51.832 | −106.613 | 1.114 |
| 5100 | 39.495 | 331.817 | 295.835 | 183.508 | −51.629 | −107.710 | 1.103 |
| 5200 | 39.565 | 332.584 | 296.534 | 187.461 | −51.413 | −108.812 | 1.093 |
| 5300 | 39.638 | 333.339 | 297.221 | 191.422 | −51.184 | −109.918 | 1.083 |
| 5400 | 39.711 | 334.080 | 297.897 | 195.389 | −50.941 | −111.028 | 1.074 |
| 5500 | 39.787 | 334.810 | 298.562 | 199.364 | −50.686 | −112.143 | 1.065 |
| 5600 | 39.863 | 335.527 | 299.215 | 203.346 | −50.419 | −113.263 | 1.056 |
| 5700 | 39.942 | 336.233 | 299.859 | 207.337 | −50.140 | −114.388 | 1.048 |
| 5800 | 40.022 | 336.929 | 300.492 | 211.335 | −49.848 | −115.518 | 1.040 |
| 5900 | 40 103 | 337.614 | 301.115 | 215.341 | −49.546 | −116.652 | 1.033 |
| 6000 | 40.185 | 338.288 | 301.729 | 219.355 | −49.232 | −117 793 | 1.025 |

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

**Sulfur Fluoride (SF)** $F_1S_1(g)$

# Sulfur Fluoride, Ion ($SF^+$) IDEAL GAS $M_r = 51.057854$ Sulfur Fluoride, Ion ($SF^+$) $F_1S_1^+(g)$

$S°(298.15\ K) = [225.405 \pm 9.2]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = 985.664 \pm 16.7\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = [991.901]\ mol^{-1}$

Electronic Levels and Quantum Weights

| State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|
| [$X^3\Sigma$] | 0 | [3] |
| [a $^1\Delta$] | [8000] | [2] |
| [b $^1\Sigma$] | [14500] | [1] |
| [B $^3\Pi$] | [30000] | [6] |

$\omega_e = [838]\ cm^{-1}$ $\omega_ex_e = [4.6]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.55686]\ cm^{-1}$ $\alpha_e = [0.0044]\ cm^{-1}$ $r_e = [1.593]$ Å

## Enthalpy of Formation

The electron impact appearance potential of $SF^+$ from SF has been measured by Hildenbrand[1] as 10.09 ± 0.1 eV. Normally, this measured AP would be identical to the vertical ionization potential of SF; however, formation of $SF^+$ involves the loss of an antibonding electron which appears to be situated primarily on the sulfur atom (IP(S) = 10.36 eV,)[2]. Thus, the geometrical changes produced upon ionization should be minimal, and therefore, the measured AP is probably very close to the true (adiabatic) ionization potential, as suggested by Hildenbrand.[1] We employ the experimental IP value as the heat of reaction, $\Delta_rH° = 232.68 \pm 2.3\ kcal{\cdot}mol^{-1}$, for the process $SF(g) + e = SF^+(g) + 2e^-$ at 0 K, and we calculate $\Delta_fH°(SF^+, g, 0\ K) = 235.6 \pm 4.0\ kcal{\cdot}mol^{-1}$ by combining the value of $\Delta_rH°(0\ K)$ with $\Delta_fH°(SF, g, 0\ K) = 2.9 \pm 1.5\ kcal{\cdot}mol^{-1}$.[3] Independent values of IP include 10.0 eV[4] and 9.9 eV.[5] Both of these values were obtained from semiempirical molecular orbital calculations and are in excellent agreement with the results adopted here.

Earlier electron impact studies which can also be used to derive $\Delta_fH°$ of $SF^+$ have been previously analyzed by O'Hare and Wahl.[6] We do not reanalyze these results since their analysis[6] has shown that the data are seriously in error.

## Heat Capacity and Entropy

As discussed in the enthalpy of formation section, one would expect that the bonding in $SF^+$ is probably not very different from that in SF, since the ionizing orbital is antibonding. Additional support for this is provided by the fact that the bond dissociation energies for $SF^+$ (87.4 $kcal{\cdot}mol^{-1}$) and SF (81.2 $kcal{\cdot}mol^{-1}$) are very similar. In addition, $SF^+$ is isoelectronic with PF, and one might therefore expect that the molecular characteristics of these two isoelectronic molecules would be quite similar. We estimate the vibrational and rotational constants to be intermediate between those for SF[3] and PF.[7] By analogy with other twelve valence electron molecules,[7] we predict that the ground state is $^3\Sigma$ and expect several excited states to exist below 35000 cm$^{-1}$. The two singlet levels are estimated from those observed for NF and $O_2$.[7] We also include a triplet level at 30000 cm$^{-1}$ based on that observed for PF.[7] We assume that the vibrational and rotational constants for the excited states are identical with those for the ground state since a comparison of the constants[7] that are available for the various states of NF and PF shows that they are not significantly different. The uncertainty in our value of $S°(298.15\ K)$ is estimated as $\pm 2.2\ cal\ K^{-1}{\cdot}mol^{-1}$ and arises primarily from the effect of the ground state quantum weight. If the $SF^+$ ground state is singlet, then our entropy value at 298.15 K should be decreased by $2.18\ cal\ K^{-1}\ mol^{-1}$. The electronic contribution to the entropy from the estimated excited states is negligible below 2000 K but increases to $0.4\ cal\ K^{-1}{\cdot}mol^{-1}$ at 4500 K.

## References

[1] D. L. Hildenbrand, J. Phys. Chem. 77, 897 (1973).
[2] J. L. Franklin, J. G. Dillard *et al.*, U.S. Nat. Bur. Stand., NSRDS–NBS 26, (1969).
[3] JANAF Thermochemical Tables: SF(g), 6–30–76.
[4] A. L. Companion, Theoret. Chim. Acta, **25**, 268 (1972).
[5] P. A. G. O'Hare, J. Chem. Phys. 59, 3842 (1973).
[6] P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. 53, 2834 (1970).
[7] B. Rosen, ed., "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, (1970).

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ (J·K$^{-1}$mol$^{-1}$) | $S°$ (J·K$^{-1}$mol$^{-1}$) | $-[G°-H°(T_r)]/T$ (J·K$^{-1}$mol$^{-1}$) | $H°-H°(T_r)$ (kJ·mol$^{-1}$) | $\Delta_fH°$ (kJ·mol$^{-1}$) | $\Delta_fG°$ (kJ·mol$^{-1}$) | log $K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0. | 0. | INFINITE | −8.864 | 985.664 | | |
| 100 | 29.116 | 192.820 | 252.379 | −5.956 | | | |
| 200 | 29.886 | 213.148 | 228.243 | −3.019 | | | |
| 250 | 30.766 | 219.908 | 225.922 | −1.503 | | | |
| 298.15 | 31.679 | 225.405 | 225.405 | 0. | 991.901 | 958.230 | −167.878 |
| 300 | 31.713 | 225.601 | 225.406 | 0.059 | 991.927 | 958.021 | −166.806 |
| 350 | 32.590 | 230.557 | 225.795 | 1.667 | 992.614 | 952.315 | −142.125 |
| 400 | 33.348 | 234.960 | 226.671 | 3.316 | 991.056 | 946.601 | −123.613 |
| 450 | 33.985 | 238.926 | 227.816 | 4.999 | 991.020 | 941.037 | −109.233 |
| 500 | 34.513 | 242.535 | 229.110 | 6.712 | 990.920 | 935.491 | −97.730 |
| 600 | 35.313 | 248.902 | 231.892 | 10.206 | 991.171 | 924.388 | −80.475 |
| 700 | 35.874 | 254.390 | 234.723 | 13.767 | 991.688 | 913.219 | −68.145 |
| 800 | 36.280 | 259.208 | 237.489 | 17.376 | 992.359 | 901.965 | −58.892 |
| 900 | 36.585 | 263.500 | 240.145 | 21.020 | 939.998 | 891.702 | −51.753 |
| 1000 | 36.824 | 267.367 | 242.677 | 24.691 | 942.047 | 886.225 | −46.292 |
| 1100 | 37.021 | 270.887 | 245.084 | 28.383 | 944.086 | 880.544 | −41.814 |
| 1200 | 37.191 | 274.115 | 247.371 | 32.094 | 946.116 | 874.678 | −38.074 |
| 1300 | 37.346 | 277.098 | 249.544 | 35.821 | 948.134 | 868.643 | −34.903 |
| 1400 | 37.494 | 279.871 | 251.612 | 39.563 | 950.141 | 862.453 | −32.179 |
| 1500 | 37.640 | 282.463 | 253.584 | 43.319 | 952.138 | 856.120 | −29.813 |
| 1600 | 37.789 | 284.897 | 255.465 | 47.091 | 954.125 | 849.654 | −27.738 |
| 1700 | 37.942 | 287.193 | 257.265 | 50.877 | 956.105 | 843.064 | −25.904 |
| 1800 | 38.100 | 289.366 | 258.988 | 54.679 | 958.079 | 836.357 | −24.270 |
| 1900 | 38.263 | 291.430 | 260.642 | 58.498 | 960.051 | 829.541 | −22.806 |
| 2000 | 38.431 | 293.397 | 262.231 | 62.332 | 962.022 | 822.621 | −21.485 |
| 2100 | 38.602 | 295.276 | 263.760 | 66.184 | 963.996 | 815.603 | −20.287 |
| 2200 | 38.776 | 297.076 | 265.234 | 70.053 | 965.977 | 808.490 | −19.196 |
| 2300 | 38.952 | 298.804 | 266.656 | 73.939 | 967.965 | 801.287 | −18.198 |
| 2400 | 39.129 | 300.465 | 268.030 | 77.843 | 969.966 | 793.997 | −17.281 |
| 2500 | 39.305 | 302.066 | 269.360 | 81.765 | 971.980 | 786.624 | −16.436 |
| 2600 | 39.480 | 303.611 | 270.648 | 85.704 | 974.011 | 779.170 | −15.654 |
| 2700 | 39.653 | 305.104 | 271.897 | 89.661 | 976.061 | 771.637 | −14.928 |
| 2800 | 39.823 | 306.549 | 273.108 | 93.635 | 978.132 | 764.028 | −14.253 |
| 2900 | 39.989 | 307.950 | 274.286 | 97.625 | 980.225 | 756.344 | −13.623 |
| 3000 | 40.152 | 309.308 | 275.431 | 101.632 | 982.341 | 748.588 | −13.034 |
| 3100 | 40.310 | 310.627 | 276.545 | 105.656 | 984.482 | 740.761 | −12.482 |
| 3200 | 40.463 | 311.910 | 277.630 | 109.694 | 986.649 | 732.865 | −11.963 |
| 3300 | 40.611 | 313.157 | 278.688 | 113.748 | 988.841 | 724.900 | −11.474 |
| 3400 | 40.755 | 314.371 | 279.720 | 117.816 | 991.060 | 716.869 | −11.013 |
| 3500 | 40.893 | 315.555 | 280.727 | 121.899 | 993.305 | 708.772 | −10.578 |
| 3600 | 41.026 | 316.709 | 281.710 | 125.995 | 995.575 | 700.610 | −10.166 |
| 3700 | 41.155 | 317.835 | 282.671 | 130.104 | 997.872 | 692.385 | −9.775 |
| 3800 | 41.278 | 318.934 | 283.611 | 134.225 | 1000.195 | 684.098 | −9.404 |
| 3900 | 41.397 | 320.008 | 284.531 | 138.359 | 1002.542 | 675.749 | −9.051 |
| 4000 | 41.512 | 321.057 | 285.431 | 142.505 | 1004.913 | 667.340 | −8.715 |
| 4100 | 41.623 | 322.083 | 286.312 | 146.662 | 1007.308 | 658.871 | −8.394 |
| 4200 | 41.729 | 323.088 | 287.176 | 150.829 | 1009.725 | 650.343 | −8.088 |
| 4300 | 41.832 | 324.071 | 288.023 | 155.007 | 1012.165 | 641.757 | −7.796 |
| 4400 | 41.932 | 325.034 | 288.853 | 159.196 | 1014.626 | 633.115 | −7.516 |
| 4500 | 42.029 | 325.977 | 289.667 | 163.394 | 1017.107 | 624.416 | −7.248 |
| 4600 | 42.122 | 326.902 | 290.467 | 167.601 | 1019.608 | 615.662 | −6.991 |
| 4700 | 42.213 | 327.809 | 291.252 | 171.818 | 1022.128 | 606.854 | −6.744 |
| 4800 | 42.302 | 328.699 | 292.023 | 176.044 | 1024.665 | 597.991 | −6.507 |
| 4900 | 42.388 | 329.572 | 292.780 | 180.278 | 1027.220 | 589.076 | −6.280 |
| 5000 | 42.473 | 330.429 | 293.525 | 184.521 | 1029.791 | 580.108 | −6.060 |
| 5100 | 42.556 | 331.271 | 294.256 | 188.773 | 1032.377 | 571.089 | −5.849 |
| 5200 | 42.638 | 332.098 | 294.976 | 193.033 | 1034.979 | 562.019 | −5.646 |
| 5300 | 42.718 | 332.911 | 295.684 | 197.300 | 1037.594 | 552.898 | −5.449 |
| 5400 | 42.797 | 333.710 | 296.381 | 201.576 | 1040.223 | 543.728 | −5.260 |
| 5500 | 42.875 | 334.496 | 297.067 | 205.860 | 1042.866 | 534.510 | −5.076 |
| 5600 | 42.952 | 335.269 | 297.742 | 210.151 | 1045.521 | 525.243 | −4.899 |
| 5700 | 43.029 | 336.030 | 298.407 | 214.450 | 1048.187 | 515.928 | −4.728 |
| 5800 | 43.105 | 336.779 | 299.063 | 218.757 | 1050.866 | 506.567 | −4.562 |
| 5900 | 43.180 | 337.517 | 299.708 | 223.071 | 1053.555 | 497.160 | −4.402 |
| 6000 | 43.255 | 338.243 | 300.344 | 227.393 | 1056.255 | 487.707 | −4.246 |

PREVIOUS: June 1976 (1 atm)    CURRENT: June 1976 (1 bar)

## Sulfur Fluoride, Ion (SF$^-$) IDEAL GAS $M_r = 51.058952$ Sulfur Fluoride, Ion (SF$^-$) $F_1S_1^-(g)$

$S°(298.15\ K) = [218.956 \pm 0.8]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = [-180.649 \pm 54.4]\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = [-186.590]\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

| State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|
| [$X^1\Sigma^+$] | [0] | [1] |
| [$A^3\Pi$] | [20000] | [6] |

$\omega_e = [627]\ cm^{-1}$ $\omega_ex_e = [5.06]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.45620]\ cm^{-1}$ $\alpha = [0.0046]\ cm^{-1}$ $r_e = [1.76]$ Å

### Enthalpy of Formation

The adopted value of $\Delta_fH°(0\ K) = 43.2 \pm 13\ 0$ kcal·mol$^{-1}$ is calculated as the difference between the $\Delta_fH°$(SF, g, 0 K) = 2.94 ± 1.5 kcal·mol$^{-1}$ [1] and an estimated EA (SF) = 2 0 ± 0.5 eV (46.121 kcal·mol$^{-1}$). We estimate EA based on a consideration of trends in the electron affinities for other S–F Species.[1] These data follow a regular pattern among the even– and odd– electron molecules, with the odd electron molecules having, as expected, the higher EA's. Within each even– and odd–electron series, the EA values become progressively larger as the number of fluorine atoms in the ion is increased. Our $\Delta_fH°$(0 K) value corresponds to a fluoride ion affinity IA (S) and bond dissociation energy (SF$^-$ = S + F$^-$) of 48.9 ± 13.5 kcal·mol$^{-1}$. Correcting $\Delta_fH°$(0 K) to a temperature of 298.15 K, we obtain the value of −44.6 kcal·mol$^{-1}$.

Several pieces of information are available which tend to provide support for our estimated EA value Formation of SF$^-$ involves the addition of an electron to an antibonding orbital of SF[2] which is located primarily on the sulfur atom. It is reasonable, therefore, to assume that EA(SF)≃EA(S) = 2.0772 ± 0.005 eV.[3] O'Hare[2] has pointed out that Koopmans' theorem[4] gives reliable estimates of electron affinities and ionization potentials provided that the parent molecule or ion have a closed shell electronic configuration. Application of this theorem to SF$^-$ which has the required closed–shell structure leads to EA = 1.7 eV.[2] Other estimates of EA based on MO calculations have included (all in eV) 2.8,[5] 2.5 ± 0.5,[6] and <3.2.[2]

JANAF data[1] suggest that SF$^-$ should be reasonably stable at moderate temperatures, with dissociative ionization becoming thermodynamically favorable above 2000 K. These predictions are supported qualitatively by the observations of Harland and Thynne[7,8] who have identified SF$^-$ in the negative ion mass spectra of $SF_4$, $SF_6$, and $SF_5Cl$. The temperature of the ion source was reported as around 325 K.[8]

### Heat Capacity and Entropy

The additional antibonding electron in SF$^-$ should weaken the bonding in the ion relative to the parent molecule, as evidenced by a reduction (~32 kcal·mol$^{-1}$) in the S–F bond strength for SF when compared with that for SF.[1] In addition, MO calculations[9] on OF and OF$^-$ show that the O–F bond length in OF increases by 0 159 Å upon forming the negative ion. We apply this difference to $r_e$(SF) = 1.5967 Å,[1] and we obtain $r_e$(SF$^-$) = 1.76 Å. The value of $B_e$ is calculated from our estimate of $r_e$. We use Badger's rule[10] to estimate a value for $\omega_e$. We write the equation in the form $\omega_e^2 = 3.159 \times 10^6/\mu(r_e\ d_{ij})$,[3] and we set $d_{ij}$ equal to 0.8833 based on molecular data for ClF.[11] Barrow and Caunt[12] have shown that the product $x_e\mu^{1/2}$ is reasonably constant for a series of similar molecules. Using $x_e\mu^{1/2} = 0.0279$ from ClF,[11] we calculate $x_e = 0.008068$ and $\omega_ex_e = 5.06$ cm$^{-1}$ for SF$^-$. The value of $\alpha_e$ is obtained from the other constants, assuming a Morse potential function.[13]

The electronic states and levels are estimated by analogy with those for ClF.[11] The effect of the triplet level at 20000 cm$^{-1}$ on our entropies is insignificant below 3000 K, but this level does contribute 0.15 cal K$^{-1}$·mol$^{-1}$ to S at 4500 K. We assign an uncertainty of ±0.2 cal K$^{-1}$·mol$^{-1}$ to the value of $S°$(298.15 K) based on conservative estimates of the uncertainties in the vibrational and rotational data.

### References

[1] JANAF Thermochemical Tables: SF(g), 6–30–76; $SF_2^-$(g), $SF_3^-$(g), $SF_4^-$(g), and $SF_5^-$(g), 12–31–76, F$^-$(g), 12–31–71; S(g), 6–30–71; $SF_6^-$(g), 6–30–77.
[2] P. A. G. O'Hare, J. Chem. Phys. 59, 3842 (1973).
[3] J. L. Franklin and P. W. Harland, Ann. Rev. Phys. Chem. 25, 485 (1974).
[4] T. Koopmans, Physica (Utr.) 1, 104 (1934).
[5] A. L. Companion, Theoret. Chim. Acta (Berl.) 25, 268 (1972).
[6] P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. 53, 2834 (1970).
[7] P. W. Harland and J. C. J. Thynne, J. Phys. Chem. 73, 4031 (1969).
[8] P. W. Harland and J. C. J. Thynne, J. Phys. Chem. 75, 3517 (1971).
[9] P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. 53, 2469 (1970).
[10] R. M. Badger, J. Chem. Phys. 2, 128 (1934).
[11] B. Rosen, ed., "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, (1970).
[12] R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London) 219A, 120 (1953).
[13] G. Herzberg, "Spectra of Diatomic Molecules," 2nd. ed., D. Van Nostrand Co., Inc., New York, (1963).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −9.082 | −180.649 | | |
| 100 | 29.204 | 185.367 | 247.084 | −6.172 | | | |
| 200 | 31.130 | 206.084 | 221.942 | −3.172 | | | |
| 250 | 32.368 | 213.166 | 219.500 | −1.584 | | | |
| 298.15 | 33.380 | 218.956 | 218.956 | 0. | −186.590 | −205.828 | 36.060 |
| 300 | 33 414 | 219.163 | 218.957 | 0.062 | −186.637 | −205.948 | 35.859 |
| 350 | 34.243 | 224.379 | 219.367 | 1.754 | −187.945 | −209.063 | 31.201 |
| 400 | 34 889 | 228.995 | 220.287 | 3.483 | −191.501 | −211.901 | 27.671 |
| 450 | 35.395 | 233.135 | 221.489 | 5.241 | −193.542 | −214.337 | 24 880 |
| 500 | 35.795 | 236.886 | 222.844 | 7.021 | −195.653 | −216.533 | 22.621 |
| 600 | 36.378 | 243.467 | 225.748 | 10.631 | −199.443 | −220.346 | 19.183 |
| 700 | 36.779 | 249.106 | 228.692 | 14.290 | −202.985 | −223.548 | 16 681 |
| 800 | 37.071 | 254.038 | 231.558 | 17.984 | −206.386 | −226.252 | 14.773 |
| 900 | 37.295 | 258.417 | 234.304 | 21.702 | −262.830 | −227.455 | 13.201 |
| 1000 | 37.476 | 262.356 | 236.915 | 25 441 | −264.871 | −223.415 | 11.670 |
| 1100 | 37.626 | 265.936 | 239.393 | 29.196 | −266.925 | −219.170 | 10.408 |
| 1200 | 37.756 | 269.215 | 241.744 | 32.966 | −268 995 | −214.737 | 9.347 |
| 1300 | 37 871 | 272.242 | 243.975 | 36.747 | −271.079 | −210.131 | 8.443 |
| 1400 | 37.974 | 275.052 | 246.095 | 40.539 | −273.179 | −205.364 | 7.662 |
| 1500 | 38.070 | 277.675 | 248.114 | 44.342 | −275.294 | −200.447 | 6.980 |
| 1600 | 38.159 | 280.135 | 250.040 | 48.153 | −277.423 | −195.388 | 6.379 |
| 1700 | 38.244 | 282.451 | 251.879 | 51 973 | −279.567 | −190.195 | 5.844 |
| 1800 | 38.326 | 284.640 | 253.638 | 55.802 | −281.724 | −184.875 | 5.365 |
| 1900 | 38.404 | 286.714 | 255.325 | 59.638 | −283.891 | −179 436 | 4.933 |
| 2000 | 38 482 | 288.686 | 256.944 | 63.483 | −286.067 | −173.882 | 4.541 |
| 2100 | 38.560 | 290.565 | 258.501 | 67.335 | −288.250 | −168.219 | 4.184 |
| 2200 | 38.638 | 292.361 | 259.999 | 71.195 | −290 436 | −162.452 | 3.857 |
| 2300 | 38.719 | 294.080 | 261.444 | 75.063 | −292.623 | −156.586 | 3.556 |
| 2400 | 38.803 | 295.730 | 262.839 | 78.939 | −294.807 | −150.624 | 3.278 |
| 2500 | 38.893 | 297.315 | 264.186 | 82.823 | −296.987 | −144.572 | 3 021 |
| 2600 | 38.988 | 298.843 | 265.490 | 86.717 | −299.159 | −138.432 | 2.781 |
| 2700 | 39.092 | 300.316 | 266.753 | 90.621 | −301.319 | −132.209 | 2.558 |
| 2800 | 39 206 | 301.740 | 267.977 | 94.536 | −303 464 | −125 907 | 2.349 |
| 2900 | 39.330 | 303.118 | 269.165 | 98.463 | −305.592 | −119.528 | 2.153 |
| 3000 | 39.467 | 304.453 | 270.319 | 102.403 | −307.701 | −113.076 | 1.969 |
| 3100 | 39.617 | 305.750 | 271.441 | 106.357 | −309.786 | −106.554 | 1.795 |
| 3200 | 39.782 | 307 010 | 272.533 | 110.327 | −311.845 | −99.965 | 1.632 |
| 3300 | 39.963 | 308.237 | 273.597 | 114.314 | −313.877 | −93.313 | 1.477 |
| 3400 | 40.160 | 309.433 | 274.633 | 118.320 | −315.877 | −86.599 | 1.330 |
| 3500 | 40.374 | 310.600 | 275.644 | 122.346 | −317.846 | −79.826 | 1.191 |
| 3600 | 40.605 | 311.741 | 276.631 | 126.395 | −319.779 | −72.998 | 1.059 |
| 3700 | 40.854 | 312.857 | 277.595 | 130.468 | −321.676 | −66.117 | 0.933 |
| 3800 | 41.120 | 313.950 | 278.537 | 134.566 | −323.534 | −59.185 | 0.814 |
| 3900 | 41.403 | 315.021 | 279.459 | 138.692 | −325.352 | −52.205 | 0.699 |
| 4000 | 41.703 | 316.073 | 280.361 | 142.847 | −327.128 | −45.178 | 0.590 |
| 4100 | 42.019 | 317 107 | 281.245 | 147.033 | −328.862 | −38.108 | 0.486 |
| 4200 | 42.351 | 318.123 | 282.111 | 151.252 | −330.550 | −30.996 | 0.385 |
| 4300 | 42.697 | 319 124 | 282.960 | 155.504 | −332.194 | −23.844 | 0.290 |
| 4400 | 43.057 | 320.110 | 283.793 | 159.792 | −333.791 | −16.655 | 0.198 |
| 4500 | 43.429 | 321.081 | 284.611 | 164.116 | −335.340 | −9.429 | 0.109 |
| 4600 | 43.813 | 322.040 | 285.415 | 168.478 | −336.842 | −2.171 | 0.025 |
| 4700 | 44.206 | 322.987 | 286.204 | 172.879 | −338.296 | 5 121 | −0.057 |
| 4800 | 44.608 | 323.921 | 286.980 | 177.319 | −339.701 | 12.442 | −0.135 |
| 4900 | 45.018 | 324.845 | 287.743 | 181.801 | −341.057 | 19.793 | −0.211 |
| 5000 | 45.433 | 325.759 | 288.494 | 186.323 | −342.364 | 27.171 | −0.284 |
| 5100 | 45.853 | 326.663 | 289.234 | 190.887 | −343.622 | 34.574 | −0.354 |
| 5200 | 46.275 | 327.557 | 289.962 | 195.494 | −344.831 | 42.001 | −0.422 |
| 5300 | 46.700 | 328.443 | 290.680 | 200.143 | −345.991 | 49 452 | −0.487 |
| 5400 | 47.125 | 329.320 | 291.388 | 204.834 | −347.104 | 56.923 | −0.551 |
| 5500 | 47.548 | 330.188 | 292.085 | 209.567 | −348.169 | 64.415 | −0.612 |
| 5600 | 47.970 | 331.049 | 292.773 | 214.343 | −349.186 | 71.926 | −0.671 |
| 5700 | 48.388 | 331.902 | 293.452 | 219.161 | −350.158 | 79.454 | −0.728 |
| 5800 | 48.801 | 332.747 | 294.123 | 224.021 | −351.084 | 86.999 | −0.784 |
| 5900 | 49.208 | 333.584 | 294.784 | 228.921 | −351.966 | 94.560 | −0.837 |
| 6000 | 49.608 | 334.415 | 295.438 | 233.862 | −352.804 | 102.136 | −0.889 |

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

Sulfur Fluoride, Ion (SF$^-$) $F_1S_1^-(g)$

## Fluorosilylidyne (SiF) IDEAL GAS $M_r = 47.083903$ Fluorosilylidyne (SiF) $F_1Si_1(g)$

$S°(298.15\ K) = 225.786 \pm 0.17\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -21.912 \pm 12.6\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -20.083 \pm 12.6\ kJ \cdot mol^{-1}$

Electronic Levels and Molecular Constants ($\sigma = 1$)

| State | $\epsilon_i$, cm$^{-1}$ | $g_i$ | $r_e$, Å | $B_e$, cm$^{-1}$ | $\alpha_e$, cm$^{-1}$ | $\omega_e$, cm$^{-1}$ | $\omega_e x_e$, cm$^{-1}$ |
|---|---|---|---|---|---|---|---|
| $X^2\Pi_{1/2}$ | 0 | 2 | 1.6008 | 0.58138 | 0.00494 | 857.20 | 4.735 |
| $^2\Pi_{3/2}$ | 161.93 | 2 | 1.6008 | 0.58138 | 0.00494 | 857.20 | 4.735 |
| $A^2\Sigma^+$ | 22858.84 | 2 | 1.6049 | 0.57839 | 0.00941 | 718.5 | 10.167 |
| $a^4\Sigma$ | 29805.06 | 4 | 1.604 | 0.5786 | 0.00502 | 863.16 | 5.730 |
| $B^2\Sigma^+$ | 34561.5 | 2 | 1.5714 | 0.62707 | 0.00462 | 1011.2 | 4.825 |
| $C^2\Delta$ | 39438.4 | 4 | 1.5714 | 0.60338 | 0.00539 | 829.41 | 7.01 |
| $C'^2\Pi$ | 41964.9 | 4 | — | 0.6376 | 0.0039 | 1031.9 | 4.45 |
| $D'^2\Pi$ | 46606.7 | 4 | — | 0.6329 | 0.0044 | 1032.9 | 5.28 |
| $D^2\Sigma^+$ | 47418.6 | 2 | 1.54 | 0.625 | 0.005 | 1003.2 | 5.64 |

### Enthalpy of Formation

Ehlert and Margrave[1] have studied mass spectrometrically the reaction $Si(g) + SiF_2(g) \rightarrow 2\ SiF(g)$ by monitoring the intensities of the $Si^+$, $SiF_2^+$ and $SiF^+$ ions in an equilibrium system containing $CaF_2$ and Si. The ionization cross sections are assumed to cancel so that equilibrium constants can be obtained directly from the ion intensities. Eleven data points were reported in the 1395 to 1543 K range. We have analyzed their data using present JANAF functions[2] and obtain $\Delta_f H°(298.15\ K) = 23.5 \pm 3\ kcal \cdot mol^{-1}$ by the 3rd law technique with a drift of $-0.8 \pm 11\ cal\ K^{-1} \cdot mol^{-1}$; the 2nd law value is $23.9 \pm 7\ kcal \cdot mol^{-1}$. Farber[6] also has determined equilibrium constants mass–spectrometrically for the $Si(g) + SiF_2(g) = 2\ SiF(g)$ reaction; ten data points over a 1590 to 1782 K range were obtained. Our analysis yields a 3rd law $\Delta_r H°(298.15\ K) = 21.08 \pm 0.59\ kcal \cdot mol^{-1}$ with a drift of $-1.9 \pm 1.5\ cal\ K^{-1} \cdot mol^{-1}$; the 2nd law value is $24.18 \pm 2.5\ kcal \cdot mol^{-1}$. The two groups of data are in good agreement. We adopt an average value and calculate $\Delta_f H°(SiF, g, 298.15\ K) = -4.8 \pm 3\ kcal \cdot mol^{-1}$.

$D_0° = 130 \pm 4\ kcal \cdot mol^{-1}$ is calculated from the resulting $\Delta_f H°(0\ K)$ and auxiliary data.[2] Johns and Barrow[3] recommended $125 \pm 10\ kcal \cdot mol^{-1}$ from Birge–Sponer extrapolations of several states. Gaydon[4] preferred $115 \pm 12\ kcal \cdot mol^{-1}$ from a Birge–Sponer extrapolation of the ground state.

### Heat Capacity and Entropy

The molecular constants and electronic levels are those given by Suchard.[5] Five higher levels are given but are not used since they do not significantly affect the calculations. The ground state is treated as two distinct levels due to the splitting of this state as expressed by the spin coupling constant ($A = 161.93\ cm^{-1}$). This approximation gives slightly biased results at lower temperatures. An error of $\pm 0.04\ cal\ K^{-1} \cdot mol^{-1}$ has been assigned to $S°(298.15\ K)$ to allow for this.

### Reference

[1] T. C. Ehlert and J. L. Margrave, J. Chem. Phys. **41**, 1066 (1964).
[2] JANAF Thermochemical Tables: Si(g), 3–31–67; $SiF_2(g)$, 6–31–76; F(g), 9–30–65.
[3] J. W. C. Johns and R. F. Barrow, Proc. Phys. Soc. (London) **71**, 476 (1958).
[4] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed., Chapman and Hall Ltd., London, (1968).
[5] S. N. Suchard, The Aerospace Corporation, Air Force Space and Missile Systems Organization Contract F04701 73 C 0074, (March 29, 1974).
[6] M. Farber, Space Sciences, Inc., personal communication, (October 18, 1976).

Enthalpy Reference Temperature = $T_r$ = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ (J·K⁻¹mol⁻¹) | $S°$ (J·K⁻¹mol⁻¹) | $-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹) | $H°-H°(T_r)$ (kJ·mol⁻¹) | $\Delta_f H°$ (kJ·mol⁻¹) | $\Delta_f G°$ (kJ·mol⁻¹) | log $K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0. | 0. | INFINITE | −9.460 | −21.912 | −21 912 | INFINITE |
| 100 | 32.762 | 190.572 | 254.370 | −6.380 | −20.552 | −30.708 | 16.040 |
| 200 | 31.864 | 212.954 | 228.738 | −3.157 | −19.972 | −41.165 | 10.751 |
| 250 | 32.126 | 220.085 | 226.320 | −1.559 | −19.976 | −46.466 | 9.709 |
| 298.15 | 32.650 | 225.786 | 225.786 | 0. | −20.083 | −51.559 | 9.033 |
| 300 | 32.672 | 225.988 | ·225.786 | 0.060 | −20.089 | −51.755 | 9.011 |
| 350 | 33.289 | 231.070 | 226.186 | 1.709 | −20.269 | −57.019 | 8.510 |
| 400 | 33.874 | 235.554 | 227.083 | 3.389 | −20.492 | −62.254 | 8.130 |
| 450 | 34.392 | 239.575 | 228.251 | 5.096 | −20.742 | −67.459 | 7.830 |
| 500 | 34.836 | 243.222 | 229.569 | 6.827 | −21.014 | −72.636 | 7.588 |
| 600 | 35.530 | 249.638 | 232.393 | 10.347 | −21.607 | −82.905 | 7.218 |
| 700 | 36.029 | 255.155 | 235.260 | 13.926 | −22.251 | −93.071 | 6.945 |
| 800 | 36.396 | 259.991 | 238.055 | 17.548 | −22.943 | −103.142 | 6.734 |
| 900 | 36.674 | 264.295 | 240.736 | 21.203 | −23.678 | −113.123 | 6.565 |
| 1000 | 36.891 | 268.170 | 243.289 | 24.881 | −24.455 | −123.020 | 6.426 |
| 1100 | 37.065 | 271.695 | 245.714 | 28.579 | −25.273 | −132.837 | 6.308 |
| 1200 | 37.208 | 274.926 | 248.015 | 32.293 | −26.131 | −142.578 | 6.206 |
| 1300 | 37.329 | 277.909 | 250.201 | 36.020 | −27.029 | −152.246 | 6.117 |
| 1400 | 37.432 | 280.679 | 252.281 | 39.758 | −27.968 | −161.844 | 6.038 |
| 1500 | 37.523 | 283.265 | 254.261 | 43.506 | −28.950 | −171.372 | 5.968 |
| 1600 | 37.604 | 285.690 | 256.150 | 47.263 | −29.974 | −180.834 | 5.904 |
| 1700 | 37.678 | 287.972 | 257.956 | 51.027 | −81.217 | −189.783 | 5.831 |
| 1800 | 37.745 | 290.127 | 259.684 | 54.798 | −82.096 | −196.144 | 5.692 |
| 1900 | 37.807 | 292.170 | 261.340 | 58.576 | −82.973 | −202.456 | 5.566 |
| 2000 | 37.866 | 294.110 | 262.931 | 62.359 | −83.850 | −208.722 | 5.451 |
| 2100 | 37.921 | 295.959 | 264.460 | 66.149 | −84.724 | −214.944 | 5.346 |
| 2200 | 37.973 | 297.724 | 265.932 | 69.943 | −85.593 | −221.125 | 5.250 |
| 2300 | 38.024 | 299.414 | 267.351 | 73.743 | −86.457 | −227.266 | 5.161 |
| 2400 | 38.072 | 301.033 | 268.721 | 77.548 | −87.314 | −233.370 | 5.079 |
| 2500 | 38.120 | 302.588 | 270.045 | 81.358 | −88.161 | −239.438 | 5.003 |
| 2600 | 38.166 | 304.084 | 271.325 | 85.172 | −88.997 | −245.472 | 4.932 |
| 2700 | 38.211 | 305.525 | 272.566 | 88.991 | −89.821 | −251.475 | 4.865 |
| 2800 | 38.256 | 306.916 | 273.768 | 92.814 | −90.631 | −257.447 | 4.803 |
| 2900 | 38.301 | 308.259 | 274.934 | 96.642 | −91.426 | −263.391 | 4.744 |
| 3000 | 38.346 | 309.558 | 276.067 | 100.474 | −92.204 | −269.307 | 4.689 |
| 3100 | 38.391 | 310.816 | 277.167 | 104.311 | −92.964 | −275.198 | 4.637 |
| 3200 | 38.436 | 312.036 | 278.238 | 108.153 | −93.705 | −281.065 | 4.588 |
| 3300 | 38.483 | 313.219 | 279.280 | 111.998 | −94.427 | −286.909 | 4.541 |
| 3400 | 38.530 | 314.369 | 280.295 | 115.849 | −95.128 | −292.731 | 4.497 |
| 3500 | 38.579 | 315.486 | 281.285 | 119.705 | −95.808 | −298.533 | 4.455 |
| 3600 | 38.629 | 316.574 | 282.250 | 123.565 | −480.618 | −293.855 | 4.264 |
| 3700 | 38.681 | 317.633 | 283.192 | 127.430 | −480.841 | −288.664 | 4.075 |
| 3800 | 38.735 | 318.665 | 284.112 | 131.301 | −481.042 | −283.467 | 3.897 |
| 3900 | 38.791 | 319.672 | 285.011 | 135.177 | −481.223 | −278.265 | 3.727 |
| 4000 | 38.850 | 320.655 | 285.890 | 139.060 | −481.382 | −273.059 | 3.566 |
| 4100 | 38.911 | 321.615 | 286.750 | 142.947 | −481.519 | −267.849 | 3.412 |
| 4200 | 38.974 | 322.553 | 287.591 | 146.842 | −481.633 | −262.637 | 3.266 |
| 4300 | 39.041 | 323.471 | 288.415 | 150.742 | −481.724 | −257.421 | 3.127 |
| 4400 | 39.111 | 324.370 | 289.222 | 154.650 | −481.792 | −252.204 | 2.994 |
| 4500 | 39.184 | 325.249 | 290.013 | 158.565 | −481.837 | −246.986 | 2.867 |
| 4600 | 39.260 | 326.111 | 290.788 | 162.487 | −481.858 | −241.766 | 2.745 |
| 4700 | 39.340 | 326.957 | 291.549 | 166.417 | −481.856 | −236.547 | 2.629 |
| 4800 | 39.423 | 327.786 | 292.295 | 170.355 | −481.830 | −231.328 | 2.517 |
| 4900 | 39.510 | 328.599 | 293.028 | 174.302 | −481.781 | −226.110 | 2.410 |
| 5000 | 39.601 | 329.399 | 293.747 | 178.257 | −481.708 | −220.893 | 2.308 |
| 5100 | 39.696 | 330.184 | 294.454 | 182.222 | −481.611 | −215.677 | 2.209 |
| 5200 | 39.794 | 330.955 | 295.148 | 186.196 | −481.491 | −210.464 | 2.114 |
| 5300 | 39.897 | 331.714 | 295.831 | 190.181 | −481.347 | −205.253 | 2.023 |
| 5400 | 40.004 | 332.461 | 296.503 | 194.176 | −481.180 | −200.045 | 1.935 |
| 5500 | 40.114 | 333.196 | 297.163 | 198.182 | −480.990 | −194.841 | 1.850 |
| 5600 | 40.229 | 333.920 | 297.813 | 202.199 | −480.777 | −189.640 | 1.769 |
| 5700 | 40.348 | 334.633 | 298.453 | 206.228 | −480.541 | −184.443 | 1.690 |
| 5800 | 40.471 | 335.336 | 299.083 | 210.269 | −480.282 | −179.251 | 1.614 |
| 5900 | 40.597 | 336.029 | 299.703 | 214.322 | −480.002 | −174.063 | 1.541 |
| 6000 | 40.728 | 336.712 | 300.314 | 218.388 | −479.698 | −168.880 | 1.470 |

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$\Delta_f H°(0\ K) = -292.859 \pm 8.4\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 239.919 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -294.554 \pm 8.4\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

| State | $\epsilon_i$, $cm^{-1}$ | $g_i$ | State | $\epsilon_i$, $cm^{-1}$ | $g_i$ |
|---|---|---|---|---|---|
| $X^2\Sigma^+$ | 0 | 2 | $D\ ^2\Sigma$ | 28296.6 | 2 |
| $A^2\Pi$ | 15067.8 | 2 | $E^2\Pi$ | 31528.7 | 2 |
|  | 15348.5 | 2 |  | 31614.8 | 2 |
| $B^2\Sigma$ | 17303.4 | 2 | $F^2\Sigma$ | 32822.0 | 2 |
| $C^2\Pi$ | 27383.7 | 4 | $G^2\Pi$ | 34759.2 | 4 |

$\omega_e = 498.0\ cm^{-1}$ $\omega_e x_e = 2.15\ cm^{-1}$ $\sigma = 1$

$B_e = 0.2506\ cm^{-1}$ $\alpha_e = [0.00148]\ cm^{-1}$ $r_e = 2.0757 \pm 0.0005$ Å

## Enthalpy of Formation

Equilibrium constants for four dissociation equilibria have been determined from observations made on the condensed phase systems $SrF_2$–B,[1] $SrF_2$–Al,[2] and $SrF_2$–$BaF_2$–Al[2] by the mass spectrometric Knudsen effusion method. Enthalpies of reaction have been calculated from these Kp data by both the 2nd and 3rd law methods. Results of our analysis are given below, using JANAF auxiliary data.[4] Also included below is a value for the enthalpy of dissociation of SrF which was determined from spectrophotometric studies[3] of reaction equilibria in $H_2$–$O_2$–$N_2$ flames.

| Source | Reaction | $T$/K | Data Points | $\Delta_r H°$(298.15), kcal·mol$^{-1}$ 2nd law | 3rd law | Drift cal $K^{-1}$ $mol^{-1}$ | $\Delta_f H°$(298.15 K) kcal $mol^{-1}$ |
|---|---|---|---|---|---|---|---|
| Hildenbrand[1] | A | 1476–1585 | 10 | 23.4 | 25.1±0.9 | 1.2±4.7 | −70.1±2.7 |
| Hildenbrand[1] | B | 1436–1525 | 9 | 4.3 | 2.0±0.7 | −1.5±4.0 | −71.0±1.0 |
| Ehlert *et al.*[2] | C | 1174–1290 | 9[a] | 8.1 | 10.6±0.3 | 2.0±1.0 | −70.0±4.0 |
| Ehlert *et al.*[2] | D | 1125–1292 | 10 | 127.6 | −116.5±1.5 | 9.1±2.7 | −67.6±1.3 |
| Ryabova and Gurvich[3] | E |  |  | 132 ± 7 |  |  | −73.9±8.0 |

Reactions. (A) $2Sr(g) + BF_3(g) = 2SrF(g) + BF(g)$ (D) $2SrF(g) = Sr(g) + SrF_2(cr)$

(B) $Sr(g) + SrF_2(g) = 2SrF(g)$ (E) $SrF(g) = Sr(g) + F(g)$

(C) $Sr(g) + BaF(g) = Ba(g) + SrF(g)$

[a] One point rejected due to failure of a statistical test.

It is believed that the Kp data for the three homogeneous reactions (A, B, and C) are more reliable than those for the heterogeneous reaction (D) due to the need for a machine calibration constant which appears in the equilibrium expression for the latter. Ehlert *et al.*[2] determined this constant from vaporization experiments performed with silver contained in their Knudsen cell. This belief is further substantiated by the appearance of the rather large positive drift in the third law analysis of their Kp data for reaction (D). Also, it is felt that the $\Delta_f H°$ value obtained from the flame spectrophotometric studies[3] is perhaps somewhat less reliable than the three values derived from the Kp data for the homogeneous reactions. Thus, a median value $\Delta_f H°$(SrF, g, 298.15 K) = −70.4±2.0 kcal·mol$^{-1}$ of the latter results is adopted. The adopted value corresponds to a dissociation energy of $D_0^\circ$ (Sr–F) = 127.7 kcal·mol$^{-1}$ (5.54 cal $K^{-1}$·mol$^{-1}$).

Spectroscopic values for $D_0^\circ$ based on a linear Birge–Sponer extrapolation of the ground state ($X^2\Sigma$) vibrational levels (v, 0–4) have been reported as 3.2[5] and 3.5 eV.[6] However, it is well established now that the linear extrapolation[5, 6] generally underestimates $D_0^\circ$ if the binding of the molecule is partially ionic. Based on the ionic character correction suggested by Hildenbrand,[6] these values adjust to 4.9 and 5.4 eV. The latter value is now in reasonable agreement with the adopted thermochemical value Other spectroscopic values[7] include 4.6 (from $X^2\Sigma$), 4.7 (from $A^2\Pi$), and 5.2 eV (from $C^2\Pi$). The products of dissociation from the two excited states of SrF were assumed to be $Sr(^3P) + F(^2P)$.

## Heat Capacity and Entropy

The spectroscopic data with the exception of the value for $\alpha_e$ are those given by Rosen.[8] $\alpha_e$ is calculated from the other constants assuming a Morse potential function. The electronic states and levels are also taken from the compilation of Rosen.[8]

## References

[1] D. L. Hildenbrand, J Chem. Phys. 48, 3657 (1968)

[2] T. C. Ehlert, G. D. Blue, J. W. Green, and J. L. Margrave, J. Chem. Phys. **41**, 2250 (1964).

[3] V. G. Ryabova and L. V Gurvich, Teplofiz. Vysokikh Temperature, Akad. Nauk SSSR **2**, 834 (1964).

[4] JANAF Thermochemical Tables: Sr(g) and Ba(g), 12–31–70; $BF_3(g)$, 6–30–69; BF(g), 12–31–64; $SrF_2$(cr, g) and BaF(g), 12–31–72; F(g), 9–30–65.

[5] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed., Chapman and Hill Ltd., London, (1968).

[6] D. L Hildenbrand in "Advances in High Temperature Chemistry," Vol. 1, Ed. by L. Eyring, Academic Press, New York, (1967).

[7] M. M. Novikov and L. V. Gurvich, Optics and Spectroscopy **22**, 395 (1967).

[8] B. Rosen, "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, (1970).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

|  | J·K$^{-1}$mol$^{-1}$ |  |  | kJ·mol$^{-1}$ |  |  |  |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p^\circ$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −9.286 | −292.859 | −292.859 | INFINITE |
| 100 | 29.458 | 205.319 | 269.038 | −6.372 | −292.898 | −302.106 | 157.804 |
| 200 | 32.336 | 226.565 | 243.014 | −3.290 | −293.768 | −310.974 | 81.218 |
| 250 | 33.590 | 233.922 | 240.482 | −1.640 | −294.172 | −315.234 | 65.865 |
| 298.15 | 34.487 | 239.919 | 239.919 | 0. | −294.554 | −319.250 | 55.931 |
| 300 | 34.516 | 240.133 | 239.920 | 0.064 | −294.568 | −319.403 | 55.613 |
| 350 | 35.190 | 245.507 | 240.343 | 1.807 | −294.972 | −323.510 | 48.281 |
| 400 | 35.687 | 250.240 | 241.290 | 3.580 | −295.391 | −327.559 | 42.775 |
| 450 | 36.060 | 254.466 | 242.523 | 5.374 | −295.832 | −331.554 | 38.486 |
| 500 | 36.347 | 258.280 | 243.911 | 7.184 | −296.297 | −335.498 | 35.049 |
| 600 | 36.756 | 264.946 | 246.878 | 10.841 | −297.307 | −343.245 | 29.882 |
| 700 | 37.031 | 270.634 | 249.875 | 14.531 | −298.426 | −350.814 | 26.178 |
| 800 | 37.229 | 275.592 | 252.786 | 18.245 | −299.657 | −358.216 | 23.389 |
| 900 | 37.381 | 279.987 | 255.569 | 21.976 | −301.628 | −365.384 | 21.206 |
| 1000 | 37.503 | 283.932 | 258.212 | 25.720 | −302.762 | −372.407 | 19.453 |
| 1100 | 37.606 | 287.511 | 260.715 | 29.476 | −311.803 | −378.951 | 17.995 |
| 1200 | 37.694 | 290.787 | 263.086 | 33.241 | −313.857 | −384.965 | 16.757 |
| 1300 | 37.773 | 293.807 | 265.335 | 37.014 | −315.914 | −390.807 | 15.703 |
| 1400 | 37.845 | 296.609 | 267.470 | 40.795 | −317.975 | −396.491 | 14.793 |
| 1500 | 37.912 | 299.223 | 269.501 | 44.583 | −320.038 | −402.027 | 14.000 |
| 1600 | 37.977 | 301.671 | 271.436 | 48.377 | −322.104 | −407.426 | 13.301 |
| 1700 | 38.040 | 303.976 | 273.283 | 52.178 | −461.087 | −411.516 | 12.644 |
| 1800 | 38.103 | 306.152 | 275.049 | 55.985 | −461.296 | −408.594 | 11.857 |
| 1900 | 38.168 | 308.214 | 276.740 | 59.799 | −461.509 | −405.660 | 11.152 |
| 2000 | 38.236 | 310.173 | 278.364 | 63.619 | −461.729 | −402.715 | 10.518 |
| 2100 | 38.310 | 312.040 | 279.923 | 67.446 | −461.957 | −399.759 | 9.943 |
| 2200 | 38.390 | 313.824 | 281.424 | 71.281 | −462.195 | −396.791 | 9.421 |
| 2300 | 38.479 | 315.533 | 282.870 | 75.125 | −462.447 | −393.813 | 8.944 |
| 2400 | 38.577 | 317.172 | 284.265 | 78.977 | −462.715 | −390.823 | 8.506 |
| 2500 | 38.686 | 318.749 | 285.613 | 82.840 | −463.004 | −387.822 | 8.103 |
| 2600 | 38.808 | 320.269 | 286.917 | 86.715 | −463.321 | −384.808 | 7.731 |
| 2700 | 38.942 | 321.736 | 288.180 | 90.602 | −463.670 | −381.782 | 7.386 |
| 2800 | 39.091 | 323.155 | 289.404 | 94.504 | −464.058 | −378.742 | 7.066 |
| 2900 | 39.253 | 324.530 | 290.591 | 98.421 | −464.493 | −375.687 | 6.767 |
| 3000 | 39.431 | 325.863 | 291.745 | 102.355 | −464.981 | −372.617 | 6.488 |
| 3100 | 39.623 | 327.159 | 292.867 | 106.308 | −465.532 | −369.529 | 6.227 |
| 3200 | 39.829 | 328.421 | 293.958 | 110.280 | −466.151 | −366.423 | 5.981 |
| 3300 | 40.051 | 329.649 | 295.021 | 114.274 | −466.846 | −363.296 | 5.750 |
| 3400 | 40.286 | 330.849 | 296.057 | 118.291 | −467.624 | −360.147 | 5.533 |
| 3500 | 40.536 | 332.020 | 297.068 | 122.332 | −468.492 | −356.973 | 5.328 |
| 3600 | 40.798 | 333.166 | 298.055 | 126.398 | −469.456 | −353.773 | 5.133 |
| 3700 | 41.073 | 334.287 | 299.019 | 130.492 | −470.520 | −350.545 | 4.949 |
| 3800 | 41.360 | 335.386 | 299.962 | 134.613 | −471.689 | −347.288 | 4.774 |
| 3900 | 41.658 | 336.464 | 300.884 | 138.764 | −472.965 | −343.997 | 4.607 |
| 4000 | 41.966 | 337.523 | 301.787 | 142.945 | −474.350 | −340.673 | 4.449 |
| 4100 | 42.284 | 338.563 | 302.671 | 147.158 | −475.845 | −337.313 | 4.297 |
| 4200 | 42.611 | 339.586 | 303.538 | 151.402 | −477.447 | −333.915 | 4.153 |
| 4300 | 42.946 | 340.592 | 304.388 | 155.680 | −479.159 | −330.478 | 4.015 |
| 4400 | 43.288 | 341.584 | 305.222 | 159.992 | −480.976 | −326.999 | 3.882 |
| 4500 | 43.636 | 342.560 | 306.041 | 164.338 | −482.896 | −323.478 | 3.755 |
| 4600 | 43.990 | 343.523 | 306.845 | 168.719 | −484.848 | −319.919 | 3.633 |
| 4700 | 44.348 | 344.473 | 307.636 | 173.136 | −486.939 | −316.311 | 3.515 |
| 4800 | 44.711 | 345.411 | 308.413 | 177.589 | −489.111 | −312.658 | 3.402 |
| 4900 | 45.076 | 346.336 | 309.177 | 182.078 | −491.359 | −308.959 | 3.294 |
| 5000 | 45.444 | 347.251 | 309.930 | 186.604 | −493.670 | −305.213 | 3.189 |
| 5100 | 45.813 | 348.154 | 310.670 | 191.167 | −496.023 | −301.423 | 3.087 |
| 5200 | 46.183 | 349.047 | 311.400 | 195.767 | −498.445 | −297.583 | 2.989 |
| 5300 | 46.553 | 349.931 | 312.119 | 200.404 | −500.911 | −293.697 | 2.895 |
| 5400 | 46.923 | 350.804 | 312.827 | 205.078 | −503.412 | −289.764 | 2.803 |
| 5500 | 47.291 | 351.669 | 313.525 | 209.788 | −505.940 | −285.785 | 2.714 |
| 5600 | 47.658 | 352.524 | 314.214 | 214.536 | −508.486 | −281.759 | 2.628 |
| 5700 | 48.021 | 353.371 | 314.894 | 219.320 | −511.043 | −277.687 | 2.545 |
| 5800 | 48.382 | 354.209 | 315.564 | 224.140 | −513.604 | −273.571 | 2.464 |
| 5900 | 48.739 | 355.039 | 316.226 | 228.996 | −515.951 | −269.435 | 2.385 |
| 6000 | 49.092 | 355.861 | 316.880 | 233.888 | −518.467 | −265.235 | 2.309 |

PREVIOUS. December 1972 (1 atm) CURRENT: December 1972 (1 bar)

$S°(298.15 K) = [232.846 \pm 8.4]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = 192.679 \pm 41.8\ kJ\ mol^{-1}$
$\Delta_fH°(298\ 15\ K) = [197\ 066]\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

| State | $\epsilon_i$, $cm^{-1}$ | $g_i$ |
|---|---|---|
| $X^1\Sigma^+$ | 0 | 1 |
| $a^3\Pi$ | [1000] | 6 |
| $A'^1\Pi$ | [12000] | 2 |
| $B'^1\Delta$ | [15000] | 2 |
| $A^1\Sigma^+$ | [18000] | 1 |
| $b^3\Sigma^-$ | [20000] | 3 |
| $B^1\Sigma^+$ | [35000] | 1 |

$\omega_e = [561]\ cm^{-1}$  $\omega_ex_e = [2.42]\ cm^{-1}$  $\sigma = 1$
$B_e = [0.27265]\ cm^{-1}$  $\alpha_e = [0.00157]\ cm^{-1}$  $r_e = [1\ 99]$ Å

## Enthalpy of Formation

The appearance potential of $SrF^+$ from SrF(g) has been measured mass spectrometrically by Hildenbrand,[1] Green *et al* [2] and Ehlert *et al.*[3] as 5.0 ± 0.3 eV, 4.9 ± 0.3 eV, and 5.2 ± 0.3 eV, respectively. For the process $e^- + SrF(g) \rightarrow SrF^+(g) + 2e^-$, the corresponding $\Delta_fH°(SrF^+, g, 0\ K)$ are derived to be 45.3 ± 9.0, and 49.9± 9.0 $kcal{\cdot}mol^{-1}$ with $\Delta_fH°(SrF, g, 0\ K) = -70.0 \pm 2.0\ kcal{\cdot}mol^{-1}$.[4]

Hildenbrand[1] has also reported AP = 13.0 ± 1.0 eV for $SrF^+$ from $SrF_2(g)$. Green *et al.*[2] obtained an ionization efficiency curve for $SrF^+$ which extrapolates (high–energy portion) to 10.5 eV at zero ion current. Assuming the process to be $e^- + SrF_2(g) \rightarrow SrF^+(g) + F(g) + 2e^-$, we obtain $\Delta_fH°(SrF^+, g, 0\ K)$ equal to 98.7 ± 25.0 and 41 1 $kcal{\cdot}mol^{-1}$ by combining the above results with $\Delta_fH°(SrF_2, g, 0\ K) = 182.7 \pm 1.0\ kcal{\cdot}mol^{-1}$ and $\Delta_fH°(F, g, 0\ K) = 18.36 \pm 0.4\ kcal{\cdot}mol^{-1}$.[4]

The adopted $\Delta_fH°(0\ K)$ is based on the three mass spectral results[1 2, 3] for the direct ionization process of SrF(g) The value of $\Delta_fH°$ at 298.15 K is 47.1 ± 10.0 $kcal{\cdot}mol^{-1}$, and the corresponding ionization potential for SrF(g) is 5.03 eV.

## Heat Capacity and Entropy

The internuclear distance ($r_e$) is the value estimated by Barrow and Beale[5] from spectroscopic work on SrF The value of $\omega_e$ is calculated from Badger's rule[6] which can be written in the form $\omega_e^2 = 3.159 \times 10^6/\mu(r_e - d_{ij})$.[3] Molecular data for the ground states of SrF,[4] SrO,[7] and RbF[8] were used to determine the constant $d_{ij}$. The product $x_e\mu^{1/2}$ has been shown to be constant within a group of similar molecules by Barrow and Caunt.[9] Since $\mu^{1/2}(SrF^+) \cong \mu^{1/2}(SrF)$, we assume $x_e(SrF^+) = x_e(SrF)$ and obtain $\omega_ex_e$ equal to 2.42 $cm^{-1}$ with our estimated value $\omega_e = 561\ cm^{-1}$. The value of $\alpha_e$ is obtained from the other constants assuming a Morse potential function.

$SrF^+$ has eight valence electrons; thus, the ground state configuration ($^1\Sigma^+$) and electronic level for the B state are estimated from those for the isoelectronic molecule SrS.[7] By analogy with the gaseous alkaline earth oxides,[10] $C_2$,[4] BeS,[11] and BaS,[12] *low lying triplet states are to be* expected. The two estimated triplet levels are based on those which have been observed directly in $C_2$,[4] BeS,[11] and indirectly (through perturbative effects) in BaS.[12] Also included are additional states at 12,000 $cm^{-1}$ ($^1\Pi$), 15,000 $cm^{-1}$ ($^1\Delta$), and 18,000 $cm^{-1}$ ($^1\Sigma$). These three levels are also estimated from those for $C_2$,[4] Bes,[11] and BaS.[12] The adopted electronic entropies are believed to represent minimal values. Probable *upper limits for the electronic contributions can be established by decreasing the two triplet levels to* 1000 $cm^{-1}$ ($^3\Pi$) and 5000 $cm^{-1}$ ($^3\Sigma$) and neglecting the other excited states. This increases the entropy by 3.9 cal $K^{-1}{\cdot}mol^{-1}$ and 2.6 cal $K^{-1}$ $mol^{-1}$ at 2000 K and 4000 K, respectively.

## References

[1] D. L. Hildenbrand, J. Chem. Phys. 48, 3657 (1968).
[2] J. W Green, G. D Blue, T. C. Ehlert, and J. L. Margrave, J. Chem. Phys. 41, 2245 (1964).
[3] T. C. Ehlert, G D. Blue, J. W. Green, and J. L. Margrave, J. Chem. Phys. 41, 2250 (1964).
[4] JANAF Thermochemical Tables· SrF(g) and $SrF_2$(g), 12–31–72; F(g), 9–30–65; $C_2$(g), 12–31–69.
[5] R. F. Barrow and J. R. Beale, Chem. Comm. **1967**, 606 (1967).
[6] R. M. Badger, J Chem. Phys. **2**, 128 (1934).
[7] M. Marcano and R. F. Barrow, Trans. Faraday Soc. **66**, 1917 (1970).
[8] B. Rosen, "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, (1970).
[9] R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London) **219A**, 120 (1953).
[10] L. Brewer and G M Rosenblatt in "Advances in High Temperature Chemistry," Vol. 2, Ed. by L. Eyring, Academic Press, New York, (1969).
[11] C. J. Cheetham, W. J. M. Gissane, and R. F. Barrow, Trans. Faraday Soc. **61**, 1308 (1965).
[12] R. F. Barrow, W. G Burton, and P. A. Jones, Trans. Faraday Soc. **67**, 902 (1971).

Enthalpy Reference Temperature = $T_r$ = 298.15 K  Standard State Pressure = $p°$ = 0.1 MPa

|  | $J{\cdot}K^{-1}mol^{-1}$ |  |  | $kJ{\cdot}mol^{-1}$ |  |  |  |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −9.171 | 192.679 |  |  |
| 100 | 29.288 | 198.822 | 261.416 | −6.259 |  |  |  |
| 200 | 31.664 | 219.755 | 235.882 | −3.225 |  |  |  |
| 250 | 32.928 | 226.961 | 233.399 | −1.610 |  |  |  |
| 298.15 | 33.891 | 232.846 | 232.846 | 0. | 197.066 | 168.224 | −29.472 |
| 300 | 33.923 | 233.056 | 232.847 | 0.063 | 197.089 | 168.045 | −29.259 |
| 350 | 34 677 | 238.345 | 233.263 | 1.779 | 197.697 | 163.157 | −24.350 |
| 400 | 35.245 | 243.014 | 234.196 | 3.527 | 198.294 | 158.181 | −20.656 |
| 450 | 35.679 | 247.191 | 235.412 | 5.301 | 198.871 | 153.132 | −17.775 |
| 500 | 36.016 | 250.969 | 236.782 | 7.094 | 199.428 | 148.020 | −15.464 |
| 600 | 36.497 | 257.581 | 239.713 | 10.721 | 200.467 | 137.639 | −11.983 |
| 700 | 36.819 | 263.233 | 242.679 | 14.388 | 201.403 | 127.093 | −9 484 |
| 800 | 37.049 | 268.165 | 245.563 | 18.082 | 202.231 | 116.419 | −7.601 |
| 900 | 37.223 | 272.539 | 248.322 | 21.796 | 202.322 | 105.720 | −6.136 |
| 1000 | 37.364 | 276.469 | 250.943 | 25.526 | 203.252 | 94.936 | −4.959 |
| 1100 | 37.488 | 280.036 | 253.428 | 29.268 | 196.277 | 84.426 | −4.009 |
| 1200 | 37.611 | 283.303 | 255.784 | 33.023 | 196.292 | 74.257 | −3.232 |
| 1300 | 37.748 | 286.319 | 258.018 | 36.791 | 196.307 | 64.086 | −2.575 |
| 1400 | 37.913 | 289.122 | 260.141 | 40.574 | 196.327 | 53.915 | −2.012 |
| 1500 | 38.124 | 291.745 | 262.161 | 44.375 | 196.355 | 43.742 | −1.523 |
| 1600 | 38.394 | 294.213 | 264.088 | 48.200 | 196.399 | 33.566 | −1.096 |
| 1700 | 38 734 | 296.551 | 265.930 | 52.056 | 59.550 | 24.567 | −0.755 |
| 1800 | 39 153 | 298.776 | 267.693 | 55 950 | 61.506 | 22.453 | −0.652 |
| 1900 | 39.657 | 300.906 | 269.385 | 59.890 | 63 497 | 20.229 | −0.556 |
| 2000 | 40.247 | 302.955 | 271.013 | 63.884 | 65.530 | 17 899 | −0.467 |
| 2100 | 40.923 | 304.935 | 272.581 | 67.942 | 67.611 | 15.467 | −0.385 |
| 2200 | 41.678 | 306.856 | 274.096 | 72.071 | 69.746 | 12.934 | −0.307 |
| 2300 | 42.506 | 308.726 | 275.561 | 76.280 | 71.939 | 10.303 | −0.234 |
| 2400 | 43.398 | 310.554 | 276.981 | 80.575 | 74.192 | 7.575 | −0.165 |
| 2500 | 44.340 | 312.344 | 278.360 | 84.961 | 76.504 | 4.752 | −0 099 |
| 2600 | 45.322 | 314.103 | 279.701 | 89.444 | 78.875 | 1.835 | −0.037 |
| 2700 | 46.328 | 315.832 | 281.007 | 94.026 | 81.299 | −1.174 | 0 023 |
| 2800 | 47.345 | 317.535 | 282.281 | 98.710 | 83.771 | −4.273 | 0.080 |
| 2900 | 48.361 | 319.214 | 283.526 | 103.495 | 86.284 | −7.462 | 0.134 |
| 3000 | 49.361 | 320.871 | 284.743 | 108.382 | 88.826 | −10.738 | 0.187 |
| 3100 | 50.335 | 322.505 | 285.935 | 113.367 | 91.387 | −14 099 | 0.238 |
| 3200 | 51.271 | 324.118 | 287.103 | 118.447 | 93.955 | −17.543 | 0.286 |
| 3300 | 52.160 | 325 709 | 288.249 | 123.619 | 96.516 | −21.067 | 0.333 |
| 3400 | 52.994 | 327.279 | 289.374 | 128.877 | 99.058 | −24.668 | 0.379 |
| 3500 | 53.768 | 328.827 | 290.479 | 134.216 | 101.566 | −28.344 | 0.423 |
| 3600 | 54.475 | 330.351 | 291.566 | 139.629 | 104.027 | −32.090 | 0.466 |
| 3700 | 55.114 | 331.853 | 292.634 | 145.109 | 106.428 | −35.905 | 0.507 |
| 3800 | 55.682 | 333.330 | 293.686 | 150.649 | 108.757 | −39.783 | 0.547 |
| 3900 | 56.179 | 334.783 | 294.721 | 156.243 | 111.002 | −43.721 | 0.586 |
| 4000 | 56.606 | 336.211 | 295.740 | 161.883 | 113 154 | −47.716 | 0.623 |
| 4100 | 56.963 | 337.613 | 296.745 | 167.562 | 115.204 | −51.763 | 0.659 |
| 4200 | 57.253 | 338.990 | 297.734 | 173.273 | 117.148 | −55.860 | 0.695 |
| 4300 | 57.481 | 340.340 | 298.709 | 179.010 | 118.974 | −60.001 | 0.729 |
| 4400 | 57.647 | 341.663 | 299.671 | 184.767 | 120.680 | −64.183 | 0.762 |
| 4500 | 57.758 | 342.960 | 300.618 | 190.538 | 122.264 | −68.402 | 0.794 |
| 4600 | 57.817 | 344.230 | 301.553 | 196.317 | 123.788 | −72.661 | 0.825 |
| 4700 | 57.828 | 345.474 | 302.474 | 202.100 | 125 142 | −76.946 | 0.855 |
| 4800 | 57.796 | 346.691 | 303.382 | 207.881 | 126.377 | −81.259 | 0.884 |
| 4900 | 57.724 | 347.882 | 304.278 | 213.658 | 127.494 | −85.597 | 0.912 |
| 5000 | 57.618 | 349.047 | 305.162 | 219.425 | 128.503 | −89.957 | 0.940 |
| 5100 | 57.480 | 350.187 | 306.034 | 225.180 | 129.422 | −94.337 | 0.966 |
| 5200 | 57.315 | 351.302 | 306.894 | 230.920 | 130.218 | −98.732 | 0.992 |
| 5300 | 57.127 | 352.392 | 307.742 | 236.642 | 130.916 | −103.142 | 1.017 |
| 5400 | 56.919 | 353.457 | 308.579 | 242.345 | 131.522 | −107.564 | 1.040 |
| 5500 | 56.693 | 354.500 | 309.404 | 248.026 | 132.043 | −111.997 | 1.064 |
| 5600 | 56.454 | 355.519 | 310.219 | 253.683 | 132.486 | −116.438 | 1.086 |
| 5700 | 56.203 | 356.516 | 311.022 | 259.316 | 132.856 | −120.886 | 1.108 |
| 5800 | 55.942 | 357.491 | 311.815 | 264.923 | 133.161 | −125.341 | 1.129 |
| 5900 | 55.675 | 358.445 | 312.597 | 270.504 | 133.617 | −129.824 | 1.149 |
| 6000 | 55.403 | 359.379 | 313.369 | 276.058 | 133.842 | −134.291 | 1.169 |

PREVIOUS: December 1972 (1 atm)  CURRENT: December 1972 (1 bar)

## Titanium Fluoride (TiF) IDEAL GAS $M_r = 66.878403$

$S°(298.15\ K) = 237.31 \pm 8.4\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = [-66.941 \pm 41.8]\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [-66.944 \pm 41.8]\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

| $\epsilon_i$, cm$^{-1}$ | $g_i$ | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|---|
| 0 | [4] | [6000] | [4] |
| [1000] | [4] | [8000] | [4] |
| [2000] | [4] | [10000] | [4] |
| [4000] | [4] | | |

$\omega_e = [590] cm^{-1}$
$B_e = [0.328]\ cm^{-1}$
$\omega_e x_e = [6.6]\ cm^{-1}$
$\alpha_e = [0.0036]\ cm^{-1}$
$\sigma = 1$
$r_e = [1.95]\ Å$

### Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°$(TiF, g, 298.15 K), is calculated from the dissociation energy. The dissociation energy is estimated as 148 ± 6 kcal·mol$^{-1}$ using the corresponding quantity for $TiF_2(g)$ and the relation $D_0°(MF)/\Delta_{at}H°(MF_2) = 0.46 \pm 0.02$ which Zmbov and Margrave[1] found held for other mono- and di-fluorides.

### Heat Capacity and Entropy

The vibrational frequency, $\omega_e$, and anharmonic vibrational term, $\omega_e x_e$, are estimated from those of the alkali and mercury monohalides. The interatomic distance, $r_e$, is estimated from those of TiCl(g), $TiF_2(g)$ and $TiF_3(g)$. $B_e$ is calculated from $r_e$. The ground state term and electronic levels are estimated from the ground state multiplet of $Ti^+$.[2]

### References

[1] K. F. Zmbov and J. L Margrave, J. Phys. Chem. **71**, 2893 (1967).

[2] C. E. Moore, U S. Nat. Bur. Stand. Circ 467, (1949).

## Titanium Fluoride (TiF) $F_1Ti_1(g)$

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −9.239 | −66.941 | −66.941 | INFINITE |
| 100 | 29.254 | 203.037 | 266.316 | −6.328 | −66.044 | −77.003 | 40.222 |
| 200 | 31.809 | 223.943 | 240.429 | −3.297 | −66.394 | −87.872 | 22.950 |
| 250 | 33.638 | 231.236 | 237.881 | −1.661 | −66.673 | −93.210 | 19.475 |
| 298.15 | 35.339 | 237.309 | 237.309 | 0. | −66.944 | −98.296 | 17.221 |
| 300 | 35.401 | 237.528 | 237.309 | 0.065 | −66.954 | −98.490 | 17.149 |
| 350 | 36.971 | 243.105 | 237.746 | 1.876 | −67.226 | −103.725 | 15.480 |
| 400 | 38.309 | 248.132 | 238.736 | 3.759 | −67.484 | −108.921 | 14.224 |
| 450 | 39.417 | 252.711 | 240.038 | 5.703 | −67.731 | −114.086 | 13.243 |
| 500 | 40.316 | 256.912 | 241.518 | 7.697 | −67.969 | −119.224 | 12.455 |
| 600 | 41.599 | 264.385 | 244.722 | 11.798 | −68.430 | −129.431 | 11.268 |
| 700 | 42.376 | 270.861 | 248.004 | 16.000 | −68.892 | −139.561 | 10.414 |
| 800 | 42.830 | 276.552 | 251.224 | 20.262 | −69.359 | −149.625 | 9.770 |
| 900 | 43.089 | 281.613 | 254.325 | 24.559 | −69.880 | −159.628 | 9.265 |
| 1000 | 43.240 | 286.161 | 257.285 | 28.876 | −70.529 | −169.567 | 8.857 |
| 1100 | 43.333 | 290.287 | 260.100 | 33.205 | −71.375 | −179.432 | 8.521 |
| 1200 | 43.402 | 294.061 | 262.775 | 37.542 | −76.406 | −189.090 | 8.231 |
| 1300 | 43.461 | 297.537 | 265.318 | 41.885 | −76.928 | −198.460 | 7.974 |
| 1400 | 43.520 | 300.760 | 267.735 | 46.235 | −77.533 | −207.786 | 7.753 |
| 1500 | 43.584 | 303.765 | 270.038 | 50.590 | −78.233 | −217.066 | 7.559 |
| 1600 | 43.652 | 306.580 | 272.235 | 54.951 | −79.041 | −226.296 | 7.388 |
| 1700 | 43.725 | 309.228 | 274.334 | 59.320 | −79.967 | −235.472 | 7.235 |
| 1800 | 43.801 | 311.730 | 276.343 | 63.696 | −81.025 | −244.589 | 7.098 |
| 1900 | 43.879 | 314.100 | 278.268 | 68.080 | −82.224 | −253.644 | 6.973 |
| 2000 | 43.958 | 316.353 | 280.117 | 72.472 | −98.265 | −262.178 | 6.847 |
| 2100 | 44.037 | 318.499 | 281.894 | 76.872 | −100.533 | −270.318 | 6.724 |
| 2200 | 44.113 | 320.550 | 283.604 | 81.280 | −102.794 | −278.350 | 6.609 |
| 2300 | 44.186 | 322.512 | 285.254 | 85.695 | −105.047 | −286.280 | 6.502 |
| 2400 | 44.255 | 324.394 | 286.846 | 90.117 | −107.290 | −294.111 | 6.401 |
| 2500 | 44.320 | 326.202 | 288.384 | 94.545 | −109.522 | −301.850 | 6.307 |
| 2600 | 44.381 | 327.942 | 289.872 | 98.981 | −111.742 | −309.499 | 6.218 |
| 2700 | 44.437 | 329.618 | 291.313 | 103.422 | −113.948 | −317.063 | 6.134 |
| 2800 | 44.488 | 331.235 | 292.710 | 107.868 | −116.139 | −324.546 | 6.054 |
| 2900 | 44.534 | 332.797 | 294.066 | 112.319 | −118.315 | −331.950 | 5.979 |
| 3000 | 44.575 | 334.307 | 295.382 | 116.774 | −120.474 | −339.280 | 5.907 |
| 3100 | 44.612 | 335.769 | 296.662 | 121.234 | −122.615 | −346.539 | 5.839 |
| 3200 | 44.645 | 337.186 | 297.906 | 125.697 | −124.739 | −353.728 | 5.774 |
| 3300 | 44.674 | 338.560 | 299.117 | 130.163 | −126.845 | −360.851 | 5.712 |
| 3400 | 44.700 | 339.894 | 300.297 | 134.631 | −128.932 | −367.911 | 5.652 |
| 3500 | 44.723 | 341.191 | 301.447 | 139.103 | −131.000 | −374.910 | 5.595 |
| 3600 | 44.742 | 342.451 | 302.569 | 143.576 | −133.050 | −381.849 | 5.540 |
| 3700 | 44.760 | 343.677 | 303.663 | 148.051 | −544.179 | −380.944 | 5.378 |
| 3800 | 44.775 | 344.871 | 304.732 | 152.528 | −544.957 | −376.522 | 5.176 |
| 3900 | 44.789 | 346.034 | 305.776 | 157.006 | −545.772 | −372.079 | 4.983 |
| 4000 | 44.800 | 347.168 | 306.797 | 161.485 | −546.623 | −367.614 | 4.801 |
| 4100 | 44.811 | 348.274 | 307.795 | 165.966 | −547.508 | −363.128 | 4.626 |
| 4200 | 44.821 | 349.354 | 308.772 | 170.448 | −548.426 | −358.620 | 4.460 |
| 4300 | 44.830 | 350.409 | 309.728 | 174.930 | −549.376 | −354.090 | 4.301 |
| 4400 | 44.838 | 351.440 | 310.664 | 179.414 | −550.356 | −349.537 | 4.150 |
| 4500 | 44.847 | 352.448 | 311.581 | 183.898 | −551.364 | −344.962 | 4.004 |
| 4600 | 44.855 | 353.433 | 312.481 | 188.383 | −552.400 | −340.364 | 3.865 |
| 4700 | 44.863 | 354.398 | 313.362 | 192.869 | −553.462 | −335.743 | 3.731 |
| 4800 | 44.871 | 355.343 | 314.227 | 197.355 | −554.547 | −331.099 | 3.603 |
| 4900 | 44.880 | 356.268 | 315.076 | 201.843 | −555.655 | −326.432 | 3.480 |
| 5000 | 44.889 | 357.175 | 315.909 | 206.331 | −556.783 | −321.743 | 3.361 |
| 5100 | 44.899 | 358.064 | 316.726 | 210.821 | −557.930 | −317.031 | 3.247 |
| 5200 | 44.909 | 358.936 | 317.530 | 215.311 | −559.094 | −312.296 | 3.137 |
| 5300 | 44.920 | 359.791 | 318.319 | 219.803 | −560.274 | −307.539 | 3.031 |
| 5400 | 44.932 | 360.631 | 319.095 | 224.295 | −561.467 | −302.759 | 2.929 |
| 5500 | 44.944 | 361.456 | 319.858 | 228.789 | −562.673 | −297.957 | 2.830 |
| 5600 | 44.958 | 362.266 | 320.608 | 233.284 | −563.889 | −293.133 | 2.734 |
| 5700 | 44.972 | 363.061 | 321.346 | 237.781 | −565.115 | −288.287 | 2.642 |
| 5800 | 44.988 | 363.844 | 322.072 | 242.279 | −566.348 | −283.420 | 2.552 |
| 5900 | 45.004 | 364.613 | 322.786 | 246.778 | −567.587 | −278.531 | 2.466 |
| 6000 | 45.021 | 365.369 | 323.490 | 251.279 | −568.832 | −273.621 | 2.382 |

PREVIOUS December 1967 (1 atm) CURRENT: December 1967 (1 bar)

Titanium Fluoride (TiF) $F_1Ti_1(g)$

## Tungsten Fluoride (WF) IDEAL GAS $M_r = 202.848403$ Tungsten Fluoride (WF) $F_1W_1(g)$

$S°(298.15\ K) = [251.141]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = [386.518 \pm 62.8]\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [386.183 \pm 62.8]\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

| State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|
| $[^2\Delta]$ | 0 | [4] |
| | [5000] | [2] |
| | [15000] | [20] |

$\omega_e = [726.5]\ cm^{-1}$ $\omega_e x_e = [2.9]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.292\ \ 3]\ cm^{-1}$ $\alpha_e = [0.0015]\ cm^{-1}$ $r_e = [1.83]\ Å$

### Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(WF, g, 298.15\ K) = 92.3\ kcal{\cdot}mol^{-1}$, is calculated from the bond dissociation energy $\Delta_a H°(WF, 298.15\ K) = 130 \pm 15\ kcal{\cdot}mol^{-1}$. This value of $\Delta_a H°(298.15\ K)$ is estimated to be slightly higher than the average bond dissociation energy of $WF_6(g)$ by analogy with the $WCl_x$ system.

### Heat Capacity and Entropy

The bond distance is estimated to be the same as that in $WF_6(g)$. This distance is then used with Guggenheimer's[1] relation to calculate the fundamental vibrational frequency, $\omega_e$.[1] The anharmonicity correction $x_e$ is estimated roughly by assuming $x_e = \omega_e/4(D_0^0 + 0.5\ \omega_e) = 0.0042$. The rotational constant, $B_e$, is calculated from the estimated bond distance. The value of $\alpha_e$ is calculated form the Morse potential function.

The ground state configuration, low lying electronic levels and their quantum weights are estimated based on the tentative molecular orbital diagram for TaO given by Weltner and McLeod.[2] Using this scheme, we obtain the ground state configuration as $\Pi^4\sigma\delta^4$ which yields a $^2\Sigma$ state. Higher levels are considered to be formed by transition to $\Pi^*$ antibonding orbitals, and by analogy with TaO these are assumed to lie in the 15000 cm$^{-1}$ region. The degeneracy of these levels is estimated roughly from the large number of possible configurations.

### References

[1] K. M. Guggenheimer, Proc. Phys. Soc. 58, 456 (1946).
[2] W. Weltner, Jr., and D. McLeod, Jr., J. Chem. Phys. 42, 882 (1965).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −9.051 | 386.518 | 386.518 | INFINITE |
| 100 | 29.135 | 217.762 | 279 175 | −6.141 | 387.322 | 375.025 | −195.893 |
| 200 | 30.708 | 238.278 | 254.142 | −3.173 | 386.818 | 362.882 | −94.775 |
| 250 | 32.340 | 245.300 | 251.691 | −1.598 | 386.485 | 356.937 | −74.578 |
| 298.15 | 34.026 | 251.141 | 251.141 | 0. | 386.183 | 351.274 | −61.542 |
| 300 | 34.090 | 251.351 | 251.141 | 0.063 | 386.172 | 351.057 | −61.125 |
| 350 | 35.728 | 256.732 | 251.563 | 1.809 | 385.900 | 345.227 | −51.522 |
| 400 | 37.157 | 261.598 | 252.518 | 3.632 | 385.668 | 339.433 | −44.325 |
| 450 | 38.353 | 266.046 | 253.777 | 5.521 | 385.472 | 333.665 | −38.731 |
| 500 | 39.326 | 270.139 | 255.212 | 7.464 | 385.303 | 327.918 | −34.257 |
| 600 | 40.693 | 277.441 | 258.323 | 11.471 | 385.015 | 316.469 | −27.551 |
| 700 | 41.464 | 283.778 | 261.517 | 15.583 | 384.751 | 305.066 | −22.764 |
| 800 | 41.824 | 289.342 | 264.655 | 19.750 | 384.468 | 293.701 | −19.177 |
| 900 | 41.920 | 294.275 | 267.677 | 23.939 | 384.141 | 282.375 | −16.389 |
| 1000 | 41.854 | 298.690 | 270.561 | 28.128 | 383.752 | 271.088 | −14.160 |
| 1100 | 41.697 | 302.672 | 273.303 | 32.306 | 383.291 | 259.843 | −12.339 |
| 1200 | 41.493 | 306.292 | 275.903 | 36.466 | 382.753 | 248.643 | −10.823 |
| 1300 | 41.271 | 309.604 | 278.370 | 40.604 | 382.137 | 237.492 | −9.543 |
| 1400 | 41.049 | 312.654 | 280.711 | 44.720 | 381.441 | 226.391 | −8.447 |
| 1500 | 40.835 | 315.479 | 282.936 | 48.815 | 380.668 | 215.343 | −7.499 |
| 1600 | 40.635 | 318.108 | 285.053 | 52.888 | 379.817 | 204.348 | −6.671 |
| 1700 | 40.451 | 320.566 | 287.071 | 56.942 | 378.891 | 193.409 | −5.943 |
| 1800 | 40.284 | 322.873 | 288.996 | 60.979 | 377.893 | 182.527 | −5.297 |
| 1900 | 40.133 | 325 047 | 290.837 | 64.999 | 376.826 | 171.702 | −4.720 |
| 2000 | 39.998 | 327.102 | 292.599 | 69.006 | 375.691 | 160.935 | −4.203 |
| 2100 | 39.877 | 329.051 | 294.289 | 72.999 | 374.491 | 150.227 | −3 737 |
| 2200 | 39 769 | 330.903 | 295.912 | 76.982 | 373.229 | 139.577 | −3.314 |
| 2300 | 39.674 | 332.669 | 297.472 | 80.954 | 371.909 | 128.986 | −2.929 |
| 2400 | 39.589 | 334.356 | 298.974 | 84.917 | 370.532 | 118.453 | −2.578 |
| 2500 | 39.514 | 335.970 | 300.422 | 88.872 | 369.101 | 107.979 | −2.256 |
| 2600 | 39.449 | 337.519 | 301.819 | 92.820 | 367.623 | 97.563 | −1.960 |
| 2700 | 39.391 | 339.006 | 303.169 | 96.762 | 366.072 | 87.206 | −1.687 |
| 2800 | 39.340 | 340.438 | 304.474 | 100.698 | 364.416 | 76.907 | −1.435 |
| 2900 | 39.295 | 341.818 | 305.738 | 104.630 | 362.618 | 66.670 | −1.201 |
| 3000 | 39.257 | 343.149 | 306.963 | 108.558 | 360.654 | 56.498 | −0.984 |
| 3100 | 39.223 | 344.436 | 308.152 | 112.481 | 358.480 | 46.395 | −0.782 |
| 3200 | 39.195 | 345.681 | 309.305 | 116.402 | 356.068 | 36.365 | −0.594 |
| 3300 | 39.170 | 346.886 | 310.426 | 120.321 | 353.393 | 26.415 | −0.418 |
| 3400 | 39.149 | 348.055 | 311.515 | 124.236 | 350.421 | 16.550 | −0.254 |
| 3500 | 39.132 | 349.190 | 312.576 | 128.151 | 347.089 | 6.778 | −0.101 |
| 3600 | 39.118 | 350.292 | 313.608 | 132.063 | 343.301 | −2.892 | 0.042 |
| 3700 | 39.107 | 351.364 | 314.614 | 135.974 | 304.192 | −12.260 | 0.173 |
| 3800 | 39.098 | 352.407 | 315.595 | 139.885 | 302.780 | −20.794 | 0.286 |
| 3900 | 39.092 | 353.422 | 316.552 | 143.794 | 301.385 | −29.290 | 0.392 |
| 4000 | 39.088 | 354.412 | 317.486 | 147.703 | 300.007 | −37.752 | 0.493 |
| 4100 | 39.086 | 355.377 | 318.399 | 151.612 | 298.645 | −46.179 | 0.588 |
| 4200 | 39.086 | 356.319 | 319.290 | 155.520 | 297.300 | −54.573 | 0.679 |
| 4300 | 39.088 | 357.239 | 320.162 | 159.429 | 295.971 | −62.935 | 0.765 |
| 4400 | 39.091 | 358.137 | 321.015 | 163.338 | 294.659 | −71.267 | 0.846 |
| 4500 | 39.095 | 359.016 | 321.850 | 167.247 | 293.364 | −79.568 | 0.924 |
| 4600 | 39.101 | 359.875 | 322.667 | 171.157 | 292.085 | −87.842 | 0.997 |
| 4700 | 39.108 | 360.716 | 323.468 | 175.067 | 290.822 | −96.087 | 1.068 |
| 4800 | 39.116 | 361.540 | 324.252 | 178.979 | 289.574 | −104.306 | 1.135 |
| 4900 | 39.125 | 362.346 | 325.022 | 182.891 | 288.343 | −112.499 | 1.199 |
| 5000 | 39.135 | 363.137 | 325.776 | 186.804 | 287.126 | −120.667 | 1.261 |
| 5100 | 39.146 | 363.912 | 326.516 | 190.718 | 285.925 | −128.811 | 1.319 |
| 5200 | 39.158 | 364.672 | 327.243 | 194.633 | 284.738 | −136.932 | 1.375 |
| 5300 | 39.170 | 365.418 | 327.956 | 198.549 | 283.565 | −145.030 | 1.429 |
| 5400 | 39.183 | 366.150 | 328.656 | 202.467 | 282.407 | −153.105 | 1.481 |
| 5500 | 39.197 | 366.869 | 329.345 | 206.386 | 281.262 | −161.160 | 1.531 |
| 5600 | 39.212 | 367.576 | 330.021 | 210.306 | 280.131 | −169.194 | 1.578 |
| 5700 | 39.227 | 368.270 | 330.686 | 214.228 | 279.013 | −177.208 | 1.624 |
| 5800 | 39.242 | 368.952 | 331.340 | 218.152 | 277.908 | −185.202 | 1.668 |
| 5900 | 39.259 | 369.623 | 331.983 | 222.077 | 276.815 | −193.177 | 1.710 |
| 6000 | 39.275 | 370.283 | 332.616 | 226.003 | 275.735 | −201.134 | 1.751 |

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

## Zirconium Fluoride (ZrF) IDEAL GAS $M_r$ = 110.218403 Zirconium Fluoride (ZrF) $F_1Zr_1(g)$

$S°(298.15 K) = [243.736 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°[83.669 \pm 20.9]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15 K) = [82.843 \pm 20.9]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

| $\epsilon_i$, cm$^{-1}$ | $g_i$ | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|---|
| 0 | [4] | [18000] | [4] |
| [3000] | [4] | [24000] | [4] |
| [6000] | [4] | [30000] | [4] |
| [12000] | [4] | | |

$\omega_e = [828.0]\ cm^{-1}$ $\omega_e x_e = [4.0]\ cm^{-1}$ $\sigma = 1$

$B_e = [0.29699]\ cm^{-1}$ $\alpha_e = [0.009]\ cm^{-1}$ $r_e = [1.90]$ Å

### Enthalpy of Formation

Based on $[D_0^\circ(ZrF)/\Delta_{at}H°(ZrF_2)] = 0.46$, as indicated by recent work on the fluorides of Groups II and IV elements,[1 2, 3 4, 5] and $\Delta_{at}H°(ZrF_2) = 318.1\ kcal \cdot mol^{-1}$, the $D_0^\circ(ZrF)$ is calculated as 146 3 kcal mol$^{-1}$. Using $\Delta_f H°(ZrF, g, 0 K) = 147\ 99$, $\Delta_f H°(F, g, 0 K) = 18.36$, and $D_0^\circ(ZrF, g) = 146.3\ kcal \cdot mol^{-1}$, we derive $\Delta_f H°(ZrF, g, 0 K) = 20.0$ or $\Delta_f H°(ZrF, g, 298.15 K) = 19\ 8 \pm 5\ kcal \cdot mol^{-1}$ (82.843 ± 20.9 kJ·mol$^{-1}$) which is adopted.

The $\Delta_f H°(ZrF, g, 298.15 K)$ was evaluated as approximately 16 ± 5 kcal mol$^{-1}$ by Murad and Hildenbrand,[8] employing a different $\Delta_{at}H°(ZrF_2)$ value. Their value is in agreement with the adopted one, within the assigned uncertainty.

### Heat Capacity and Entropy

The ground state configuration is taken from the ground state multiplet of $Zr^+$.[6] The electronic levels are estimated as three times higher than those of TiF(g) and the quantum weights are assumed to be the same. $\omega_e$ is taken to be approximately the same as the $ZrF_2$ stretching frequency $\nu_1$ for $ZrF_4(g)$. $B_e$ is calculated from the formula $B_e = 2.799076 \times 10^{-39}/I_e$ where $I_e = \mu r_e$, $\mu$ = reduced mass of ZrF(g), $r_e = 1.90$ Å which is estimated from those of $ZrF_4$, $CF_4$, CF and other related gaseous molecules, $\alpha_e$ is derived from $B_e$, $\omega_e$ and $\omega_e x_e$ (estimated), according to the method suggested by Herzberg.[7]

### References

[1] G D Blue, J. W. Green, R. G. Bautista, and J L. Margrave, J. Phys Chem. 67, 877 (1963).
[2] H L. Hildenbrand and E. Murad, J. Chem Phys. 44, 1524 (1966).
[3] G D Blue, J. W. Green, T. C. Ehlert, and J. L. Margrave, Nature 119, 804 (1963).
[4] T C Ehlert and J. L Margrave, J. Chem. Phys 41, 1066 (1964).
[5] R A Kent, T. C. Ehlert, and J. L. Margrave, J. Amer Chem. Soc. 86, 5080 (1964).
[6] C. E. Moore, U S. Nat. Bur Stand. Circ. 467, Vol. II, (1952).
[7] G. Herzberg, "Spectra of Diatomic Molecules," D Van Nostrand Co., Inc., New York, (1950).
[8] E. Murad and D L. Hildenbrand, J. Chem. Phys. 45, 4751 (1966).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | | J·K$^{-1}$mol$^{-1}$ | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0 | 0 | INFINITE | −9.084 | 83.669 | 83.669 | INFINITE |
| 100 | 29.199 | 210.139 | 271.878 | −6.174 | 84.239 | 73.149 | −38.209 |
| 200 | 31.136 | 230.853 | 246.724 | −3.174 | 83.581 | 62.286 | −16.267 |
| 250 | 32.394 | 237.939 | 244.280 | −1.585 | 83.203 | 57.006 | −11.911 |
| 298.15 | 33.427 | 243.736 | 243.736 | 0 | 82.843 | 51.993 | −9.109 |
| 300 | 33.462 | 243.942 | 243.736 | 0.062 | 82.829 | 51.802 | −9.019 |
| 350 | 34.316 | 249.167 | 244.147 | 1.757 | 82.459 | 46.660 | −6.964 |
| 400 | 34.996 | 253.796 | 245.069 | 3 491 | 82.089 | 41.571 | −5.429 |
| 450 | 35.552 | 257.951 | 246.274 | 5.255 | 81.715 | 36.528 | −4.240 |
| 500 | 36.027 | 261.722 | 247.633 | 7.044 | 81.335 | 31.528 | −3.294 |
| 600 | 36.856 | 268.365 | 250.549 | 10.689 | 80.552 | 21.639 | −1.884 |
| 700 | 37 629 | 274.105 | 253.513 | 14.414 | 79.734 | 11.885 | −0.887 |
| 800 | 38.392 | 279 179 | 256.410 | 18.215 | 78.881 | 2.250 | −0.147 |
| 900 | 39.142 | 283 744 | 259.198 | 22.092 | 77.983 | −7.276 | 0.422 |
| 1000 | 39.866 | 287.906 | 261.864 | 26.042 | 77.033 | −16.698 | 0 872 |
| 1100 | 40.548 | 291.738 | 264.408 | 30.064 | 76.023 | −26.023 | 1.236 |
| 1200 | 41.178 | 295.294 | 266.835 | 34.150 | 71.235 | −35.031 | 1.525 |
| 1300 | 41.752 | 298.613 | 269.153 | 38.297 | 70.629 | −43.862 | 1.762 |
| 1400 | 42.268 | 301.726 | 271.370 | 42.499 | 70.024 | −52.647 | 1 964 |
| 1500 | 42.727 | 304.659 | 273.492 | 46.749 | 69.406 | −61.387 | 2.138 |
| 1600 | 43.132 | 307.429 | 275.528 | 51.042 | 68.758 | −70.086 | 2.288 |
| 1700 | 43.486 | 310.055 | 277.482 | 55.374 | 68.066 | −78.743 | 2.419 |
| 1800 | 43 794 | 312.549 | 279.362 | 59.738 | 67.314 | −87.357 | 2.535 |
| 1900 | 44.063 | 314.925 | 281.171 | 64.131 | 66.491 | −95.928 | 2.637 |
| 2000 | 44.295 | 317.191 | 282.916 | 68.549 | 65.582 | −104.453 | 2.728 |
| 2100 | 44.496 | 319.357 | 284.600 | 72.989 | 64.575 | −112.931 | 2.809 |
| 2200 | 44.671 | 321.431 | 286.228 | 77.448 | 42 135 | −120.612 | 2.864 |
| 2300 | 44.824 | 323.420 | 287.802 | 81.923 | 40.482 | −127 973 | 2.906 |
| 2400 | 44.957 | 325.331 | 289.326 | 86.412 | 38.846 | −135.262 | 2.944 |
| 2500 | 45.076 | 327.168 | 290.803 | 90.914 | 37.226 | −142.483 | 2.977 |
| 2600 | 45.181 | 328.938 | 292.236 | 95.427 | 35.624 | −149.639 | 3.006 |
| 2700 | 45.276 | 330.645 | 293.627 | 99 950 | 34.040 | −156 735 | 3.032 |
| 2800 | 45.364 | 332.294 | 294.979 | 104.482 | 32.474 | −163.772 | 3.055 |
| 2900 | 45.445 | 333.887 | 296.293 | 109.022 | 30.927 | −170.753 | 3.076 |
| 3000 | 45.521 | 335.429 | 297.572 | 113.570 | 29.401 | −177.682 | 3.094 |
| 3100 | 45.593 | 336.923 | 298.817 | 118.126 | 27.896 | −184.560 | 3.110 |
| 3200 | 45.663 | 338.371 | 300.031 | 122.689 | 26.411 | −191.389 | 3.124 |
| 3300 | 45.731 | 339.777 | 301.214 | 127.259 | 24.949 | −198.173 | 3.137 |
| 3400 | 45.798 | 341.144 | 302.369 | 131.835 | 23.510 | −204 912 | 3.148 |
| 3500 | 45.865 | 342.472 | 303.496 | 136.418 | 22.093 | −211.610 | 3.158 |
| 3600 | 45.932 | 343.765 | 304.596 | 141.008 | 20.699 | −218.267 | 3.167 |
| 3700 | 45.999 | 345.025 | 305.672 | 145.605 | 19.330 | −224.886 | 3.175 |
| 3800 | 46.067 | 346.252 | 306.724 | 150.208 | 17.984 | −231.469 | 3.182 |
| 3900 | 46.136 | 347.450 | 307.753 | 154.818 | 16.662 | −238 016 | 3 188 |
| 4000 | 46.205 | 348.619 | 308.760 | 159.435 | 15.363 | −244.530 | 3.193 |
| 4100 | 46.276 | 349.760 | 309.746 | 164 059 | 14.089 | −251 011 | 3.198 |
| 4200 | 46.348 | 350.876 | 310.712 | 168.690 | 12.839 | −257 462 | 3.202 |
| 4300 | 46.421 | 351.968 | 311.659 | 173.329 | 11.613 | −263.883 | 3.206 |
| 4400 | 46.495 | 353.036 | 312.587 | 177.975 | 10.410 | −270.276 | 3.209 |
| 4500 | 46.570 | 354.082 | 313.498 | 182.628 | 9.231 | −276.642 | 3.211 |
| 4600 | 46.646 | 355.106 | 314.391 | 187.289 | 8.075 | −282.982 | 3.213 |
| 4700 | 46.724 | 356.110 | 315.268 | 191.957 | 6.943 | −289.297 | 3.215 |
| 4800 | 46.802 | 357.095 | 316.129 | 196.633 | −555.103 | −283.971 | 3.090 |
| 4900 | 46.881 | 358.060 | 316.975 | 201.317 | −555.842 | −278.315 | 2.967 |
| 5000 | 46.962 | 359.008 | 317.806 | 206.010 | −556.576 | −272.643 | 2.848 |
| 5100 | 47.043 | 359.939 | 318.623 | 210.710 | −557.303 | −266.957 | 2.734 |
| 5200 | 47.124 | 360.853 | 319.427 | 215.418 | −558.023 | −261.257 | 2.624 |
| 5300 | 47.207 | 361.752 | 320.217 | 220.135 | −558.735 | −255.543 | 2.519 |
| 5400 | 47.290 | 362.635 | 320.994 | 224.859 | −559.437 | −249.816 | 2.416 |
| 5500 | 47.373 | 363.503 | 321.759 | 229.593 | −560.129 | −244.076 | 2.318 |
| 5600 | 47 457 | 364.358 | 322.512 | 234.334 | −560.809 | −238.324 | 2.223 |
| 5700 | 47.541 | 365.198 | 323.254 | 239.084 | −561.477 | −232.559 | 2.131 |
| 5800 | 47 625 | 366.026 | 323.984 | 243.842 | −562.132 | −226.783 | 2.042 |
| 5900 | 47.710 | 366.841 | 324 704 | 248.609 | −562.773 | −220.995 | 1.957 |
| 6000 | 47.795 | 367.643 | 325.413 | 253.384 | −563.398 | −215.197 | 1.873 |

PREVIOUS· June 1969 (1 atm) CURRENT June 1969 (1 bar)

## Fluorine (F$_2$) REFERENCE STATE $M_r = 37.996806$ Fluorine (F$_2$) F$_2$(ref)

0 to 6000 K Ideal Diatomic Gas

$D_0^\circ = 154.56 \pm 0.60$ kJ·mol$^{-1}$
$S^\circ(298.15\ \mathrm{K}) = 202.789 \pm 0.040$ J·K$^{-1}$·mol$^{-1}$

$\Delta_f H^\circ(0\ \mathrm{K}) = 0$ kJ·mol$^{-1}$
$\Delta_f H^\circ(298.15\ \mathrm{K}) = 0$ kJ·mol$^{-1}$

Spectroscopic Data for F$_2$ in cm$^{-1}$

| v = | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| G(v)−G(0) | 0.00 | 893.90 | 1764.15 | 2610.22 | 3431.53 | 4227.43 | 4997.19 | 5740.05 | 6455.17 | 7141.63 | 7798.48 | 8424.67 |
| $B_v$ | 0.8833 | 0.8696 | 0.8560 | 0.8423 | 0.8284 | 0.8142 | 0.7996 | 0.7484 | 0.7685 | 0.7518 | 0.7343 | 0.7156 |
| $D_v \times 10^6$ | 3.3 | 3.1 | 2.7 | 4.4 | 3.6 | 2.2 | 4.6 | 4.5 | 5.2 | 5.4 | 6.5 | 6.7 |

| v = | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| G(v)−G(0) | 9019.11 | 9580.63 | 10108.02 | 10599.62 | 11053.90 | 11468.96 | 11842.62 | 12172.25 | 12452.98 | 12678.00 | 12830.38 |
| $B_v$ | 0.6958 | 0.6747 | 0.6522 | 0.6282 | 0.6025 | 0.5750 | 0.5449 | 0.5094 | 0.4711 | 0.4185 | 0.3865 |
| $D_v \times 10^6$ | 3.7 | 9.2 | 8.5 | 5.5 | 8.6 | 7.0 | 9.8 | 15.0 | 19.6 | 32.7 | 86.4 |

$r_e = 1.41193$ Å[10]

### Heat of Formation

Zero by definition. Refer to monatomic fluorine gas table for a discussion of the discussion energy.

### Heat Capacity and Entropy

The thermal functions are calculated using a direct summation technique Due to the absence of known low lying bound excited states (i.e. <93000 cm$^{-1}$) only the ground state is included in the calculation.

The G(v), $B_v$ and $D_v$ spectroscopic constants for the ground state and the dissociation energy were determined by Colbourn *et al.*[1] These are used in the computation as given (and not as the usual fitting coefficients $\omega_e$, $\omega_e x_e$, etc.). The rotational levels are weighted in accordance with the nuclear spin–rotation interaction[5] as follows· even J weight = 0.75, odd J weight = 0 25. Also, the rotational levels are extrapolated to high J values according to the method of Khachkuruzov[6] who proposed a simpler form of Wooley's method.[7] Note that there is only one stable isotope of fluorine, $^{19}$F.

The so–called quasibound rotational levels above the dissociation limit[2,3] are also included. For a given vibrational quantum number, v, the summation over rotational states is carried out up to a rotational quantum number, J, given by $J = J_{\mathrm{lim}}(1 - v/v_{\mathrm{max}})$ where $J_{\mathrm{lim}}$ amd $v_{\mathrm{max}}$ were determined by Gurvich *et al.*[4] to be 178 and 23, respectively. Our adopted value for $S^\circ$(298.15 K) differs from values recommended by CODATA,[9] Gurvich *et al.*[3] and Wagman *et al.*[11] by less than 0.01 J K$^{-1}$·mol$^{-1}$. For this comparison, the entropy values reported by CODATA[9] and Gurvich *et al.*[3] are increased by 0.1094 J K$^{-1}$·mol$^{-1}$to account for a change in the standard–state pressure from 1 atm to 1 bar.

### Phase Data

Hultgren *et al.*[8] had recommended the α→β transition temperature, 45.55 K, the triple point, 53.48 K (0 000249 atm) and the boiling point, 84.95 K (1 atm). These values should prove reasonably accurate, although they have not been evaluated by the present authors, and are furnished for the convenience of the reader. As a result of the low values, the reference state for fluorine is chosen to be the ideal diatomic gas at all temperatures. This may differ from the choice of other authors.

### References

[1] E. A. Colbourn, M. Dagenais, A. E. Douglas and J. W. Raymonda, Can. J. Phys. 54, 1343 (1976).
[2] F. M. Mies and P. S. Julienne, J. Chem. Phys.77, 6162 (1982).
[3] L. V. Gurvich, I. V. Veits *et al.*, "Thermodynamic Properties of Individual Substances," Volume I, 3rd ed., Part 1, 38–40, Nauka, Moscow, (1978).
[4] Reference [3], Part 1, 146–9.
[5] G. Herzberg, "Spectra of Diatomic Molecules," 2nd. Ed., D. Van Nostrand Co., Inc., New York, Chapter V, (1950).
[6] G. A. Khachkuruzov, Opt. Spectros. 30, 455 (1971).
[7] H. W. Wooley, R. B. Scott and F. G. Brickwedde, J. Res. Nat. Bur. Stand. 41, 379 (1948).
[8] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley and D. D. Wagman, "Selected Values of the Thermodynamic Properties of the Elements," American Society for Metals, Metals Park, Ohio, (1973).
[9] J. D. Cox, J. Chem. Thermodynamics 10, 903 (1972).
[10] K. P. Huber and G. Herzberg, "Constants of Diatomic Molecules," Van Nostrand–Reinhold Co., New York, (1979).
[11] D. D. Wagman, W. H. Evans, *et al.*, J. Phys. Chem. Ref. Data 11, Supp. 2 (1982).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p^\circ$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −8.825 | 0. | 0. | 0. |
| 100 | 29.114 | 170.370 | 229.549 | −5.918 | 0. | 0. | 0. |
| 200 | 29.685 | 190.652 | 205.596 | −2.989 | 0. | 0. | 0. |
| 250 | 30.447 | 197.354 | 203.300 | −1.486 | 0. | 0. | 0. |
| 298.15 | 31.302 | 202.789 | 202.789 | 0. | 0. | 0. | 0. |
| 300 | 31.336 | 202.983 | 202.790 | 0.058 | 0. | 0. | 0. |
| 350 | 32.207 | 207.880 | 203.175 | 1.647 | 0. | 0. | 0. |
| 400 | 32.992 | 212.233 | 204.040 | 3.277 | 0. | 0. | 0. |
| 450 | 33.674 | 216.159 | 205.172 | 4.944 | 0. | 0. | 0. |
| 500 | 34.255 | 219.738 | 206.452 | 6.643 | 0. | 0. | 0. |
| 600 | 35.166 | 226.068 | 209.208 | 10.116 | 0. | 0. | 0. |
| 700 | 35.832 | 231.542 | 212.016 | 13.668 | 0. | 0. | 0 |
| 800 | 36.336 | 236.361 | 214.764 | 17.277 | 0. | 0. | 0. |
| 900 | 36.732 | 240.664 | 217.407 | 20.932 | 0. | 0. | 0. |
| 1000 | 37.057 | 244.552 | 219.930 | 24.622 | 0. | 0. | 0. |
| 1100 | 37.334 | 248.097 | 222.332 | 28.341 | 0. | 0. | 0. |
| 1200 | 37.579 | 251.356 | 224.617 | 32.087 | 0. | 0. | 0. |
| 1300 | 37.802 | 254.373 | 226.791 | 35.857 | 0. | 0. | 0. |
| 1400 | 38.008 | 257.182 | 228.863 | 39.647 | 0. | 0. | 0. |
| 1500 | 38.199 | 259.811 | 230.839 | 43.458 | 0. | 0. | 0. |
| 1600 | 38.374 | 262.282 | 232.728 | 47.287 | 0. | 0. | 0. |
| 1700 | 38.530 | 264.613 | 234.536 | 51.132 | 0. | 0. | 0. |
| 1800 | 38.663 | 266.819 | 236.268 | 54.992 | 0. | 0 | 0. |
| 1900 | 38 770 | 268.913 | 237.932 | 58.864 | 0 | 0. | 0. |
| 2000 | 38.846 | 270.904 | 239.531 | 62.745 | 0. | 0. | 0. |
| 2100 | 38.889 | 272.800 | 241.071 | 66.632 | 0. | 0. | 0. |
| 2200 | 38.895 | 274.609 | 242.554 | 70.521 | 0 | 0. | 0. |
| 2300 | 38.864 | 276.338 | 243.986 | 74.409 | 0. | 0. | 0. |
| 2400 | 38.795 | 277.991 | 245.369 | 78.293 | 0. | 0. | 0 |
| 2500 | 38.690 | 279.572 | 246.705 | 82.167 | 0. | 0. | 0. |
| 2600 | 38.549 | 281.087 | 247.999 | 86.030 | 0. | 0. | 0. |
| 2700 | 38.375 | 282.539 | 249.251 | 89.876 | 0. | 0. | 0. |
| 2800 | 38 170 | 283.931 | 250.465 | 93.704 | 0. | 0. | 0. |
| 2900 | 37.939 | 285.266 | 251.642 | 97.509 | 0. | 0. | 0. |
| 3000 | 37.683 | 286.548 | 252.785 | 101.290 | 0. | 0. | 0. |
| 3100 | 37.406 | 287.779 | 253.894 | 105.045 | 0. | 0. | 0. |
| 3200 | 37.111 | 288.962 | 254.971 | 108.771 | 0. | 0. | 0. |
| 3300 | 36.802 | 290.100 | 256.019 | 112.467 | 0. | 0. | 0. |
| 3400 | 36.482 | 291.193 | 257.037 | 116.131 | 0. | 0. | 0. |
| 3500 | 36.152 | 292.246 | 258.028 | 119.763 | 0. | 0. | 0. |
| 3600 | 35.817 | 293.260 | 258.993 | 123.361 | 0. | 0. | 0. |
| 3700 | 35.477 | 294.237 | 259.932 | 126.926 | 0. | 0. | 0. |
| 3800 | 35.135 | 295.178 | 260.848 | 130.457 | 0. | 0. | 0. |
| 3900 | 34.793 | 296.087 | 261.740 | 133.953 | 0. | 0. | 0. |
| 4000 | 34.452 | 296.963 | 262.609 | 137.415 | 0. | 0. | 0. |
| 4100 | 34.114 | 297.810 | 263.458 | 140.844 | 0. | 0. | 0. |
| 4200 | 33.780 | 298.628 | 264.285 | 144.238 | 0. | 0. | 0. |
| 4300 | 33.450 | 299.419 | 265.093 | 147.600 | 0. | 0. | 0. |
| 4400 | 33.125 | 300.184 | 265.882 | 150.929 | 0. | 0. | 0. |
| 4500 | 32.807 | 300.925 | 266.653 | 154.225 | 0. | 0. | 0. |
| 4600 | 32.495 | 301.642 | 267.405 | 157.490 | 0. | 0. | 0. |
| 4700 | 32.191 | 302.338 | 268.141 | 160.724 | 0. | 0. | 0. |
| 4800 | 31.893 | 303.013 | 268.861 | 163.929 | 0. | 0 | 0. |
| 4900 | 31.603 | 303.667 | 269.565 | 167.103 | 0. | 0. | 0 |
| 5000 | 31.321 | 304.303 | 270.253 | 170.249 | 0. | 0. | 0. |
| 5100 | 31.046 | 304.920 | 270.927 | 173.368 | 0. | 0. | 0. |
| 5200 | 30.779 | 305.521 | 271.586 | 176.459 | 0. | 0. | 0. |
| 5300 | 30.519 | 306.104 | 272.232 | 179.524 | 0. | 0. | 0. |
| 5400 | 30.268 | 306.673 | 272.865 | 182.563 | 0. | 0. | 0. |
| 5500 | 30.023 | 307.226 | 273.484 | 185.577 | 0. | 0. | 0. |
| 5600 | 29.787 | 307.765 | 274.092 | 188.568 | 0. | 0. | 0. |
| 5700 | 29.557 | 308.290 | 274.687 | 191.535 | 0. | 0. | 0. |
| 5800 | 29.335 | 308.802 | 275.271 | 194.480 | 0. | 0. | 0. |
| 5900 | 29.119 | 309.301 | 275.843 | 197.402 | 0. | 0. | 0. |
| 6000 | 28.911 | 309.789 | 276.405 | 200.304 | 0. | 0. | 0. |

PREVIOUS: June 1977 (1 atm) CURRENT· June 1982 (1 bar)

**Iron Fluoride ($FeF_2$)** **CRYSTAL** **$M_r$ = 93.843806** **Iron Fluoride ($FeF_2$)** **$F_2Fe_1(cr)$**

$S°(298.15\ K) = 86.985 \pm 0.17\ J·K^{-1}·mol^{-1}$
$T_{fus} = [1373]\ K$

$\Delta_f H°(0\ K) = 705.266 \pm 41.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 705.841 \pm 41.8\ kJ·mol^{-1}$
$\Delta_{fus} H° = [51.882]\ kJ·mol^{-1}$

## Enthalpy of Formation

The equilibrium pressures for the reaction $FeF_2(cr) + H_2(g) = Fe(cr) + 2HF(g)$ have been measured by Jellinek and Rudat[1] at 773, 873 and 973 K. The enthalpy change of the reaction, $\Delta_r H°(298.15\ K)$, was evaluated by the 2nd and 3rd law methods to be 27.19 and 39.08 $kcal·mol^{-1}$, respectively. Based on the 3rd law value of $\Delta_r H°(298.15\ K)$, the $\Delta_f H°(FeF_2, cr, 298\ 15\ K)$ was calculated to be 168.7 ± 10 $kcal·mol^{-1}$. The drift in the 3rd law values of $\Delta_r H°(298.15\ K)$ was evaluated to be 13.3 ± 1.8 cal $K^{-1}·mol^{-1}$.

## Heat Capacity and Entropy

The low temperature (11.33–307.30 K) heat capacities were determined by Catalano and Stout.[2] The heat capacities above 307 K were estimated by comparison with those of $FeCl_2(cr)$, $MgCl_2(cr)$ and $MgF_2(cr)$. The value of $S°(298.15\ K)$ was obtained from Catalano and Stout,[2] in which a sharp maximum $C_p°$ of 17.8 cal $K^{-1}·mol^{-1}$ at 78.35 K was reported. The $S°(298.15\ K)$ value was based on $S°(15\ K) = 0.039$ cal $K^{-1}·mol^{-1}$.

## Fusion Data

$T_{fus}$ was estimated as 1100°C based on the data reported by Biltz and Rahlfs.[3] The value of $\Delta_{fus}H°$ was calculated using $\Delta_{fus}S° = 9$ cal $K^{-1}·mol^{-1}$ which was assumed to be the same as the corresponding value for $MgF_2(cr)$.

## Sublimation Data

The value of $\Delta_{sub}H°(298.15\ K) = 316.31 \pm 8.4\ kJ·mol^{-1}$ was obtained from Margrave.[4] See $FeF_2(g)$ table for details.

## References

[1] K. Jellinek and A. Rudat, Z. Anorg. Allg. Chem. **175**, 281 (1928).
[2] E. Catalano and J. W. Stout, J. Chem. Phys. **23**, 1803 (1955).
[3] W. Biltz and E. Rahlfs, Z. Anorg. Allg. Chem. **166**, 363 (1927).
[4] J. L. Margrave, "Research in Fluorine Chemistry," William Rice University, Houston, Texas, Progress Report No. 7, (January 1 to March 31, 1965).

Enthalpy Reference Temperature = $T_r$ = 298.15 K　　Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| $T/K$ | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −12.757 | −705.266 | −705.266 | INFINITE |
| 100 | 33.447 | 30.853 | 138.926 | −10.807 | −706.646 | −692.088 | 361.510 |
| 200 | 56.610 | 62.024 | 92.902 | −6.176 | −706.712 | −677.397 | 176.918 |
| 298.15 | 68.116 | 86.985 | 86.985 | 0. | −705.841 | −663.168 | 116.184 |
| 300 | 68.199 | 87.407 | 86.987 | 0.126 | −705.819 | −662.903 | 115.422 |
| 400 | 71.965 | 107.562 | 89.709 | 7.141 | −704.651 | −648.774 | 84.721 |
| 500 | 74.894 | 123.948 | 94.968 | 14.490 | −703.521 | −634.937 | 66.331 |
| 600 | 77.153 | 137.811 | 100.983 | 22.097 | −702.473 | −621.321 | 54.091 |
| 700 | 78.868 | 149.837 | 107.122 | 29.900 | −701.547 | −607.871 | 45.360 |
| 800 | 80.249 | 160.462 | 113.138 | 37.859 | −700.813 | −594.541 | 38.820 |
| 900 | 81.337 | 169.979 | 118.934 | 45.941 | −700.414 | −581.286 | 33.737 |
| 1000 | 82.132 | 178.592 | 124.476 | 54.115 | −700.676 | −568.045 | 29.672 |
| 1100 | 82.717 | 186.448 | 129.758 | 62.359 | −701.795 | −554.713 | 26.341 |
| 1200 | 83.178 | 193.666 | 134.787 | 70.655 | −702.335 | −541.337 | 23.564 |
| 1300 | 83.516 | 200.338 | 139.576 | 78.990 | −701.212 | −527.966 | 21.214 |
| 1373.000 | 83.685 | 204.906 | 142.929 | 85.094 | --- CRYSTAL <--> LIQUID --- | | |
| 1400 | 83.764 | 206.536 | 144.140 | 87.354 | −700.166 | −514.679 | 19.203 |
| 1500 | 83.983 | 212.323 | 148.495 | 95.742 | −699.200 | −501.464 | 17.463 |
| 1600 | 84.182 | 217.750 | 152.656 | 104.150 | −698.315 | −488.311 | 15.942 |
| 1700 | 84.365 | 222.859 | 156.636 | 112.578 | −698.461 | −475.192 | 14.601 |
| 1800 | 84.517 | 227.685 | 160.451 | 121.022 | −698.073 | −462.071 | 13.409 |
| 1900 | 84.637 | 232.258 | 164.111 | 129.480 | −711.865 | −448.266 | 12.324 |
| 2000 | 84.726 | 236.602 | 167.628 | 137.949 | −711.880 | −434.392 | 11.345 |

PREVIOUS:　　CURRENT: September 1965

**Iron Fluoride ($FeF_2$)** **$F_2Fe_1(cr)$**

## Iron Fluoride ($FeF_2$) LIQUID $M_r$ = 93.843806 Iron Fluoride ($FeF_2$) $F_2Fe_1(l)$

$S°(298.15\ K) = [92.537]\ J·K^{-1}·mol^{-1}$
$T_{fus} = [1373]\ K$

$\Delta_f H°(298.15\ K) = [-674.549]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [51.882]\ kJ·mol^{-1}$

### Enthalpy of Formation

$\Delta_f H°(FeF_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(FeF_2, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus} H°$, and the difference in enthalpy, $H°(1373\ K)–H°(298.15\ K)$, between the crystal and liquid.

### Heat Capacity and Entropy

The heat capacity for $FeF_2(l)$ is estimated by comparison with those for $FeCl_2(cr)$, $MgCl_2(cr)$, $MgF_2(cr)$, $CaCl_2(cr)$ and $CaF_2(cr)$. The $C_p°(FeF_2, l)$ value is assumed to be constant in the temperature range, 298.15–3000 K. $S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

### Fusion Data

Refer to the crystal table for details.

### Vaporization Data

$T_{vap}$ = 2110 K is calculated as the temperature at which the fugacity of the reaction $FeF_2(l) = FeF_2(g)$ is 1 atm. The difference between $\Delta_f H°$ for $FeF_2$ (l) and $FeF_2(g)$ at $T_{vap}$ is $\Delta_{vap} H° = 224.43\ kJ·mol^{-1}$.

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| | $J·K^{-1}mol^{-1}$ | | | $kJ·mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T/K$ | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 98.324 | 92.537 | 92.537 | 0. | −674.549 | −633.532 | 110.992 |
| 300 | 98.324 | 93.145 | 92.539 | 0.182 | −674.472 | −633.277 | 110.263 |
| 400 | 98.324 | 121.431 | 96.395 | 10.014 | −670.486 | −620.157 | 80.984 |
| 500 | 98.324 | 143.371 | 103.678 | 19.847 | −666 872 | −608.000 | 63.517 |
| 600 | 98.324 | 161.298 | 111.833 | 29.679 | −663.599 | −596.539 | 51.933 |
| 700 | 98.324 | 176.455 | 120.010 | 39.511 | −660.644 | −585.600 | 43.698 |
| 800 | 98.324 | 189.584 | 127.904 | 49.344 | −658.036 | −575.062 | 37.548 |
| 900 | 98.324 | 201.165 | 135.413 | 59.176 | −655.886 | −564.825 | 32.782 |
| 1000 | 98.324 | 211.524 | 142.516 | 69.009 | −654.491 | −554.792 | 28.979 |
| 1100 | 98.324 | 220.896 | 149.222 | 78.841 | −654.021 | −544.831 | 25.872 |
| 1200 | 98.324 | 229.451 | 155.556 | 88.673 | −653.025 | −534.968 | 23.287 |
| 1300 | 98.324 | 237.321 | 161.547 | 98.506 | −650.405 | −525.237 | 21.104 |
| 1373.000 | 98.324 | 242.693 | 165.720 | 105.684 | --- CRYSTAL <--> LIQUID --- | | |
| 1400 | 98.324 | 244.608 | 167.223 | 108.338 | −647.891 | −515.703 | 19.241 |
| 1500 | 98.324 | 251.391 | 172.611 | 118.171 | −645.480 | −506.346 | 17.633 |
| 1600 | 98.324 | 257.737 | 177.735 | 128.003 | −643.170 | −497.147 | 16.230 |
| 1700 | 98.324 | 263.698 | 182.618 | 137.835 | −641.911 | −488.069 | 14.997 |
| 1800 | 98.324 | 269.318 | 187.280 | 147.668 | −640.135 | −479.072 | 13.902 |
| 1900 | 98.324 | 274.634 | 191.739 | 157.500 | −652.553 | −469.468 | 12.907 |
| 2000 | 98.324 | 279.677 | 196.011 | 167.333 | −651.204 | −459.867 | 12.010 |
| 2100 | 98.324 | 284.475 | 200.110 | 177.165 | −649.861 | −450.333 | 11.201 |
| 2200 | 98.324 | 289.049 | 204.050 | 186.997 | −648.521 | −440.863 | 10.467 |
| 2300 | 98.324 | 293.419 | 207.841 | 196.830 | −647.179 | −431.454 | 9.799 |
| 2400 | 98.324 | 297.604 | 211.495 | 206.662 | −645.832 | −422.104 | 9.187 |
| 2500 | 98.324 | 301.618 | 215.020 | 216.495 | −644.477 | −412.809 | 8.625 |
| 2600 | 98.324 | 305.474 | 218.425 | 226.327 | −643.109 | −403.570 | 8.108 |
| 2700 | 98.324 | 309.185 | 221.718 | 236.159 | −641.725 | −394.383 | 7.630 |
| 2800 | 98.324 | 312.761 | 224.906 | 245.992 | −640.323 | −385.248 | 7.187 |
| 2900 | 98.324 | 316.211 | 227.996 | 255.824 | −638.899 | −376.163 | 6.775 |
| 3000 | 98.324 | 319.544 | 230.992 | 265.657 | −637.450 | −367.128 | 6.392 |

PREVIOUS:    CURRENT: September 1965

## Iron Fluoride (FeF$_2$) CRYSTAL-LIQUID

$M_r = 93.843806$ Iron Fluoride (FeF$_2$) F$_2$Fe$_1$(cr,l)

0 to 1373 K crystal
above 1373 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = $T_r$ = 298.15 K | Standard State Pressure = $p^\circ$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log K$_f$ |
| 0 | 0. | 0. | INFINITE | −12.757 | −705.266 | −705.266 | INFINITE |
| 100 | 33.447 | 30.853 | 138.926 | −10.807 | −706.646 | −692.088 | 361.510 |
| 200 | 56.610 | 62.024 | 92.902 | −6.176 | −706.712 | −677.397 | 176.918 |
| 298.15 | 68.116 | 86.985 | 86.985 | 0. | −705.841 | −663.168 | 116.184 |
| 300 | 68.199 | 87.407 | 86.987 | 0.126 | −705.819 | −662.903 | 115.422 |
| 400 | 71.965 | 107.562 | 89.709 | 7.141 | −704.651 | −648.774 | 84.721 |
| 500 | 74.894 | 123.948 | 94.968 | 14.490 | −703.521 | −634.937 | 66.331 |
| 600 | 77.153 | 137.811 | 100.983 | 22.097 | −702.473 | −621.321 | 54.091 |
| 700 | 78.868 | 149.837 | 107.122 | 29.900 | −701.547 | −607.871 | 45.360 |
| 800 | 80.249 | 160.462 | 113.138 | 37.859 | −700.813 | −594.541 | 38.820 |
| 900 | 81.337 | 169.979 | 118.934 | 45.941 | −700 414 | −581.286 | 33.737 |
| 1000 | 82.132 | 178.592 | 124.476 | 54.115 | −700.676 | −568.045 | 29.672 |
| 1100 | 82.717 | 186.448 | 129.758 | 62.359 | −701.795 | −554 713 | 26.341 |
| 1200 | 83.178 | 193.666 | 134.787 | 70.655 | −702.335 | −541.337 | 23.564 |
| 1300 | 83.516 | 200.338 | 139.576 | 78.990 | −701.212 | −527 966 | 21.214 |
| 1373.000 | 83.685 | 204.906 | 142.929 | 85.094 | CRYSTAL <−−> LIQUID | | |
| 1373.000 | 98.324 | 242.693 | 142.929 | 136.975 | TRANSITION | | |
| 1400 | 98.324 | 244.608 | 144.872 | 139.630 | −647.891 | −515 703 | 19.241 |
| 1500 | 98.324 | 251.391 | 151.750 | 149.462 | −645.480 | −506.346 | 17.633 |
| 1600 | 98.324 | 257.737 | 158.178 | 159.295 | −643.170 | −497 147 | 16.230 |
| 1700 | 98.324 | 263.698 | 164.211 | 169.127 | −641.911 | −488.069 | 14 997 |
| 1800 | 98.324 | 269.318 | 169.896 | 178.960 | −640.135 | −479.072 | 13.902 |
| 1900 | 98.324 | 274.634 | 175.270 | 188.792 | −652.553 | −469.468 | 12.907 |
| 2000 | 98.324 | 279.677 | 180.365 | 198.624 | −651.204 | −459.867 | 12.010 |
| 2100 | 98.324 | 284.475 | 185.209 | 208.457 | −649.861 | −450.333 | 11.201 |
| 2200 | 98.324 | 289.049 | 189.826 | 218.289 | −648.521 | −440.863 | 10.467 |
| 2300 | 98.324 | 293.419 | 194.236 | 228.122 | −647.179 | −431.454 | 9.799 |
| 2400 | 98.324 | 297.604 | 198.456 | 237.954 | −645.832 | −422.104 | 9.187 |
| 2500 | 98.324 | 301.618 | 202.503 | 247.786 | −644.477 | −412.809 | 8.625 |
| 2600 | 98.324 | 305.474 | 206.390 | 257.619 | −643.109 | −403.570 | 8.108 |
| 2700 | 98.324 | 309.185 | 210.129 | 267.451 | −641.725 | −394.383 | 7.630 |
| 2800 | 98.324 | 312.761 | 213.731 | 277.284 | −640.323 | −385.248 | 7.187 |
| 2900 | 98.324 | 316.211 | 217.205 | 287.116 | −638.899 | −376.163 | 6.775 |
| 3000 | 98.324 | 319.544 | 220.561 | 296.948 | −637.450 | −367.128 | 6.392 |

PREVIOUS. CURRENT. September 1965

Iron Fluoride (FeF$_2$) F$_2$Fe$_1$(cr,l)

## Iron Fluoride (FeF$_2$) IDEAL GAS $M_r = 93.843806$ Iron Fluoride (FeF$_2$) F$_2$Fe$_1$(g)

$S°(298.15\ K) = [265.205]\ J\ K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -388.870 \pm 14.2\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -389.530 \pm 14.2\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights

| $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|
| 0 | [5] |
| [1000] | [10] |
| [4000] | [5] |
| [6000] | |

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ |
|---|
| [550](1) |
| [190](2) |
| [714](1) |

Point Group: $[D_{\infty h}]$ $\sigma = 2$
Bond Distance: Fe–F = [1.8] Å
Bond Angle: F–Fe–F = [180]°
Rotational constant: $B_0 = 0.136932\ cm^{-1}$

### Enthalpy of Formation

The rate of sublimation of FeF$_2$(cr) was measured between 965 and 1149 K by the Knudsen technique employing the high temperature magnetic mass spectrometer by Margrave.[1] The only vapor species of importance is FeF$_2$(g) From the vapor pressure data, the 3rd law enthalpy of sublimation, $\Delta_{sub}H°(298.15\ K)$, was reported as 75.6 ± 2.0 kcal·mol$^{-1}$. The sum of the values $\Delta_{sub}H°(298.15\ K)$ and $\Delta_f H°(298.15\ K)$ for FeF$_2$(cr) is $\Delta_f H°(FeF_2, g, 298.15\ K)$.

### Heat Capacity and Entropy

The molecular structure was assumed to be linear. The Fe–F bond distance was estimated from that in FeF$_2$(cr) reported by Baur.[2] The vibrational frequencies, $\nu_1$ and $\nu_3$, were estimated by Brewer *et al.*[3] The values of $\nu_2$, electronic levels and quantum weights were estimated by comparison with those for FeCl$_2$(g). See the ideal gas table for details.

### References

[1] J. L. Margrave, "Research in Fluorine Chemistry," William Marsh Rice University, Houston, Texas, Progress Report No. 7, Jan. 1 to March 31, (1965).

[2] W. H. Baur, Acta Cryst. 11, 488 (1958).

[3] L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log K$_f$ |
| 0 | 0. | 0. | INFINITE | −12.671 | −388.870 | −388.870 | INFINITE |
| 100 | 38.559 | 214.824 | 309.258 | −9.443 | −388.972 | −392.811 | 205.183 |
| 200 | 47.902 | 244.563 | 270.063 | −5.100 | −389.326 | −396.519 | 103.560 |
| 250 | 52.104 | 255.709 | 266.103 | −2.599 | −389.465 | −398.300 | 83.220 |
| 298.15 | 55.747 | 265.205 | 265.205 | 0. | −389.530 | −399.994 | 70.077 |
| 300 | 55.876 | 265.551 | 265.206 | 0.103 | −389.532 | −400.059 | 69.656 |
| 350 | 58.995 | 274 407 | 265.899 | 2.978 | −389.532 | −401.813 | 59.967 |
| 400 | 61.390 | 282.449 | 267.473 | 5.991 | −389.491 | −403.570 | 52.701 |
| 450 | 63.115 | 289.786 | 269.551 | 9.106 | −389.441 | −405.332 | 47.050 |
| 500 | 64.284 | 296.500 | 271.915 | 12.293 | −389.408 | −407.100 | 42.529 |
| 600 | 65.466 | 308.344 | 277.026 | 18.791 | −389.469 | −410 636 | 35.749 |
| 700 | 65.785 | 318.466 | 282.241 | 25.358 | −389.780 | −414.144 | 30.904 |
| 800 | 65.747 | 327.251 | 287.331 | 31.936 | −390.425 | −417.585 | 27.265 |
| 900 | 65.601 | 334.986 | 292.205 | 38.504 | −391.541 | −420.919 | 24.429 |
| 1000 | 65.452 | 341.890 | 296.834 | 45.056 | −393.425 | −424.092 | 22.152 |
| 1100 | 65.339 | 348.123 | 301.218 | 51.595 | −396.248 | −427.008 | 20.277 |
| 1200 | 65.266 | 353.805 | 305.367 | 58.125 | −398.555 | −429.722 | 18.705 |
| 1300 | 65.229 | 359.027 | 309.296 | 64.650 | −399.243 | −432.292 | 17.370 |
| 1400 | 65.219 | 363.861 | 313.023 | 71.172 | −400.038 | −434.805 | 16.223 |
| 1500 | 65.226 | 368.360 | 316.564 | 77.694 | −400.937 | −437.258 | 15.227 |
| 1600 | 65.244 | 372.570 | 319.935 | 84.218 | −401.937 | −439.647 | 14.353 |
| 1700 | 65.265 | 376.526 | 323.148 | 90.743 | −403.985 | −441.952 | 13.580 |
| 1800 | 65.286 | 380.257 | 326.218 | 97.270 | −405.514 | −444.142 | 12.889 |
| 1900 | 65.304 | 383.788 | 329.156 | 103.800 | −421.235 | −445.542 | 12.249 |
| 2000 | 65.316 | 387.138 | 331.972 | 110.331 | −423.187 | −446.771 | 11.668 |
| 2100 | 65.323 | 390.325 | 334.676 | 116.863 | −425.144 | −447.902 | 11.141 |
| 2200 | 65.323 | 393.364 | 337.275 | 123.395 | −427.104 | −448.940 | 10.659 |
| 2300 | 65.316 | 396.267 | 339 777 | 129.927 | −429.063 | −449.888 | 10.217 |
| 2400 | 65.302 | 399.047 | 342.189 | 136.458 | −431.017 | −450.752 | 9.810 |
| 2500 | 65.283 | 401.712 | 344.517 | 142.988 | −432.965 | −451.534 | 9.434 |
| 2600 | 65.258 | 404.272 | 346.766 | 149.515 | −434.903 | −452.239 | 9.086 |
| 2700 | 65.228 | 406.734 | 348.942 | 156.039 | −436.827 | −452.869 | 8.761 |
| 2800 | 65.193 | 409.106 | 351.049 | 162.560 | −438.736 | −453.428 | 8.459 |
| 2900 | 65.155 | 411.393 | 353.090 | 169.078 | −440.627 | −453.919 | 8.176 |
| 3000 | 65.114 | 413.601 | 355.071 | 175.591 | −442.497 | −454.346 | 7.911 |
| 3100 | 65.070 | 415.736 | 356.994 | 182.100 | −444.345 | −454.710 | 7.662 |
| 3200 | 65.024 | 417.801 | 358.862 | 188.605 | −794.468 | −447.591 | 7.306 |
| 3300 | 64.976 | 419.801 | 360.678 | 195.105 | −794.366 | −436.753 | 6.913 |
| 3400 | 64.927 | 421.740 | 362.446 | 201.600 | −794.269 | −425.918 | 6.543 |
| 3500 | 64.877 | 423.621 | 364.167 | 208.090 | −794.179 | −415.085 | 6.195 |
| 3600 | 64.827 | 425.448 | 365.844 | 214.576 | −794.094 | −404.255 | 5.866 |
| 3700 | 64.776 | 427.224 | 367.479 | 221.056 | −794.015 | −393.427 | 5.554 |
| 3800 | 64.726 | 428.951 | 369.074 | 227.531 | −793.943 | −382.602 | 5.259 |
| 3900 | 64.675 | 430.631 | 370.631 | 234.001 | −793.879 | −371.778 | 4.979 |
| 4000 | 64.625 | 432.268 | 372.151 | 240.466 | −793.822 | −360.955 | 4.714 |
| 4100 | 64.575 | 433.863 | 373.637 | 246.926 | −793.775 | −350.134 | 4.461 |
| 4200 | 64.525 | 435.419 | 375.090 | 253.381 | −793.739 | −339.314 | 4.220 |
| 4300 | 64.477 | 436.936 | 376.511 | 259.831 | −793.715 | −328.495 | 3.990 |
| 4400 | 64.429 | 438.418 | 377.901 | 266.276 | −793.704 | −317.676 | 3.771 |
| 4500 | 64.382 | 439.865 | 379.262 | 272.717 | −793.709 | −306.857 | 3.562 |
| 4600 | 64.336 | 441.280 | 380.595 | 279.152 | −793.730 | −296.038 | 3.362 |
| 4700 | 64.290 | 442.663 | 381.901 | 285.584 | −793.770 | −285.218 | 3.170 |
| 4800 | 64.246 | 444.016 | 383.181 | 292.011 | −793.829 | −274.397 | 2.986 |
| 4900 | 64.203 | 445.340 | 384.436 | 298.433 | −793.911 | −263.575 | 2.810 |
| 5000 | 64.161 | 446.637 | 385.667 | 304.851 | −794.017 | −252.751 | 2.640 |
| 5100 | 64.119 | 447.907 | 386.875 | 311.265 | −794.148 | −241.924 | 2.478 |
| 5200 | 64.079 | 449.152 | 388.061 | 317.675 | −794.308 | −231.095 | 2.321 |
| 5300 | 64.040 | 450.372 | 389.225 | 324.081 | −794.497 | −220.262 | 2.171 |
| 5400 | 64.002 | 451.569 | 390.368 | 330.483 | −794.719 | −209.425 | 2.026 |
| 5500 | 63.965 | 452.743 | 391.492 | 336.881 | −794.975 | −198.584 | 1.886 |
| 5600 | 63.928 | 453.895 | 392.596 | 343.276 | −795.269 | −187.738 | 1.751 |
| 5700 | 63.893 | 455.026 | 393.681 | 349.667 | −795.602 | −176.887 | 1.621 |
| 5800 | 63.859 | 456.137 | 394.748 | 356.055 | −795.979 | −166.029 | 1.495 |
| 5900 | 63.825 | 457.228 | 395.798 | 362.439 | −796.401 | −155.164 | 1.374 |
| 6000 | 63.793 | 458.301 | 396.831 | 368.820 | −796.873 | −144.292 | 1.256 |

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

## Potassium Fluoride (K(HF$_2$)) CRYSTAL $M_r = 78.103046$

$S°(298.15\ K) = 104.264 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 469.85\ K$
$T_{fus} = 511.95\ K$

$\Delta_f H°(0\ K) = -926.386 \pm 1.26\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -931.233 \pm 1.26\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 11.221 \pm 0.04\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 6.619 \pm 0.013\ kJ \cdot mol^{-1}$

### Enthalpy of Formation

Davis and Westrum[1] measured directly the enthalpy of the decomposition reaction $KHF_2(cr) \rightarrow KF(cr) + HF(g)$ in an adiabatic calorimeter as $\Delta_{dcm} H° = 18.52 \pm 0.05\ kcal \cdot mol^{-1}$ at 500 K. Reducing to 298.15 K, we obtain $\Delta_{dcm} H°(298\ 15\ K) = 21.533 \pm 0.05\ kcal \cdot mol^{-1}$ which leads to the enthalpy of formation, $\Delta_f H°(KHF_2, cr, 298.15\ K) = -222.57 \pm 0.3\ kcal\ mol^{-1}$, using JANAF auxiliary data. This value is adopted in the tabulation.

Westrum and Pitzer[3] measured the dissociation vapor pressures of $KHF_2$ (cr, l) by a static method. Their pressure data have been analyzed by both 2nd law and 3rd law methods as given below. The enthalpy of formation derived from the 3rd law analysis differs by about 0.3 $kcal \cdot mol^{-1}$ from the value adopted, which is greater than the combined experimental errors.

| Reaction | T/K | Data Points | $\Delta_{dcm} H°(298.15\ K)$, $kcal \cdot mol^{-1}$ 2nd law | 3rd law | Drift $cal\ K^{-1} \cdot mol^{-1}$ | $\Delta_f H°(298.15\ K)$ $kcal \cdot mol^{-1}$ |
|---|---|---|---|---|---|---|
| $KHF_2(cr) \rightarrow KF(cr) + HF(g)$ | 478–500 | 14 | 21.21 ± 0.12 | 21.31 ± 0.01 | 0.2 ± 0.2 | −222.35 |
| $KHF_2(l) \rightarrow KF(cr) + HF(g)$ | 504–577 | 5 | 19.82 ± 0.08 | 17.73 ± 0.24 | −3.9 ± 0.2 | −222.28** |

**This value is derived from the adopted heat of melting, $\Delta_{fus} H°(298.15\ K) = 3.504\ kcal \cdot mol^{-1}$ and $\Delta_f H°(KHF_2, l, 298.15\ K) = -218.773\ kcal \cdot mol^{-1}$. The latter is calculated from the 3rd law $\Delta_{dcm} H°(298.15\ K)$.

### Heat Capacity and Entropy

Westrum and Pitzer[3] measured both low temperature $C_p°$ data (16–315 K) in an adiabatic calorimeter and high temperature enthalpy data (321.6−465 K for α phase and 471.3−505.9 K for β phase) in a drop calorimeter. We use their experimental $C_p°$ data to derive $S°(298.15\ K) = 24.92 \pm 0.1\ cal\ K^{-1} \cdot mol^{-1}$, based on $S° = 0.0643\ cal\ K^{-1} \cdot mol^{-1}$ at 15 K. The low temperature $C_p°$ and high temperature enthalpy data for the α phase are smoothly joined at 298.15 K by a polynomial curve fitting method. The deviations of the observed enthalpy data from the adopted values are 0.68% at 321.6 K and 0.09% at 463.7 K. The constant heat capacity, 23.96 $cal\ K^{-1} \cdot mol^{-1}$, in the β phase is derived from the measured enthalpy data,[3] and is assumed to be the same when the temperature is above the melting point.

### Transition and Fusion Data

Davis and Westrum[1] measured the heat of the αβ transition, $\Delta_{trs} H° = 2.682 \pm 0.01\ kcal \cdot mol^{-1}$ at 196.7°C, and the heat of melting, $\Delta_{fus} H° = 1.582 \pm 0.003\ kcal \cdot mol^{-1}$ at 238.8°C in an adiabatic calorimeter. Their data are adopted in the tabulation. Based on the drop calorimetric measurements,[3] we have derived $\Delta_{fus} H° = 1.554\ kcal \cdot mol^{-1}$ which is in good agreement with the value adopted.

### References

[1] M. L. Davis and E. F. Westrum, Jr., J. Phys. Chem. 65, 338 (1961).
[2] JANAF Thermochemical Tables: HF(g), 12–31–68; KF(cr), 6–30–69.
[3] E. F. Westrum, Jr. and K. S. Pitzer, J. Amer. Chem. Soc. 71, 1940 (1949).

## Potassium Fluoride (K(HF$_2$)) $F_2H_1K_1(cr)$

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

|  | $J \cdot K^{-1} mol^{-1}$ |  |  | $kJ \cdot mol^{-1}$ |  |  |  |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −15.294 | −926.386 | −926.386 | INFINITE |
| 100 | 48.961 | 34.988 | 165.420 | −13.043 | −930.274 | −908.140 | 474.363 |
| 200 | 67.070 | 75.565 | 110.999 | −7.087 | −931.188 | −885.531 | 231.277 |
| 298.15 | 76.940 | 104.264 | 104.264 | 0. | −931.233 | −863.095 | 151.211 |
| 300 | 77.111 | 104.741 | 104.266 | 0.142 | −931.230 | −862.672 | 150.205 |
| 400 | 86.065 | 128.152 | 107.398 | 8.302 | −933.221 | −839.415 | 109.616 |
| 469.850 | 92.450 | 142.501 | 111.566 | 14.535 | ALPHA <--> BETA |  |  |
| 469.850 | 100 .249 | 166.384 | 111.566 | 25.757 | TRANSITION |  |  |
| 500 | 100.249 | 172.619 | 115.061 | 28.779 | −920.678 | −816.803 | 85.331 |
| 511.950 | 100.249 | 174.987 | 116.432 | 29.977 | ---- BETA <--> LIQUID ---- |  |  |
| 600 | 100.249 | 190.897 | 126.224 | 38.804 | −918.631 | −796.221 | 69.317 |
| 700 | 100.249 | 206.350 | 136.595 | 48.829 | −916.622 | −775.979 | 57.904 |
| 800 | 100.249 | 219.737 | 146.169 | 58.854 | −914.660 | −756.021 | 49.363 |
| 900 | 100.249 | 231.544 | 155.012 | 68.879 | −912.760 | −736.306 | 42.734 |
| 1000 | 100.249 | 242.106 | 163.203 | 78.903 | −910.939 | −716.799 | 37.442 |
| 1100 | 100.249 | 251.661 | 170.817 | 88.928 | −988.173 | −692.859 | 32.901 |
| 1200 | 100.249 | 260.384 | 177.923 | 98.953 | −985.512 | −666.130 | 28.996 |
| 1300 | 100.249 | 268.408 | 184.579 | 108.978 | −982.895 | −639.621 | 25.700 |
| 1400 | 100.249 | 275.837 | 190.835 | 119.003 | −980.322 | −613.312 | 22.883 |
| 1500 | 100.249 | 282.754 | 196.735 | 129.028 | −977.791 | −587.186 | 20.448 |
| 1600 | 100.249 | 289.224 | 202.316 | 139.053 | −975.301 | −561.227 | 18.322 |
| 1700 | 100.249 | 295.301 | 207.609 | 149.077 | −972.851 | −535.423 | 16.452 |
| 1800 | 100.249 | 301.031 | 212.641 | 159.102 | −970.438 | −509.761 | 14.793 |
| 1900 | 100.249 | 306.451 | 217.437 | 169.127 | −968.060 | −484.233 | 13.313 |
| 2000 | 100.249 | 311.594 | 222.017 | 179.152 | −965.716 | −458.829 | 11.983 |

PREVIOUS: December 1963    CURRENT: June 1971

Potassium Fluoride (K(HF$_2$)) $F_2H_1K_1(cr)$

# Potassium Fluoride (K(HF$_2$)) LIQUID $M_r$ = 78.103046 Potassium Fluoride (K(HF$_2$)) F$_2$H$_1$K$_1$(l)

$S°(298.15\ K) = [132.764]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$T_{fus} = 511.95\ K$

$\Delta_f H°(298.15\ K) = [-916.573]\ kJ{\cdot}mol^{-1}$

$\Delta_{fus}H° = 6.619 \pm 0.013\ kJ{\cdot}mol^{-1}$

## Enthalpy of Formation

The enthalpy of formation is calculated from that of the crystal by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(511.95\ K)-H°(298.15\ K)$, between the crystal and liquid.

## Heat Capacity and Entropy

Westrum and Pitzer[1] measured high temperature enthalpy data by drop calorimetry in a narrow range of 510.6–523.2 K and derived a constant heat capacity of approximately 25 cal $K^{-1}{\cdot}mol^{-1}$ which is adopted in the tabulation.

A glass transition is assumed at 314 K. Below 314 K, the heat capacities are assumed to be the same as those of the crystal. Between 314 K and the melting point, the $C_p°$ is assumed to be the same as that of the liquid.

The entropy is calculated in a manner similar to that used for the enthalpy of formation.

## Fusion Data

Refer to the crystal table for details.

## Decomposition Data

The decomposition temperature, $T_{dcm} = 750$ K, is calculated as the temperature at which $\Delta_f G = 0$ for $KHF_2(l) \rightarrow KF(cr) + HF(g)$. At $T_{dcm}$, the vapor pressure of HF(g) reaches one atmosphere.

Westrum and Pitzer[1] determined the decomposition vapor pressures of $KHF_2$(cr, l) by a static method. Their data lead to the decomposition temperature, 700 K when the pressure of HF reaches one atmosphere. JANAF analyses of their data are given in $KHF_2$(cr) table. Their data over the crystal phase are suspected to be high by approximately 11.5%; and the data over the liquid phase are probably in error as indicated by the 3rd law drift (3.9 cal $K^{-1}{\cdot}mol^{-1}$) in the JANAF analyses.

## Reference

[1] E. F. Westrum, Jr. and K. S. Pitzer, J. Amer. Chem. Soc. 71, 1940 (1949).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 76.944 | 132.764 | 132.764 | 0. | −916.573 | −856.932 | 150.131 |
| 300 | 76.944 | 133.240 | 132.766 | 0.142 | −916.569 | −856.562 | 149.141 |
| 314.000 | 78.408 | 136.784 | 132.866 | 1.230 | GLASS <--> LIQUID | | |
| 314.000 | 104.600 | 136.784 | 132.866 | 1.230 | TRANSITION | | |
| 400 | 104.600 | 162.105 | 136.540 | 10.226 | −916.636 | −836.412 | 109.224 |
| 500 | 104.600 | 185.446 | 144 074 | 20.686 | −914.111 | −816.649 | 85.315 |
| 511.950 | 104.600 | 187.916 | 145.069 | 21.936 | ---- BETA <--> LIQUID ---- | | |
| 600 | 104.600 | 204.517 | 152.607 | 31.146 | −911.629 | −797.391 | 69.419 |
| 700 | 104.600 | 220.641 | 161.204 | 41.606 | −909.185 | −778.545 | 58.096 |
| 800 | 104.600 | 234.608 | 169.526 | 52.066 | −906.788 | −760.046 | 49.626 |
| 900 | 104.600 | 246.928 | 177.455 | 62.526 | −904.452 | −741.844 | 43.056 |
| 1000 | 104.600 | 257.949 | 184.963 | 72.986 | −902.197 | −723.898 | 37.813 |
| 1100 | 104.600 | 267.918 | 192.059 | 83.446 | −978.995 | −701.564 | 33.314 |
| 1200 | 104.600 | 277.020 | 198.765 | 93.906 | −975.898 | −676.480 | 29.446 |
| 1300 | 104.600 | 285.392 | 205.111 | 104.366 | −972.847 | −651.652 | 26.184 |
| 1400 | 104.600 | 293.144 | 211.125 | 114.826 | −969.839 | −627.058 | 23.396 |
| 1500 | 104.600 | 300.361 | 216.837 | 125.286 | −966.873 | −602.678 | 20.987 |
| 1600 | 104.600 | 307.111 | 222.270 | 135.746 | −963.948 | −578.494 | 18.886 |
| 1700 | 104.600 | 313.453 | 227.449 | 146.206 | −961.062 | −554.491 | 17.037 |
| 1800 | 104.600 | 319.431 | 232.395 | 156.666 | −958.214 | −530.658 | 15.399 |
| 1900 | 104.600 | 325.087 | 237.126 | 167 126 | −955.401 | −506.982 | 13.938 |
| 2000 | 104.600 | 330.452 | 241.659 | 177.586 | −952.622 | −483.452 | 12.626 |

PREVIOUS: December 1963 CURRENT: June 1971

**Potassium Fluoride (K(HF$_2$))** **CRYSTAL(α–β)-LIQUID** $M_r = 78.103046$ **Potassium Fluoride (K(HF$_2$))** **$F_2H_1K_1(cr,l)$**

0 to 469.85 K crystal, alpha
467.85 to 511.95 K crystal, beta
above 511.95 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p^\circ$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −15.294 | −926.386 | −926.386 | INFINITE |
| 100 | 48.961 | 34.988 | 165.420 | −13.043 | −930.274 | −908.140 | 474.363 |
| 200 | 67.070 | 75.565 | 110.999 | −7.087 | −931.188 | −885.531 | 231.277 |
| 298.15 | 76.940 | 104.264 | 104.264 | 0. | −931.233 | −863.095 | 151.211 |
| 300 | 77.111 | 104.741 | 104.266 | 0.142 | −931.230 | −862.672 | 150.205 |
| 400 | 86.065 | 128.152 | 107.398 | 8.302 | −933.221 | −839.415 | 109.616 |
| 469.850 | 92.450 | 142.501 | 111.566 | 14.535 | ALPHA <- -> BETA | TRANSITION | |
| 469.850 | 100.249 | 166.384 | 111.566 | 25.757 | | | |
| 500 | 100.249 | 172.619 | 115.061 | 28.779 | −920.678 | −816.803 | 85.331 |
| 511 950 | 100.249 | 174.987 | 116.432 | 29.977 | BETA <- -> LIQUID | TRANSITION | |
| 511 950 | 104.600 | 187.916 | 116.432 | 36.596 | | | |
| 600 | 104.600 | 204.517 | 128.173 | 45.806 | −911.629 | −797.391 | 69.419 |
| 700 | 104.600 | 220.641 | 140.261 | 56.266 | −909.185 | −778.545 | 58.096 |
| 800 | 104.600 | 234.608 | 151.200 | 66.726 | −906.788 | −760.046 | 49.626 |
| 900 | 104.600 | 246.928 | 161.166 | 77.186 | −904.452 | −741.844 | 43.056 |
| 1000 | 104.600 | 257.949 | 170.303 | 87.646 | −902.197 | −723.898 | 37.813 |
| 1100 | 104.600 | 267.918 | 178.731 | 98.106 | −978.995 | −701.564 | 33.314 |
| 1200 | 104.600 | 277.020 | 186.548 | 108.566 | −975.898 | −676.480 | 29.446 |
| 1300 | 104.600 | 285.392 | 193.834 | 119.026 | −972.847 | −651.652 | 26.184 |
| 1400 | 104.600 | 293.144 | 200.654 | 129.486 | −969.839 | −627.058 | 23.396 |
| 1500 | 104.600 | 300.361 | 207.063 | 139.946 | −966.873 | −602.678 | 20.987 |
| 1600 | 104.600 | 307.111 | 213.107 | 150.406 | −963.948 | −578.494 | 18.886 |
| 1700 | 104.600 | 313.453 | 218.826 | 160.866 | −961.062 | −554.491 | 17.037 |
| 1800 | 104.600 | 319.431 | 224.250 | 171.326 | −958.214 | −530.658 | 15.399 |
| 1900 | 104.600 | 325.087 | 229.410 | 181.786 | −955 401 | −506.982 | 13.938 |
| 2000 | 104.600 | 330.452 | 234.329 | 192.246 | −952.622 | −483.452 | 12.626 |

PREVIOUS:    CURRENT: June 1971

**Potassium Fluoride (K(HF$_2$))** **$F_2H_1K_1(cr,l)$**

## Hydrogen Fluoride ((HF)$_2$) IDEAL GAS $M_r = 40.012686$ Hydrogen Fluoride ((HF)$_2$) $F_2H_2(g)$

$S°(298.15\ K) = 238.849 \pm 8.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -566.600 \pm 3.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -572.664 \pm 3.3\ kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, cm$^{-1}$ |
|---|
| [4000](1) |
| [3400](1) |
| [1200](2) |
| [720](1) |
| [350](1) |

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: $C_s$
Bond Distances. F–H = 0.92 Å; H ··· F = 1.87 Å
Bond Angles: H ··· F–H = 108°; F–H ··· F = 180°
Product of the Moments of Inertia: $I_A I_B I_C = 1.98556 \times 10^{-116}\ g^3 \cdot cm^6$

### Enthalpy of Formation

The enthalpy of 2 HF(g) → $H_2F_2(g)$ was taken as the mean of the 3rd law values which were obtained from the following equilibrium data. Briegleb and Strohmeier[1] measured the vapor density of associated HF(g) between 26 and 56°C and between 30 and 700 torr. Franck and Meyer[2] measured the heat capacity between 20 and 100°*C* and between 100 and 700 torr. Their 2nd law values differed by 1.2 kcal·mol$^{-1}$; and using the molecular constants discussed below gave respectively mean 3rd law values which differed by 0.34 kcal·mol$^{-1}$, a 0.14 kcal·mol$^{-1}$ temperature trend for Briegleb and Strohmeier,[1] and a 0.02 kcal·mol$^{-1}$ temperature trend for Franck and Meyer.[2] $\Delta_f H°(H_2F_2$, g, 298.15 K) was calculated using auxiliary JANAF data.[3]

### Heat Capacity and Entropy

The structure of the semi rigid hydrogen bonded dimer is taken from Dyke *et al.*[4] Using bond distances and angles given by these authors we obtain $I_A = 0.1203 \times 10^{-39}$, $I_B = 12.7869 \times 10^{-39}$, and $I_C = 12.9022 \times 10^{-39}\ \cdot cm^2$. Dyke *et al.*[4] observed a doubling of the rotational energy levels of the dimer and attributed this to a tunneling motion involving breaking of the hydrogen bond, interchange of the two HF units, and formation of a new hydrogen bond. Thus there are two identical configurations for the dimer separated by a low energy barrier so that quantum mechanical tunneling occurs at a significant rate. Therefore the overall symmetry number is 2 even though the external symmetry number is 1.

Reliable experimental values of the vibrational frequencies of $H_2F_2(g)$ are not available. The estimated frequencies are similar to those used for the higher polymers which were obtained from data on HF solid. The infrared absorption bands observed in the vapor (350 to 400 cm$^{-1}$, 700 to 800 cm$^{-1}$, and 1000–1200 cm$^{-1}$ regions) are largely due to the higher polymers, such as the tetramer and hexamer. Calculated values (610, 443, and 144 cm$^{-1}$) were obtained from force constants given in a paper on theory of molecular interactions of the HF polymers by Del Bene and Pople.[5] The potential energy surface computed for the dimer suggests very anharmonic low frequency motions for the external hydrogen (estimated at 600 ± 200 cm$^{-1}$) and for the hydrogen bond stretching mode.

The National Bureau of Standards prepared this table[6] by critical analysis of data existing in 1972. Using our $I_A I_B I_C$ with other molecular constants and $\Delta_f H°$ selected by NBS,[6] we recalculate the table in terms of 1973 fundamental constants,[7] 1975 atomic weights[8] and current JANAF reference states for the elements.

### References

[1] G. Briegleb and W. Strohmeier, Z. Elektrochem. 57, 668 (1953).
[2] E. U Franck and F. Meyer, Z. Elektrochem. 63, 571 (1959).
[3] JANAF Thermochemical Tables: HF(g), 6–30–77.
[4] T. R. Dyke, B. J. Howard and W. Klemperer, J. Chem. Phys. 56, 2442 (1972).
[5] J. E. Del Bene and J. A. Pople, J. Chem. Phys. 55, 2296 (1971).
[6] S. Abramowitz *et al.*, U.S. Nat. Bur. Stand. Report 10904, 239, (1972).
[7] CODATA Task Group on Fundamental Constants, CODATA Bulletin 11, (December 1973).
[8] IUPAC Commission on Atomic Weights, Pure Appl. Chem. 47, 75 (1976).

Enthalpy Reference Temperature = $T_r$ = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −11.228 | −566.600 | −566.600 | INFINITE |
| 100 | 34.675 | 196.439 | 275.181 | −7.874 | −569.152 | −561.686 | 293.395 |
| 200 | 39.777 | 222.014 | 242.789 | −4.155 | −571.056 | −553.446 | 144.545 |
| 250 | 42.385 | 231.170 | 239.574 | −2.101 | −571.901 | −548.945 | 114.696 |
| 298.15 | 44.874 | 238.849 | 238.849 | 0. | −572.664 | −544.453 | 95.386 |
| 300 | 44.968 | 239.127 | 238.850 | 0.083 | −572.692 | −544.278 | 94.767 |
| 350 | 47.433 | 246.246 | 239.407 | 2.394 | −573.419 | −539.484 | 80.514 |
| 400 | 49.702 | 252.731 | 240.673 | 4.823 | −574.077 | −534.590 | 69.810 |
| 450 | 51.736 | 258.705 | 242.349 | 7.360 | −574.668 | −529.618 | 61.477 |
| 500 | 53.536 | 264.251 | 244.265 | 9.993 | −575.196 | −524.584 | 54.803 |
| 600 | 56.536 | 274.287 | 248.450 | 15.502 | −576.089 | −514.374 | 44.780 |
| 700 | 58.952 | 283.190 | 252.789 | 21.281 | −576.800 | −504.030 | 37.611 |
| 800 | 61.000 | 291.199 | 257.098 | 27.281 | −577.363 | −493.594 | 32.228 |
| 900 | 62.809 | 298.490 | 261.298 | 33.473 | −577.799 | −483.096 | 28.038 |
| 1000 | 64.449 | 305.194 | 265.357 | 39.837 | −578.129 | −472.555 | 24.684 |
| 1100 | 65.953 | 311.408 | 269.264 | 46.358 | −578.366 | −461.985 | 21.938 |
| 1200 | 67.335 | 317.207 | 273.020 | 53.023 | −578.525 | −451.397 | 19.649 |
| 1300 | 68.602 | 322.647 | 276.631 | 59.821 | −578.617 | −440.799 | 17.712 |
| 1400 | 69.761 | 327.774 | 280.103 | 66.740 | −578.653 | −430.196 | 16.051 |
| 1500 | 70.818 | 332.624 | 283.444 | 73.770 | −578.642 | −419.592 | 14.611 |
| 1600 | 71.778 | 337.225 | 286.663 | 80.900 | −578.591 | −408.990 | 13.352 |
| 1700 | 72.651 | 341.603 | 289.767 | 88.123 | −578.508 | −398.392 | 12.241 |
| 1800 | 73.442 | 345.779 | 292.763 | 95.428 | −578.396 | −387.801 | 11.254 |
| 1900 | 74.159 | 349.769 | 295.659 | 102.808 | −578.261 | −377.216 | 10.370 |
| 2000 | 74.809 | 353.590 | 298.461 | 110.257 | −578.103 | −366.638 | 9.576 |
| 2100 | 75.399 | 357.254 | 301.174 | 117.768 | −577.924 | −356.069 | 8.857 |
| 2200 | 75.934 | 360.774 | 303.804 | 125.335 | −577.726 | −345.509 | 8.203 |
| 2300 | 76.421 | 364.161 | 306.355 | 132.953 | −577.507 | −334.959 | 7.607 |
| 2400 | 76.864 | 367.423 | 308.832 | 140.618 | −577.267 | −324.418 | 7.061 |
| 2500 | 77.268 | 370.569 | 311.239 | 148.325 | −577.004 | −313.888 | 6.558 |
| 2600 | 77.637 | 373.606 | 313.579 | 156.071 | −576.719 | −303.369 | 6.095 |
| 2700 | 77.975 | 376.543 | 315.857 | 163.852 | −576.409 | −292.862 | 5.666 |
| 2800 | 78.284 | 379.384 | 318.076 | 171.665 | −576.072 | −282.366 | 5.268 |
| 2900 | 78.568 | 382.137 | 320.237 | 179.507 | −575.709 | −271.883 | 4.897 |
| 3000 | 78.829 | 384.805 | 322.345 | 187.377 | −575.317 | −261.413 | 4.552 |
| 3100 | 79.069 | 387.393 | 324.402 | 195.273 | −574.897 | −250.956 | 4.229 |
| 3200 | 79.291 | 389.907 | 326.410 | 203.191 | −574.447 | −240.514 | 3.926 |
| 3300 | 79.495 | 392.350 | 328.371 | 211.130 | −573.967 | −230.085 | 3.642 |
| 3400 | 79.685 | 394.726 | 330.288 | 219.089 | −573.456 | −219.672 | 3.375 |
| 3500 | 79.860 | 397.039 | 332.163 | 227.067 | −572.915 | −209.275 | 3.123 |
| 3600 | 80.023 | 399.291 | 333.996 | 235.061 | −572.344 | −198.893 | 2.886 |
| 3700 | 80.175 | 401.485 | 335.791 | 243.071 | −571.744 | −188.527 | 2.662 |
| 3800 | 80.316 | 403.625 | 337.548 | 251.095 | −571.114 | −178.179 | 2.449 |
| 3900 | 80.448 | 405.713 | 339.269 | 259.134 | −570.455 | −167.847 | 2.248 |
| 4000 | 80.571 | 407.752 | 340.956 | 267.185 | −569.769 | −157.532 | 2.057 |
| 4100 | 80.686 | 409.743 | 342.609 | 275.248 | −569.055 | −147.235 | 1.876 |
| 4200 | 80.793 | 411.688 | 344.231 | 283.322 | −568.315 | −136.955 | 1.703 |
| 4300 | 80.894 | 413.591 | 345.822 | 291.406 | −567.550 | −126.694 | 1.539 |
| 4400 | 80.989 | 415.451 | 347.383 | 299.500 | −566.760 | −116.451 | 1.382 |
| 4500 | 81.077 | 417.272 | 348.916 | 307.604 | −565.946 | −106.226 | 1.233 |
| 4600 | 81.161 | 419.055 | 350.422 | 315.716 | −565.109 | −96.019 | 1.090 |
| 4700 | 81.240 | 420.802 | 351.900 | 323.836 | −564.251 | −85.830 | 0.954 |
| 4800 | 81.314 | 422.513 | 353.354 | 331.963 | −563.371 | −75.660 | 0.823 |
| 4900 | 81.384 | 424.190 | 354.782 | 340.098 | −562.470 | −65.509 | 0.698 |
| 5000 | 81.450 | 425.835 | 356.187 | 348.240 | −561.550 | −55.376 | 0.579 |
| 5100 | 81.513 | 427.449 | 357.569 | 356.388 | −560.610 | −45.262 | 0.464 |
| 5200 | 81.572 | 429.032 | 358.928 | 364.542 | −559.652 | −35.166 | 0.353 |
| 5300 | 81.628 | 430.586 | 360.265 | 372.703 | −558.675 | −25.089 | 0.247 |
| 5400 | 81.681 | 432.113 | 361.582 | 380.868 | −557.681 | −15.031 | 0.145 |
| 5500 | 81.732 | 433.612 | 362.878 | 389.039 | −556.668 | −4.992 | 0.047 |
| 5600 | 81.780 | 435.085 | 364.154 | 397.214 | −555.639 | 5.030 | −0.047 |
| 5700 | 81.825 | 436.533 | 365.411 | 405.395 | −554.592 | 15.032 | −0.138 |
| 5800 | 81.869 | 437.956 | 366.650 | 413.579 | −553.527 | 25.016 | −0.225 |
| 5900 | 81.910 | 439.356 | 367.870 | 421.768 | −552.446 | 34.982 | −0.310 |
| 6000 | 81.949 | 440.733 | 369.073 | 429.961 | −551.347 | 44.929 | −0.391 |

PREVIOUS June 1977 (1 atm) CURRENT June 1977 (1 bar)

Hydrogen Fluoride ((HF)$_2$) $F_2H_2(g)$

$S°(298.15\ K) = 262.130 \pm 2.1\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = [-782.254 \pm 20.9]\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [-790.776 \pm 20.9]\ kJ{\cdot}mol^{-1}$

| Vibrational Frequencies and Degeneracies | | |
|---|---|---|
| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
| 2246(1) | 322(1) | 730(1) |
| 982(1) | 730(1) | 981(1) |
| 869(1) | 2251(1) | 903(1) |

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: $C_{2v}$
Bond Distances: Si–H = 1.471 Å; Si–F = 1.5767 Å
Bond Angles: H–Si–H = 112.02°; F–Si–F = 107.93°
Product of the Moments of Inertia: $I_A I_B I_C = 4.815754 \times 10^{-115}\ g^3{\cdot}cm^6$

## Enthalpy of Formation

There are no reported experimental studies leading to the enthalpy of formation of $SiH_2F_2(g)$. We estimate this value via a linear interpolation between the established $\Delta_f H°(298.15\ K)$ values of $SiH_4(g)$ and $SiF_4(g)$.[1] The reasonableness of this approach has been demonstrated by Lapidus *et al.*,[2] Hunt and Sirtl,[3] and Seiter and Sirtl.[4]

## Heat Capacity and Entropy

The adopted vibrational frequencies are from the gas phase infrared study of Cradock *et al.*[6] Two frequencies ($\nu_5$ and $\nu_6$) were quite uncertain and were discussed in terms of a strong Coriolis interaction.

These frequencies appear quite reasonable when a comparison of the dihalosilanes and dihalomethanes (halogen is fluorine, chlorine, and bromine) is made.[1,5]

The adopted bond distances and bond angles are obtained from the microwave spectrum study by Laurie.[7] The individual moments of inertia are: $I_A = 3.4021 \times 10^{-39}$, $I_B = 10.7552 \times 10^{-39}$, and $I_C = 13.1614 \times 10^{-39}\ g{\cdot}cm^2$.

## References

[1] JANAF Thermochemical Tables: $SiH_4(g)$ and $SiF_4(g)$, 6–30–76; $CH_2F_2$, 12–31–69.
[2] I. I. Lapidus, L. A. Nisel'son, and A. L. Seifer in "Thermophysical Properties of Gases and Liquids," No. 1, V. A. Rabinovich, Ed., Israel Program for Scientific Translations, Jerusalem, pp. 102–135, (1970).
[3] L. P. Hunt and E. Sirtl, J. Electrochem. Soc. **119**, 1741 (1972).
[4] H. Seiter and E. Sirtl, Z. Naturforsch. **21a**, 1956 (1966).
[5] T. Shimanouchi, NSRDS–NBS–39, 1972; J. Phys. Chem. Ref. Data **2**, 121 (1973).
[6] S. Cradock, E. A. V. Ebsworth, and A. G. Robiette, Trans. Faraday Soc. **60**, 1502 (1964).
[7] V. W. Laurie, J. Chem. Phys. **26**, 1359 (1957).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −11.988 | −782.254 | −782.254 | INFINITE |
| 100 | 35.089 | 216.460 | 302.698 | −8.624 | −785.062 | −779.215 | 407.020 |
| 200 | 42.974 | 242.890 | 266.723 | −4.766 | −788.006 | −772.238 | 201.688 |
| 250 | 48.646 | 253.078 | 262.992 | −2.478 | −789.467 | −768.126 | 160.491 |
| 298.15 | 54.268 | 262.130 | 262.130 | 0. | −790.776 | −763.895 | 133.831 |
| 300 | 54.479 | 262.466 | 262.131 | 0.101 | −790.824 | −763.728 | 132.977 |
| 350 | 59.903 | 271.278 | 262.814 | 2.962 | −792.035 | −759.114 | 113.292 |
| 400 | 64.714 | 279.598 | 264.397 | 6.081 | −793.090 | −754.338 | 98.506 |
| 450 | 68.914 | 287.469 | 266.527 | 9.424 | −793.999 | −749.437 | 86.992 |
| 500 | 72.575 | 294.923 | 268.998 | 12.963 | −794.774 | −744.443 | 77.771 |
| 600 | 78.609 | 308.712 | 274.487 | 20.535 | −795.981 | −734.257 | 63.923 |
| 700 | 83.350 | 321.200 | 280.283 | 28.642 | −796.811 | −723.899 | 54.018 |
| 800 | 87.139 | 332.586 | 286.120 | 37.173 | −797.351 | −713.443 | 46.583 |
| 900 | 90.201 | 343.033 | 291.871 | 46.045 | −797.670 | −702.934 | 40.797 |
| 1000 | 92.697 | 352.670 | 297.475 | 55.195 | −797.825 | −692.398 | 36.167 |
| 1100 | 94.746 | 361.604 | 302.904 | 64.570 | −797.865 | −681.853 | 32.378 |
| 1200 | 96.440 | 369.923 | 308.146 | 74.132 | −797.826 | −671.307 | 29.221 |
| 1300 | 97.850 | 377.699 | 313.201 | 83.848 | −797.739 | −660.767 | 26.550 |
| 1400 | 99.033 | 384.995 | 318.071 | 93.694 | −797.631 | −650.235 | 24.261 |
| 1500 | 100.033 | 391.863 | 322.764 | 103.649 | −797.519 | −639.711 | 22.277 |
| 1600 | 100.882 | 398.347 | 327.287 | 113.696 | −797.418 | −629.194 | 20.541 |
| 1700 | 101.609 | 404.485 | 331.649 | 123.821 | −847.516 | −618.235 | 18.996 |
| 1800 | 102.236 | 410.311 | 335.859 | 134.014 | −847.236 | −604.756 | 17.550 |
| 1900 | 102.778 | 415.854 | 339.924 | 144.266 | −846.949 | −591.293 | 16.256 |
| 2000 | 103.251 | 421.138 | 343.854 | 154.568 | −846.658 | −577.845 | 15.092 |
| 2100 | 103.665 | 426.186 | 347.655 | 164.914 | −846.364 | −564.411 | 14.039 |
| 2200 | 104.029 | 431.017 | 351.335 | 175.299 | −846.067 | −550.992 | 13.082 |
| 2300 | 104.351 | 435.648 | 354.901 | 185.718 | −845.766 | −537.586 | 12.209 |
| 2400 | 104.637 | 440.096 | 358.359 | 196.168 | −845.461 | −524.194 | 11.409 |
| 2500 | 104.892 | 444.372 | 361.714 | 206.645 | −845.148 | −510.814 | 10.673 |
| 2600 | 105.120 | 448.491 | 364.973 | 217.145 | −844.827 | −497.447 | 9.994 |
| 2700 | 105.325 | 452.462 | 368.140 | 227.668 | −844.495 | −484.092 | 9.365 |
| 2800 | 105.510 | 456.296 | 371.221 | 238.210 | −844.150 | −470.750 | 8.782 |
| 2900 | 105.677 | 460.001 | 374.219 | 248.769 | −843.789 | −457.421 | 8.239 |
| 3000 | 105.828 | 463.586 | 377.138 | 259.345 | −843.412 | −444.104 | 7.733 |
| 3100 | 105.966 | 467.059 | 379.983 | 269.934 | −843.016 | −430.801 | 7.259 |
| 3200 | 106.092 | 470.425 | 382.757 | 280.537 | −842.601 | −417.510 | 6.815 |
| 3300 | 106.207 | 473.691 | 385.463 | 291.152 | −842.165 | −404.232 | 6.398 |
| 3400 | 106.313 | 476.864 | 388.105 | 301.779 | −841.707 | −390.969 | 6.007 |
| 3500 | 106.410 | 479.947 | 390.685 | 312.415 | −841.227 | −377.719 | 5.637 |
| 3600 | 106.499 | 482.946 | 393.207 | 323.060 | −1224.876 | −354.022 | 5.137 |
| 3700 | 106.581 | 485.865 | 395.672 | 333.714 | −1223.937 | −329.844 | 4.657 |
| 3800 | 106.657 | 488.708 | 398.083 | 344.376 | −1222.977 | −305.692 | 4.202 |
| 3900 | 106.728 | 491.480 | 400.442 | 355.046 | −1221.996 | −281.566 | 3.771 |
| 4000 | 106.794 | 494.183 | 402.752 | 365.722 | −1220.994 | −257.465 | 3.362 |
| 4100 | 106.855 | 496.820 | 405.014 | 376.404 | −1219.972 | −233.389 | 2.973 |
| 4200 | 106.911 | 499.396 | 407.231 | 387.092 | −1218.928 | −209.339 | 2.604 |
| 4300 | 106.964 | 501.912 | 409.404 | 397.786 | −1217.865 | −185.314 | 2.251 |
| 4400 | 107.014 | 504.372 | 411.534 | 408.485 | −1216.781 | −161.313 | 1.915 |
| 4500 | 107.060 | 506.777 | 413.624 | 419.189 | −1215.678 | −137.338 | 1.594 |
| 4600 | 107.103 | 509.131 | 415.675 | 429.897 | −1214.556 | −113.387 | 1.288 |
| 4700 | 107.144 | 511.435 | 417.688 | 440.609 | −1213.416 | −89.461 | 0.994 |
| 4800 | 107.182 | 513.691 | 419.665 | 451.326 | −1212.258 | −65.559 | 0.713 |
| 4900 | 107.218 | 515.901 | 421.606 | 462.046 | −1211.082 | −41.682 | 0.444 |
| 5000 | 107.252 | 518.068 | 423.514 | 472.769 | −1209.889 | −17.828 | 0.186 |
| 5100 | 107.284 | 520.192 | 425.389 | 483.496 | −1208.680 | 6.001 | −0.061 |
| 5200 | 107.314 | 522.275 | 427.232 | 494.226 | −1207.455 | 29.806 | −0.299 |
| 5300 | 107.343 | 524.320 | 429.045 | 504.959 | −1206.214 | 53.588 | −0.528 |
| 5400 | 107.370 | 526.327 | 430.828 | 515.695 | −1204.957 | 77.346 | −0.748 |
| 5500 | 107.395 | 528.297 | 432.582 | 526.433 | −1203.686 | 101.080 | −0.960 |
| 5600 | 107.420 | 530.232 | 434.308 | 537.174 | −1202.400 | 124.792 | −1.164 |
| 5700 | 107.443 | 532.134 | 436.008 | 547.917 | −1201.099 | 148.480 | −1.361 |
| 5800 | 107.464 | 534.003 | 437.681 | 558.662 | −1199.785 | 172.146 | −1.550 |
| 5900 | 107.485 | 535.840 | 439.330 | 569.410 | −1198.456 | 195.788 | −1.733 |
| 6000 | 107.505 | 537.646 | 440.953 | 580.159 | −1197.113 | 219.408 | −1.910 |

PREVIOUS· June 1976 (1 atm) CURRENT· June 1976 (1 bar)

## Mercury Fluoride (HgF$_2$) CRYSTAL $M_r$ = 238.586806 Mercury Fluoride (HgF$_2$) F$_2$Hg$_1$(cr)

$S^\circ$(298.15 K) = [116.315 ± 8.4] J·K$^{-1}$·mol$^{-1}$ $\Delta_f H^\circ$(298.15 K) = [−422.584 ± 41.8] kJ·mol$^{-1}$

$T_{fus}$ = 918 K $\Delta_{fus}H^\circ$ = [23.012 ± 4.2] kJ·mol$^{-1}$

### Enthalpy of Formation

Estimated by comparison of the mercurous and mercuric halides.

### Heat Capacity and Entropy

The heat capacity is assumed to be a *linear* function of temperature and was estimated to be 7.0 cal K$^{-1}$·g–atom$^{-1}$ at the melting point. The entropy is estimated by comparison with the other mercuric and mercurous halides and use of additive entropy constants for the halogens.[1]

### Fusion Data

$T_{fus}$ was given by Ruff and Bahlau.[2] The heat of melting was from Brewer.[3]

### References

[1] K. K. Kelley, U.S. Bur. Mines, personal communication, (1960).

[2] O. Ruff and G. Bahlau, Ber. 51, 1752 (1918).

[3] L. Brewer, in 'Thermodynamics,' McGraw Hill, National Nuclear Energy Series 4–19B paper 7 (1950).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p^\circ$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 74.856 | 116.315 | 116.315 | 0. | −422.584 | −374.134 | 65.547 |
| 300 | 74.894 | 116.778 | 116.317 | 0.139 | −422.555 | −373.833 | 65.090 |
| 400 | 76.986 | 138.610 | 119.279 | 7.732 | −420.946 | −357.833 | 46.728 |
| 500 | 79.078 | 156.014 | 124.943 | 15.536 | −419.236 | −342.250 | 35.755 |
| 600 | 81.170 | 170.616 | 131.370 | 23.548 | −417.411 | −327.022 | 28.470 |
| 700 | 83.262 | 183.286 | 137.901 | 31.770 | −474.215 | −305.539 | 22.800 |
| 800 | 85.354 | 194.541 | 144.290 | 40.200 | −471.472 | −281.627 | 18.388 |
| 900 | 87.446 | 204.714 | 150.448 | 48.840 | −468.565 | −258.070 | 14.978 |
| 918.000 | 87.822 | 206.450 | 151.529 | 50.418 | --- CRYSTAL <--> LIQUID --- | | |
| 1000 | 89.538 | 214.036 | 156.347 | 57.689 | −465.485 | −234.845 | 12.267 |
| 1100 | 91.630 | 222.668 | 161.988 | 66.748 | −462.225 | −211.937 | 10.064 |
| 1200 | 93.722 | 230.731 | 167.384 | 76.015 | −458.782 | −189.334 | 8.241 |
| 1300 | 95.814 | 238.315 | 172.552 | 85.492 | −455.153 | −167.026 | 6.711 |
| 1400 | 97.906 | 245.492 | 177.508 | 95.178 | −451.336 | −145.004 | 5.410 |
| 1500 | 99.998 | 252.318 | 182.269 | 105.073 | −447.330 | −123.262 | 4.292 |
| 1600 | 102.090 | 258.839 | 186.853 | 115.178 | −443.133 | −101.793 | 3.323 |
| 1700 | 104.182 | 265.091 | 191.272 | 125.491 | −438.743 | −80.593 | 2.476 |
| 1800 | 106.274 | 271.105 | 195.541 | 136.014 | −434.159 | −59.657 | 1.731 |
| 1900 | 108.366 | 276.907 | 199.672 | 146.746 | −429.378 | −38.981 | 1.072 |
| 2000 | 110.458 | 282.518 | 203.675 | 157.687 | −424.396 | −18.561 | 0.485 |

PREVIOUS: CURRENT: March 1962

Mercury Fluoride (HgF$_2$) F$_2$Hg$_1$(cr)

## Mercury Fluoride ($HgF_2$) LIQUID $M_r$ = 238.586806 Mercury Fluoride ($HgF_2$) $F_2Hg_1(l)$

$S°(298.15\ K) = [134.246]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 918\ K$

$\Delta_f H°(298.15\ K) = [-404.897]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [23.012 \pm 4.2]\ kJ \cdot mol^{-1}$

### Enthalpy of Formation

$\Delta_f H°(HgF_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(HgF_2, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus} H°$, and the difference in enthalpy, $H°(918\ K)$ $H°(298\ 15\ K)$, between the crystal and liquid.

### Heat Capacity and Entropy

$C_p°$ is estimated by analogy with mercuric iodide and bromide. A glass type transitiion is assumed at 613 K below which the heat capacity is that of $HgF_2(cr)$. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

### Fusion and Vaporization Data

$T_{fus}$ was given by Ruff and Bahlan.[1] $T_{vap} = 920\ K$, $\Delta_{fus} H° = 23.0 \pm 4.2\ kJ \cdot mol^{-1}$, and $\Delta_{vap} H° = 92.0 \pm 16.7\ kJ \cdot mol^{-1}$ were all taken from Brewer.[2]

### References

[1] O. Ruff and G Bahlan, Ber. **51**, 1752 (1918).
[2] L. Brewer, in 'Thermodynamics' McGraw Hill, New York, National Nuclear Energy Series 4–19B paper 7, (1950).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| $T/K$ | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 74.856 | 134.246 | 134.246 | 0. | −404.897 | −361.793 | 63.385 |
| 300 | 74.894 | 134.709 | 134.248 | 0.139 | −404.868 | −361.525 | 62.947 |
| 400 | 76.986 | 156.541 | 137.210 | 7.732 | −403.259 | −347.318 | 45.355 |
| 500 | 79.078 | 173.945 | 142.874 | 15.536 | −401.549 | −333.528 | 34.843 |
| 600 | 81.170 | 188.548 | 149.301 | 23.548 | −399.724 | −320.093 | 27.867 |
| 613.000 | 81.442 | 190.290 | 150.152 | 24.605 | ——— GLASS <−−> LIQUID ——— TRANSITION | | |
| 613.000 | 102.090 | 190.290 | 150.152 | 24.605 | | | |
| 700 | 102.090 | 203.839 | 156.001 | 33.487 | −454.810 | −300.521 | 22.425 |
| 800 | 102.090 | 217.471 | 162.852 | 43.696 | −450.290 | −278.789 | 18.203 |
| 900 | 102.090 | 229.496 | 169.602 | 53.905 | −445.813 | −257.621 | 14.952 |
| 918.000 | 102.090 | 231.517 | 170.796 | 55.742 | −−− CRYSTAL <−−> LIQUID −−− | | |
| 1000 | 102.090 | 240.252 | 176.138 | 64.114 | −441.373 | −236.949 | 12.377 |
| 1100 | 102.090 | 249.982 | 182.416 | 74.323 | −436.963 | −216.720 | 10.291 |
| 1200 | 102.090 | 258.865 | 188.422 | 84.532 | −432.578 | −196.892 | 8.570 |
| 1300 | 102.090 | 267.037 | 194.159 | 94.741 | −428.217 | −177.428 | 7.129 |
| 1400 | 102.090 | 274.602 | 199.638 | 104.949 | −423.877 | −158.300 | 5.906 |
| 1500 | 102.090 | 281.646 | 204.873 | 115.158 | −419.557 | −139.481 | 4.857 |
| 1600 | 102.090 | 288.234 | 209.880 | 125.367 | −415.256 | −120.950 | 3.949 |
| 1700 | 102.090 | 294.424 | 214.673 | 135.576 | −410.971 | −102.687 | 3.155 |
| 1800 | 102.090 | 300.259 | 219.267 | 145.785 | −406.700 | −84.676 | 2.457 |
| 1900 | 102.090 | 305.779 | 223.676 | 155.994 | −402.442 | −66.902 | 1.839 |
| 2000 | 102.090 | 311.015 | 227.913 | 166.203 | −398.193 | −49.351 | 1.289 |

PREVIOUS: CURRENT March 1962

## Mercury Fluoride (HgF$_2$) CRYSTAL-LIQUID

0 to 918 K crystal
above 918 K liquid

Refer to the individual tables for details.

## $M_r$ = 238.586806 Mercury Fluoride (HgF$_2$) F$_2$Hg$_1$(cr,l)

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p^\circ$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log K$_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 74.856 | 116.315 | 116.315 | 0. | −422.584 | −374.134 | 65.547 |
| 300 | 74.894 | 116.778 | 116.317 | 0.139 | −422.555 | −373.833 | 65.090 |
| 400 | 76.986 | 138.610 | 119.279 | 7.732 | −420.946 | −357.833 | 46.728 |
| 500 | 79.078 | 156.014 | 124.943 | 15.536 | −419.236 | −342.250 | 35.755 |
| 600 | 81.170 | 170.616 | 131.370 | 23.548 | −417.411 | −327.022 | 28.470 |
| 700 | 83.262 | 183.286 | 137.901 | 31.770 | −474.215 | −305.539 | 22.800 |
| 800 | 85.354 | 194.541 | 144.290 | 40.200 | −471.472 | −281.627 | 18.388 |
| 900 | 87.446 | 204.714 | 150.448 | 48.840 | −468.565 | −258.070 | 14 978 |
| 918.000 | 87.822 | 206.450 | 151.529 | 50.418 | CRYSTAL <--> LIQUID TRANSITION | | |
| 918.000 | 102.090 | 231.517 | 151.529 | 73.430 | | | |
| 1000 | 102.090 | 240.252 | 158.451 | 81.801 | −441.373 | −236.949 | 12.377 |
| 1100 | 102.090 | 249.982 | 166.337 | 92.010 | −436.963 | −216.720 | 10.291 |
| 1200 | 102.090 | 258.865 | 173.683 | 102.219 | −432.578 | −196.892 | 8.570 |
| 1300 | 102.090 | 267.037 | 180.554 | 112.428 | −428.217 | −177.428 | 7.129 |
| 1400 | 102.090 | 274.602 | 187.005 | 122.637 | −423.877 | −158.300 | 5.906 |
| 1500 | 102.090 | 281.646 | 193.082 | 132.846 | −419.557 | −139.481 | 4.857 |
| 1600 | 102.090 | 288.234 | 198.825 | 143.055 | −415.256 | −120.950 | 3.949 |
| 1700 | 102.090 | 294.424 | 204.268 | 153.264 | −410.971 | −102.687 | 3.155 |
| 1800 | 102.090 | 300.259 | 209.441 | 163.473 | −406.700 | −84.676 | 2.457 |
| 1900 | 102.090 | 305.779 | 214.367 | 173.682 | −402.442 | −66.902 | 1.839 |
| 2000 | 102.090 | 311.015 | 219.070 | 183.891 | −398.193 | −49.351 | 1.289 |

PREVIOUS: CURRENT: March 1962

## Mercury Fluoride ($HgF_2$) IDEAL GAS $M_r = 238.586806$ Mercury Fluoride ($HgF_2$) $F_2Hg_1(g)$

$\Delta_fH°(0\ K) = -288.672\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 271.737\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = [-293.654 \pm 41.8]\ kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, cm$^{-1}$ |
|---|
| [600](1) |
| [120](2) |
| [593](1) |

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distance: Hg–F = [1.96] Å
Bond Angle. F–Hg–F = [180°]
Rotational Constant: $B_0 = [0.115488]\ cm^{-1}$

### Enthalpy of Formation

Estimated by comparison with the other gaseous mercuric halides and with the crystalline mercurous mercuric fluorides.

### Heat Capacity and Entropy

Vibrational constants were estimated by analogy with the other mercuric halides and the mercurous halides. The bond length was estimated by assuming the mercurous bond to be 0.965 of the mercuric bond by analogy with the mercury chlorides.

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −13.186 | −288.672 | −288.672 | INFINITE |
| 100 | 42.378 | 219.689 | 316.215 | −9.653 | −289.751 | −290.961 | 151.983 |
| 200 | 49.043 | 251.161 | 276.531 | −5.074 | −290.687 | −291.784 | 76.206 |
| 250 | 51.842 | 262.416 | 272.614 | −2.550 | −293.362 | −291.860 | 60.981 |
| 298.15 | 53.968 | 271.737 | 271.737 | 0. | −293.654 | −291.543 | 51.077 |
| 300 | 54.040 | 272.071 | 271.738 | 0.100 | −293.664 | −291.530 | 50.760 |
| 350 | 55.705 | 280.532 | 272.402 | 2.845 | −293.897 | −291.155 | 43.453 |
| 400 | 56.961 | 288.056 | 273.897 | 5.664 | −294.085 | −290.750 | 37.968 |
| 450 | 57.915 | 294.823 | 275.853 | 8.537 | −294.246 | −290.323 | 33.700 |
| 500 | 58.649 | 300.965 | 278.062 | 11.451 | −294.390 | −289.880 | 30.284 |
| 600 | 59.677 | 311.756 | 282.803 | 17.372 | −294.658 | −288.952 | 25.156 |
| 700 | 60.339 | 321.008 | 287.616 | 23.375 | −353.680 | −281.409 | 20.999 |
| 800 | 60.787 | 329.096 | 292.306 | 29.432 | −353.311 | −271.110 | 17.702 |
| 900 | 61.102 | 336.275 | 296.800 | 35.528 | −352.948 | −260.857 | 15.140 |
| 1000 | 61.333 | 342.725 | 301.075 | 41.650 | −352.594 | −250.643 | 13.092 |
| 1100 | 61.505 | 348.579 | 305.132 | 47.792 | −352.250 | −240.465 | 11.419 |
| 1200 | 61.638 | 353.937 | 308.979 | 53.950 | −351.917 | −230.318 | 10.025 |
| 1300 | 61.743 | 358.875 | 312.630 | 60.119 | −351.596 | −220.197 | 8.848 |
| 1400 | 61.826 | 363.454 | 316.098 | 66.298 | −351.287 | −210.102 | 7.839 |
| 1500 | 61.893 | 367.722 | 319.399 | 72.484 | −350.990 | −200.027 | 6.966 |
| 1600 | 61.949 | 371.718 | 322.546 | 78.676 | −350.705 | −189.972 | 6.202 |
| 1700 | 61.995 | 375.475 | 325.550 | 84.873 | −350.432 | −179.935 | 5.529 |
| 1800 | 62.034 | 379.020 | 328.423 | 91.075 | −350.168 | −169.913 | 4.931 |
| 1900 | 62.067 | 382.375 | 331.175 | 97.280 | −349.914 | −159.906 | 4.396 |
| 2000 | 62.095 | 385.559 | 333.815 | 103.488 | −349.665 | −149.912 | 3.915 |
| 2100 | 62.119 | 388.589 | 336.352 | 109.699 | −349.420 | −139.931 | 3.481 |
| 2200 | 62.140 | 391.480 | 338.793 | 115.912 | −349.175 | −129.961 | 3.086 |
| 2300 | 62.159 | 394.242 | 341.144 | 122.126 | −348.927 | −120.002 | 2.725 |
| 2400 | 62.175 | 396.888 | 343.412 | 128.343 | −348.673 | −110.054 | 2.395 |
| 2500 | 62.189 | 399.426 | 345.602 | 134.561 | −348.408 | −100.117 | 2.092 |
| 2600 | 62.202 | 401.866 | 347.719 | 140.781 | −348.129 | −90.191 | 1.812 |
| 2700 | 62.213 | 404.214 | 349.768 | 147.002 | −347.833 | −80.276 | 1.553 |
| 2800 | 62.223 | 406.476 | 351.754 | 153.224 | −347.517 | −70.372 | 1.313 |
| 2900 | 62.232 | 408.660 | 353.678 | 159.446 | −347.179 | −60.480 | 1.089 |
| 3000 | 62.241 | 410.770 | 355.546 | 165.670 | −346.815 | −50.600 | 0.881 |
| 3100 | 62.248 | 412.811 | 357.361 | 171.894 | −346.424 | −40.733 | 0.686 |
| 3200 | 62.255 | 414.787 | 359.125 | 178.120 | −346.003 | −30.878 | 0.504 |
| 3300 | 62.261 | 416.703 | 360.841 | 184.345 | −345.552 | −21.037 | 0.333 |
| 3400 | 62.266 | 418.562 | 362.511 | 190.572 | −345.069 | −11.211 | 0.172 |
| 3500 | 62.272 | 420.367 | 364 139 | 196.799 | −344.552 | −1.399 | 0.021 |
| 3600 | 62.276 | 422.121 | 365.725 | 203.026 | −344.002 | 8.398 | −0.122 |
| 3700 | 62.281 | 423.827 | 367.272 | 209.254 | −343.418 | 18.179 | −0.257 |
| 3800 | 62.285 | 425.488 | 368.783 | 215.482 | −342.799 | 27.943 | −0.384 |
| 3900 | 62.288 | 427.106 | 370.257 | 221.711 | −342.146 | 37.692 | −0.505 |
| 4000 | 62.292 | 428.683 | 371.698 | 227.940 | −341.458 | 47.422 | −0.619 |
| 4100 | 62.295 | 430.222 | 373.107 | 234.169 | −340.737 | 57.135 | −0.728 |
| 4200 | 62.298 | 431.723 | 374.485 | 240.399 | −339.981 | 66.831 | −0.831 |
| 4300 | 62.301 | 433.189 | 375.833 | 246.629 | −339.193 | 76.507 | −0.929 |
| 4400 | 62.303 | 434.621 | 377.153 | 252.859 | −338.372 | 86.165 | −1.023 |
| 4500 | 62.306 | 436.021 | 378.446 | 259 089 | −337.519 | 95.805 | −1.112 |
| 4600 | 62.308 | 437.391 | 379.712 | 265.320 | −336.635 | 105.424 | −1.197 |
| 4700 | 62.310 | 438.731 | 380.954 | 271.551 | −335 721 | 115.024 | −1.278 |
| 4800 | 62.312 | 440.042 | 382.171 | 277.782 | −334.777 | 124.605 | −1.356 |
| 4900 | 62.314 | 441.327 | 383.365 | 284.013 | −333.805 | 134.165 | −1.430 |
| 5000 | 62.316 | 442.586 | 384.537 | 290.245 | −332.806 | 143.705 | −1.501 |
| 5100 | 62.317 | 443.820 | 385.688 | 296.477 | −331.780 | 153.225 | −1.569 |
| 5200 | 62.319 | 445.030 | 386.817 | 302.708 | −330.728 | 162.725 | −1.635 |
| 5300 | 62.320 | 446.217 | 387.927 | 308.940 | −329.652 | 172.205 | −1.697 |
| 5400 | 62.322 | 447.382 | 389.017 | 315.172 | −328.553 | 181.663 | −1.757 |
| 5500 | 62.323 | 448.526 | 390.089 | 321.405 | −327.432 | 191.101 | −1.815 |
| 5600 | 62.324 | 449.649 | 391.142 | 327.637 | −326.289 | 200.519 | −1.870 |
| 5700 | 62.325 | 450.752 | 392.178 | 333.869 | −325.126 | 209.916 | −1.924 |
| 5800 | 62.327 | 451.836 | 393.198 | 340.102 | −323.945 | 219.292 | −1.975 |
| 5900 | 62.328 | 452.901 | 394.201 | 346.335 | −322.746 | 228.648 | −2.024 |
| 6000 | 62.329 | 453.949 | 395.188 | 352.568 | −321.530 | 237.984 | −2.072 |

PREVIOUS. December 1961 (1 atm) CURRENT: December 1961 (1 bar)

## Mercury Fluoride ($Hg_2F_2$) CRYSTAL $M_r$ = 439.176806 Mercury Fluoride ($Hg_2F_2$) $F_2Hg_2$(cr)

$\Delta_fH°$(0 K) = unknown

$S°$(298.15 K) = [160.666 ± 8.4] $J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_fH°$(298.15 K) = [−485.344 ± 12.6] $kJ \cdot mol^{-1}$

### Enthalpy of Formation

A value of $\Delta_fG°$(298.15 K) was obtained from the cell measurements of Koerber and de Vries.[1] This was combined with $\Delta_fS°$ from the estimated entropy.

### Heat Capacity and Entropy

The heat capacity is estimated by comparison with mercurous chloride. The entropy is estimated by comparison with the other mercurous and mercuric halides and use of additive entropy constants for the halogens from Kelley.[2]

### Sublimation Data

Sublimation with decomposition to Hg(g) and $HgF_2$(g) is assumed at 949 K from the Gibbs energy change of the reaction.

### References

[1] G. G. Koerber and T. de Vries, J. Amer. Chem. Soc. 74, 5008 (1952).
[2] K. K. Kelley, U.S. Bur. Mines, personal communication, (1960).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | $J \cdot K^{-1} mol^{-1}$ | | | $kJ \cdot mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 250 | | | | | | | |
| 298.15 | 100.416 | 160.666 | 160.666 | .000 | −485.344 | −427.449 | 74.887 |
| 300 | 100.500 | 161.287 | 160.668 | .186 | −485.320 | −427.090 | 74.363 |
| 400 | 104.684 | 190.783 | 164.661 | 10.449 | −483.807 | −407.898 | 53.266 |
| 500 | 108.407 | 214.551 | 172.337 | 21.107 | −481.969 | −389.128 | 40.652 |
| 600 | 111.671 | 234.611 | 181.086 | 32.115 | −479.863 | −370.753 | 32.277 |
| 700 | 114.516 | 252.044 | 190.005 | 43.427 | −595.050 | −339.607 | 25.342 |
| 800 | 116.943 | 267.499 | 198.744 | 55.004 | −591.240 | −303.373 | 19.808 |
| 900 | 118.951 | 281.391 | 207.168 | 66.800 | −587.255 | −267.627 | 15.533 |
| 1000 | 120.748 | 294.018 | 215.231 | 78.787 | −583.115 | −232.333 | 12.136 |
| 1100 | 122.334 | 305.603 | 222.927 | 90.943 | −578.837 | −197.461 | 9.377 |
| 1200 | 123.709 | 316.308 | 230.269 | 103.247 | −574.436 | −162.984 | 7.095 |
| 1300 | 124.872 | 326.257 | 237.274 | 115.678 | −569.932 | −128.878 | 5.178 |
| 1400 | 125.825 | 335.547 | 243.966 | 128.214 | −565.343 | −95.123 | 3.549 |
| 1500 | 126.566 | 344.255 | 250.364 | 140.836 | −560.689 | −61.698 | 2.149 |

PREVIOUS: CURRENT. March 1962

## Potassium Fluoride, Ion ($KF_2^-$) IDEAL GAS $M_r$ = 77.095655 Potassium Fluoride, Ion ($KF_2^-$) $F_2K_1^-(g)$

$S^\circ$(298.15 K) = [261.868 ± 8.4] $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$

$\Delta_f H^\circ$(0 K) = −686.217 ± 41.8 $\mathrm{kJ\cdot mol^{-1}}$
$\Delta_f H^\circ$(298.15 K) = −694.544 ± 41.8 $\mathrm{kJ\cdot mol^{-1}}$

| Vibrational Frequencies and Degeneracies $\nu$, $\mathrm{cm^{-1}}$ |
|---|
| [350](1) |
| [130](1) |
| [500](1) |

Ground State Quantum Weight: [1]
Point Group: $[D_{\infty h}]$
Bond Distance: K–F = [2.17] Å
Bond Angle: F–K–F = [180°]
Rotational Constant: $B_0$ = [0.094216] $\mathrm{cm^{-1}}$
$\sigma = 2$

### Enthalpy of Formation

The enthalpy of formation is estimated from three calculated values. The methods of calculation are described as follows. In a manner analogous to $LiF_2^-(g)$, the first reaction considered is $KF(g) + F^-(g) = KF_2^-(g)$ and the $\Delta_r H^\circ$(298.15 K) value is evaluated to be between 0 and 1/2(−50) = 25 $\mathrm{kcal\cdot mol^{-1}}$ (see $LiF_2^-(g)$ table for details), yielding $\Delta_f H^\circ(KF_2^-$, g, 298.15 K) between −140 and −165 $\mathrm{kcal\cdot mol^{-1}}$. The $\Delta_f H^\circ$(298.15 K) values for the other species involved are taken from JANAF tables.

The second reaction employed for estimation is $K_2F_2(g) = KF_2^-(g) + K^+(g)$. The enthalpy change of this reaction is calculated as $\Delta_r H^\circ$(298.15 K) = (1/2)(50.0) + 138.8 = 163.8 $\mathrm{kcal\cdot mol^{-1}}$ where the $KF_2^-$ ion is considered to be converted from $K_2F_2(g)$ by breaking one of the two dimer association bonds, $\Delta_r H^\circ$(298.15 K) = 50 0 $\mathrm{kcal\cdot mol^{-1}}$, and one $K^+$–$F^-$ ionic bond, $\Delta_r H^\circ$(298.15 K) = 138.8 $\mathrm{kcal\cdot mol^{-1}}$. Using $\Delta_f H^\circ$(298.15 K) = −206.2 and 122.9 $\mathrm{kcal\cdot mol^{-1}}$ for $K_2F_2(g)$ and $K^+(g)$, we obtain the enthalpy of formation for $KF_2^-(g)$ as −165 $\mathrm{kcal\cdot mol^{-1}}$.

Based on an assumption that the electron affinity of $KF_2(g)$ is similar to that of F (refer to $LiF_2^-(g)$ table for details), i.e., $\Delta_r H^\circ$(298.15 K) = 83.5 $\mathrm{kcal\cdot mol^{-1}}$[1] for the reaction $KF_2^-(g) = KF_2(g) + e^-(g)$, we derive $\Delta_f H^\circ(KF_2^-$, g, 298.15 K) = −167.7 $\mathrm{kcal\cdot mol^{-1}}$. The $\Delta_f H^\circ(KF_2$, g, 298.15 K) is calculated as −84.2 $\mathrm{kcal\cdot mol^{-1}}$ from the value $\Delta_r H^\circ$(298.15 K) = 143.3 $\mathrm{kcal\cdot mol^{-1}}$ for the reaction $K_2F_2(g) = KF_2(g) + K(g)$ where the $\Delta_r H^\circ$(298.15 K) value is calculated as the sum of two enthalpy changes, i.e. half of the heat of dimer dissociation into two monomers or 1/2(50.0) = 25.0 $\mathrm{kcal\cdot mol^{-1}}$, and the heat of dissociation of KF(g) or 118.3 $\mathrm{kcal\cdot mol^{-1}}$.

The value of $\Delta_f H^\circ(KF_2^-$ 298.15 K) is tentatively adopted as −166 ± 10 $\mathrm{kcal\cdot mol^{-1}}$.

### Heat Capacity and Entropy

The molecular structure is assumed to be linear, according to the suggestion given by Walsh[2] that molecules with not more than 16 valency electrons are linear in their ground states. The K–F bond distance is taken to be the same as that of KF(g) reported by Veazey and Gordy.[3] The vibrational frequencies are estimated from the vibrational frequency of KF(g) using the method suggested by Herzberg.[4]

### References

[1] H. O Pritchard, Chem. Rev. 52, 529 (1953).
[2] A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).
[3] S. E. Veazey and W. Gordy, Phys. Rev. 138, A1303 (1965).
[4] G. Herzberg, 'Infrared and Raman Spectra,' p. 172, D. Van Nostrand Co., Inc., New York, (1945).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p^\circ$ = 0.1 MPa

| | $\mathrm{J\cdot K^{-1}mol^{-1}}$ | | | $\mathrm{kJ\cdot mol^{-1}}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −13 777 | −686.217 | | |
| 100 | 43.337 | 206.619 | 309.310 | −10.269 | | | |
| 200 | 52.713 | 239.908 | 266.969 | −5.412 | | | |
| 250 | 55.318 | 251.970 | 262.798 | −2.707 | | | |
| 298.15 | 57.015 | 261.868 | 261.868 | 0. | −694.544 | −686.622 | 120.293 |
| 300 | 57.069 | 262.221 | 261.869 | 0 106 | −694.589 | −686.573 | 119.543 |
| 350 | 58.272 | 271.114 | 262.569 | 2.991 | −698.224 | −685.041 | 102.237 |
| 400 | 59.122 | 278.954 | 264.137 | 5.927 | −699.544 | −683.068 | 89.200 |
| 450 | 59.739 | 285.955 | 266.179 | 8.899 | −700.842 | −680.930 | 79.040 |
| 500 | 60.200 | 292.274 | 268.478 | 11.898 | −702.125 | −678.649 | 70.898 |
| 600 | 60.824 | 303.310 | 273.390 | 17.952 | −704.663 | −673.715 | 58.652 |
| 700 | 61.215 | 312.717 | 278.352 | 24.055 | −707.185 | −668.357 | 49.873 |
| 800 | 61.475 | 320.909 | 283.171 | 30.191 | −709.715 | −662.638 | 43.266 |
| 900 | 61.656 | 328.161 | 287.775 | 36.348 | −712.273 | −656.600 | 38.108 |
| 1000 | 61.787 | 334.664 | 292.144 | 42.520 | −714.882 | −650.275 | 33.967 |
| 1100 | 61.884 | 340.558 | 296.282 | 48.704 | −796.516 | −639.075 | 30.347 |
| 1200 | 61 959 | 345 946 | 300.199 | 54.896 | −798.227 | −624.687 | 27.192 |
| 1300 | 62.017 | 350.908 | 303.912 | 61.095 | −799.954 | −610.155 | 24.516 |
| 1400 | 62.064 | 355.506 | 307.435 | 67.299 | −801.699 | −595.490 | 22.218 |
| 1500 | 62.101 | 359.789 | 310.784 | 73.508 | −803.459 | −580.699 | 20.222 |
| 1600 | 62.132 | 363.798 | 313.973 | 79.719 | −805.235 | −565.791 | 18.471 |
| 1700 | 62.158 | 367.565 | 317.016 | 85.934 | −807.027 | −550.771 | 16.923 |
| 1800 | 62.179 | 371.119 | 319.924 | 92.151 | −808.834 | −535.645 | 15.544 |
| 1900 | 62.198 | 374.481 | 322.708 | 98.370 | −810.654 | −520.418 | 14.307 |
| 2000 | 62.213 | 377.672 | 325.377 | 104.590 | −812.488 | −505.095 | 13.192 |
| 2100 | 62.227 | 380.708 | 327.940 | 110.812 | −814.333 | −489.680 | 12.180 |
| 2200 | 62.238 | 383.603 | 330.405 | 117.036 | −816.188 | −474.177 | 11.258 |
| 2300 | 62.248 | 386.370 | 332.778 | 123.260 | −818.052 | −458.589 | 10.415 |
| 2400 | 62.257 | 389.019 | 335.067 | 129.485 | −819.924 | −442.920 | 9.640 |
| 2500 | 62.265 | 391.561 | 337.276 | 135.711 | −821.803 | −427.173 | 8.925 |
| 2600 | 62.272 | 394.003 | 339.411 | 141.938 | −823.687 | −411.351 | 8.264 |
| 2700 | 62.278 | 396.353 | 341.477 | 148.166 | −825.577 | −395.456 | 7.651 |
| 2800 | 62.284 | 398 618 | 343.477 | 154.394 | −827.473 | −379.491 | 7.079 |
| 2900 | 62.289 | 400.804 | 345.417 | 160.622 | −829.373 | −363.458 | 6.547 |
| 3000 | 62.293 | 402.916 | 347.298 | 166.852 | −831.281 | −347.359 | 6.048 |
| 3100 | 62.298 | 404.958 | 349.126 | 173.081 | −833.196 | −331.197 | 5.581 |
| 3200 | 62.301 | 406.936 | 350.902 | 179.311 | −835.122 | −314.973 | 5.141 |
| 3300 | 62.305 | 408.853 | 352.629 | 185.541 | −837.050 | −298 689 | 4.728 |
| 3400 | 62.308 | 410.713 | 354.310 | 191.772 | −838.997 | −282.346 | 4.338 |
| 3500 | 62.311 | 412.520 | 355.947 | 198.003 | −840.959 | −265.945 | 3.969 |
| 3600 | 62.313 | 414.275 | 357.543 | 204.234 | −842.944 | −249.488 | 3.620 |
| 3700 | 62.316 | 415.982 | 359.100 | 210.466 | −844.952 | −232.976 | 3.289 |
| 3800 | 62.318 | 417.644 | 360.619 | 216.697 | −846.989 | −216.409 | 2.975 |
| 3900 | 62.320 | 419.263 | 362.102 | 222.929 | −849.058 | −199.788 | 2.676 |
| 4000 | 62.322 | 420.841 | 363.550 | 229.161 | −851.159 | −183.113 | 2.391 |
| 4100 | 62.323 | 422.380 | 364.967 | 235.393 | −853.303 | −166.386 | 2.120 |
| 4200 | 62.325 | 423.882 | 366.352 | 241.626 | −855.498 | −149.606 | 1.861 |
| 4300 | 62.327 | 425.348 | 367.707 | 247.858 | −857.745 | −132.773 | 1.613 |
| 4400 | 62.328 | 426.781 | 369.033 | 254.091 | −859.773 | −115.913 | 1.376 |
| 4500 | 62.329 | 428.182 | 370.332 | 260.324 | −862.073 | −98.981 | 1.149 |
| 4600 | 62.331 | 429.552 | 371.604 | 266.557 | −864.428 | −81.998 | 0.931 |
| 4700 | 62.332 | 430.892 | 372.852 | 272.790 | −866.822 | −64.965 | 0.722 |
| 4800 | 62.333 | 432.204 | 374.075 | 279.023 | −869.168 | −47.892 | 0.521 |
| 4900 | 62.334 | 433.490 | 375.274 | 285.257 | −871.680 | −30.756 | 0.328 |
| 5000 | 62.335 | 434.749 | 376.451 | 291.490 | −874.256 | −13.569 | 0.142 |
| 5100 | 62.336 | 435.983 | 377.606 | 297.724 | −876.899 | 3.671 | −0.038 |
| 5200 | 62.337 | 437.194 | 378.741 | 303.957 | −879.609 | 20.964 | −0.211 |
| 5300 | 62.337 | 438.381 | 379.855 | 310.191 | −882.387 | 38.309 | −0.378 |
| 5400 | 62.338 | 439.547 | 380.949 | 316.425 | −885.235 | 55.707 | −0.539 |
| 5500 | 62.339 | 440.690 | 382.025 | 322.659 | −888.153 | 73.158 | −0.695 |
| 5600 | 62.339 | 441.814 | 383.083 | 328.892 | −891.139 | 90.664 | −0.846 |
| 5700 | 62.340 | 442.917 | 384.123 | 335.126 | −893.850 | 108.175 | −0.991 |
| 5800 | 62.341 | 444.001 | 385.146 | 341.361 | −896.930 | 125.781 | −1.133 |
| 5900 | 62.341 | 445.067 | 386.153 | 347.595 | −900.073 | 143.442 | −1.270 |
| 6000 | 62.342 | 446.115 | 387.143 | 353.829 | −903.277 | 161.155 | −1.403 |

PREVIOUS December 1968 (1 atm) *CURRENT* December 1968 (*1 bar*)

# Potassium Fluoride, $((KF)_2)$ IDEAL GAS $M_r = 116.193406$

$S°(298.15\ K) = [319.955 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -858.080 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -862.741 \pm 8.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|
| [273](1) | [150](1) |
| [150](1) | [255](1) |
| [235](1) | [258](1) |

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: $D_{2h}$
Bond Distance: K–F = 2.2 Å
Bond Angles: F–K–F = [90°]; K–F–K = [90°]
Product of the Moments of Inertia: $I_A I_B I_C = [2.240426 \times 10^{-113}]\ g^3 \cdot cm^6$

## Enthalpy of Formation

The equilibrium constants ($K_c$) for the reaction $K_2F_2(g) = 2\ KF(g)$, in the temperature range 974–1052 K, were determined by Eisenstadt *et al.*[1] Although the reported absolute values of the vapor pressures of KF(cr) are not adopted for evaluation, the reported $K_c$ values are used to calculate the enthalpy change, $\Delta_r H°(298.15\ K)$, for the above reaction. The 2nd and 3rd law values of $\Delta_r H°(298.15\ K)$ are derived as $51.0 \pm 1.6$ and 50.0 kcal·mol$^{-1}$, respectively. Based on the 3rd law $\Delta_r H°(298.15\ K)$ and $\Delta_f H°(KF, g, 298.15\ K) = -78.1$ kcal·mol$^{-1}$, we obtain $\Delta_f H°(298.15\ K) = -206.2$ kcal·mol$^{-1}$ ($-862.74 \pm 8.4$ kJ·mol$^{-1}$) for $K_2F_2(g)$ which is tentatively adopted.

## Heat Capacity and Enthalpy

The molecular structure and K–F bond distance were determined by Akishin and Rambidi,[2] using electron diffraction with sector microphotometry. The bond angles are estimated by comparison with other alkali halide dimers. The vibrational frequencies are taken from Berkowitz[3] which were calculated based on an ionic model. The three principal moments of inertia are: $I_A = 15.2693 \times 10^{-39}$, $I_B = 31.4238 \times 10^{-39}$, and $I_C = 46.6931 \times 10^{-39}\ g \cdot cm^2$.

## References

[1] M. Eisenstadt, G. M. Rothberg, and P. Kusch, J. Chem. Phys. 29, 797 (1958).
[2] P. A. Akishin and G. Rambidi, Z. Physik. Chem. 213, 111 (1960).
[3] J. Berkowitz, J. Chem. Phys. 32, 1519 (1960).

## Potassium Fluoride $((KF)_2)$ $F_2K_2(g)$

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| $T$/K | $C_p°$ (J·K$^{-1}$mol$^{-1}$) | $S°$ (J·K$^{-1}$mol$^{-1}$) | $-[G°-H°(T_r)]/T$ (J·K$^{-1}$mol$^{-1}$) | $H°-H°(T_r)$ (kJ·mol$^{-1}$) | $\Delta_f H°$ (kJ·mol$^{-1}$) | $\Delta_f G°$ (kJ·mol$^{-1}$) | log $K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0. | 0. | INFINITE | −18.329 | −858.080 | −858.080 | INFINITE |
| 100 | 56.735 | 243.679 | 385.805 | −14.213 | −860.336 | −860.546 | 449.503 |
| 200 | 73.655 | 289.471 | 327.017 | −7.509 | −861.750 | −860.117 | 224.640 |
| 250 | 76.754 | 306.272 | 321.238 | −3.742 | −862.234 | −859.652 | 179.615 |
| 298.15 | 78.525 | 319.955 | 319.955 | 0. | −862.741 | −859.111 | 150.513 |
| 300 | 78.578 | 320.440 | 319.956 | 0.145 | −862.763 | −859.088 | 149.581 |
| 350 | 79.731 | 332.646 | 320.917 | 4.105 | −868.174 | −858.232 | 128.084 |
| 400 | 80.500 | 343.346 | 323.066 | 8.112 | −868.972 | −856.757 | 111.881 |
| 450 | 81.039 | 352.861 | 325.858 | 12.151 | −869.727 | −855.184 | 99.267 |
| 500 | 81.429 | 361.420 | 328.993 | 16.213 | −870.451 | −853.529 | 89.168 |
| 600 | 81.944 | 376.316 | 335.675 | 24.384 | −871.833 | −850.014 | 74.000 |
| 700 | 82.259 | 388.973 | 342.408 | 32.596 | −873.165 | −846.272 | 63.150 |
| 800 | 82.464 | 399.972 | 348.931 | 40.833 | −874.492 | −842.339 | 54.999 |
| 900 | 82.606 | 409.693 | 355.153 | 49.086 | −875.857 | −838.239 | 48.650 |
| 1000 | 82.707 | 418.402 | 361.050 | 57.352 | −877.307 | −833.982 | 43.563 |
| 1100 | 82.783 | 426.289 | 366.628 | 65.627 | −1036.789 | −820.355 | 38.955 |
| 1200 | 82.840 | 433 494 | 371.904 | 73.908 | −1036.411 | −800.696 | 34.853 |
| 1300 | 82.885 | 440.127 | 376.900 | 82.195 | −1036.052 | −781.068 | 31.384 |
| 1400 | 82.921 | 446.271 | 381.639 | 90.485 | −1035.710 | −761.467 | 28.411 |
| 1500 | 82.949 | 451.993 | 386.140 | 98.779 | −1035.386 | −741.889 | 25.835 |
| 1600 | 82.973 | 457.347 | 390.425 | 107.075 | −1035.080 | −722.333 | 23.582 |
| 1700 | 82.992 | 462.378 | 394.511 | 115.373 | −1034 792 | −702.795 | 21.594 |
| 1800 | 83.009 | 467.122 | 398.415 | 123.673 | −1034.522 | −683.273 | 19.828 |
| 1900 | 83.023 | 471.610 | 402.150 | 131.975 | −1034.271 | −663.767 | 18.248 |
| 2000 | 83.034 | 475.869 | 405.730 | 140.278 | −1034.037 | −644.272 | 16.827 |
| 2100 | 83.045 | 479.921 | 409.168 | 148.582 | −1033.823 | −624 790 | 15.541 |
| 2200 | 83.053 | 483 784 | 412.472 | 156.886 | −1033.629 | −605.316 | 14.372 |
| 2300 | 83.061 | 487.476 | 415.653 | 165.192 | −1033 455 | −585.852 | 13.305 |
| 2400 | 83.068 | 491.011 | 418.720 | 173.499 | −1033.302 | −566.394 | 12.327 |
| 2500 | 83.074 | 494.402 | 421.680 | 181.806 | −1033.173 | −546.942 | 11 428 |
| 2600 | 83.079 | 497.661 | 424.540 | 190 113 | −1033.068 | −527.495 | 10.598 |
| 2700 | 83.084 | 500.796 | 427.307 | 198.422 | −1032.991 | −508.052 | 9.829 |
| 2800 | 83.088 | 503.818 | 429.986 | 206.730 | −1032.945 | −488.610 | 9.115 |
| 2900 | 83.092 | 506.734 | 432.582 | 215.039 | −1032.932 | −469.170 | 8.451 |
| 3000 | 83.095 | 509.551 | 435.101 | 223.349 | −1032.957 | −449.730 | 7.830 |
| 3100 | 83.098 | 512.275 | 437.547 | 231.658 | −1033.026 | −430.288 | 7.250 |
| 3200 | 83 101 | 514.914 | 439.924 | 239.968 | −1033.143 | −410.843 | 6.706 |
| 3300 | 83 104 | 517.471 | 442.235 | 248.278 | −1033.296 | −391.395 | 6.195 |
| 3400 | 83.106 | 519.952 | 444.485 | 256.589 | −1033.521 | −371.940 | 5.714 |
| 3500 | 83.108 | 522.361 | 446.675 | 264.900 | −1033.807 | −352.478 | 5.260 |
| 3600 | 83.110 | 524.702 | 448.810 | 273.211 | −1034.172 | −333.007 | 4.832 |
| 3700 | 83.112 | 526.979 | 450.892 | 281.522 | −1034.618 | −313.524 | 4.426 |
| 3800 | 83.114 | 529.196 | 452.924 | 289.833 | −1035.156 | −294.028 | 4 042 |
| 3900 | 83.115 | 531.355 | 454.907 | 298.144 | −1035.794 | −274.516 | 3.677 |
| 4000 | 83.117 | 533 459 | 456.845 | 306.456 | −1036.528 | −254.988 | 3.330 |
| 4100 | 83.118 | 535.511 | 458.739 | 314 768 | −1037.383 | −235.441 | 3.000 |
| 4200 | 83 119 | 537.514 | 460.591 | 323.080 | −1038.374 | −215.869 | 2.685 |
| 4300 | 83.120 | 539.470 | 462.402 | 331.392 | −1039.503 | −196.273 | 2.384 |
| 4400 | 83.121 | 541.381 | 464.176 | 339.704 | −1040.227 | −176.703 | 2.098 |
| 4500 | 83.122 | 543.249 | 465.912 | 348.016 | −1041.525 | −157.062 | 1.823 |
| 4600 | 83.123 | 545.076 | 467.613 | 356.328 | −1042.967 | −137.392 | 1.560 |
| 4700 | 83.124 | 546.864 | 469.281 | 364 641 | −1044.518 | −117.693 | 1.308 |
| 4800 | 83.125 | 548.614 | 470.915 | 372.953 | −1046.002 | −97.983 | 1.066 |
| 4900 | 83.126 | 550.328 | 472.519 | 381.266 | −1047.849 | −78.214 | 0.834 |
| 5000 | 83.127 | 552.007 | 474.092 | 389.578 | −1049.853 | −58.406 | 0 610 |
| 5100 | 83.127 | 553.653 | 475.636 | 397.891 | −1052.016 | −38.555 | 0.395 |
| 5200 | 83.128 | 555.268 | 477.151 | 406.204 | −1054.342 | −18.661 | 0.187 |
| 5300 | 83.128 | 556.851 | 478.640 | 414.516 | −1056.832 | 1.279 | −0.013 |
| 5400 | 83.129 | 558.405 | 480.103 | 422.829 | −1059.486 | 21.268 | −0.206 |
| 5500 | 83.130 | 559.930 | 481.541 | 431.142 | −1062.304 | 41.308 | −0.392 |
| 5600 | 83.130 | 561.428 | 482.954 | 439.455 | −1065.285 | 61.400 | −0.573 |
| 5700 | 83.131 | 562.899 | 484.344 | 447.768 | −1067.737 | 81.452 | −0.746 |
| 5800 | 83.131 | 564.345 | 485.711 | 456.081 | −1070.950 | 101.641 | −0.915 |
| 5900 | 83.131 | 565.766 | 487.055 | 464.394 | −1074.311 | 121.887 | −1.079 |
| 6000 | 83.132 | 567.164 | 488.379 | 472.708 | −1077.815 | 142.190 | −1.238 |

PREVIOUS: June 1969 (1 atm) CURRENT. June 1969 (1 bar)

## Lithium Fluoride, Ion ($LiF_2^-$) IDEAL GAS $M_r = 44.938355$ Lithium Fluoride, Ion ($LiF_2^-$) $F_2Li_1^-(g)$

$S°(298.15\ K) = [229.618 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-702.735 \pm 62.8]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-711.280 \pm 62.8]\ kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ |
|---|
| [1300](1) |
| [350](2) |
| [550](1) |

Ground State Quantum Weight: [1] $\sigma = [2]$

Point Group: $[D_{\infty h}]$

Bond Distance: Li–F = [1.57] Å

Bond Angle: F–Li–F = [180]°

Rotational Constant: $B_0 = [0.179988]\ cm^{-1}$

Enthalpy Reference Temperature = $T_r$ = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
|---|---|---|---|---|---|---|---|
| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
| 0 | 0. | 0. | INFINITE | −11.100 | −702.735 | | |
| 100 | 32.069 | 186.362 | 267.697 | −8.133 | | | |
| 200 | 41.808 | 211.729 | 233.812 | −4.417 | | | |
| 250 | 45.181 | 221.439 | 230.390 | −2.238 | | | |
| 298.15 | 47.670 | 229.618 | 229.618 | 0. | −711.280 | −704.353 | 123.400 |
| 300 | 47.754 | 229.914 | 229.619 | 0.088 | −711.334 | −704.309 | 122.631 |
| 350 | 49.802 | 237.434 | 230.209 | 2.529 | −712.784 | −703.024 | 104.921 |
| 400 | 51.483 | 244.198 | 231.542 | 5.062 | −714.258 | −701.530 | 91.610 |
| 450 | 52.886 | 250.345 | 233.295 | 7.673 | −715.777 | −699.848 | 81.236 |
| 500 | 54.066 | 255.980 | 235.285 | 10.347 | −720.350 | −697.687 | 72.887 |
| 600 | 55.910 | 266.009 | 239.591 | 15.851 | −723.382 | −692.868 | 60.319 |
| 700 | 57.248 | 274.734 | 244.002 | 21.513 | −726.276 | −687.551 | 51.306 |
| 800 | 58.233 | 282.446 | 248.334 | 27.289 | −729.084 | −681.827 | 44.519 |
| 900 | 58.973 | 289.349 | 252.515 | 33.151 | −731.845 | −675.754 | 39.220 |
| 1000 | 59.538 | 295.593 | 256.516 | 39.078 | −734.573 | −669.375 | 34.965 |
| 1100 | 59.977 | 301.289 | 260.331 | 45.054 | −737.276 | −662.724 | 31.470 |
| 1200 | 60.324 | 306.523 | 263.965 | 51.070 | −739.961 | −655.828 | 28.547 |
| 1300 | 60.602 | 311.363 | 267.427 | 57.117 | −742.634 | −648.708 | 26.065 |
| 1400 | 60.828 | 315.863 | 270.728 | 63.189 | −745.298 | −641.383 | 23.930 |
| 1500 | 61.014 | 320.066 | 273.879 | 69.281 | −747.952 | −633.868 | 22.073 |
| 1600 | 61.169 | 324.009 | 276.890 | 75.391 | −750.599 | −626.176 | 20.443 |
| 1700 | 61.298 | 327.721 | 279.772 | 81.514 | −898.477 | −611.142 | 18.778 |
| 1800 | 61.408 | 331.228 | 282.534 | 87.650 | −900.361 | −594.186 | 17.243 |
| 1900 | 61.502 | 334.551 | 285.185 | 93.795 | −902.247 | −577.125 | 15.866 |
| 2000 | 61.582 | 337.708 | 287.733 | 99.950 | −904.136 | −559.964 | 14.625 |
| 2100 | 61.652 | 340.714 | 290.185 | 106.111 | −906.027 | −542.710 | 13.499 |
| 2200 | 61.713 | 343.584 | 292.547 | 112.280 | −907.916 | −525.364 | 12.474 |
| 2300 | 61.767 | 346.328 | 294.827 | 118.454 | −909.804 | −507.933 | 11.536 |
| 2400 | 61.814 | 348.958 | 297.028 | 124.633 | −911.689 | −490.420 | 10.674 |
| 2500 | 61.856 | 351.482 | 299.156 | 130.816 | −913.567 | −472.829 | 9.879 |
| 2600 | 61.893 | 353.909 | 301.215 | 137.004 | −915.438 | −455.162 | 9.144 |
| 2700 | 61.926 | 356.245 | 303.210 | 143.195 | −917.301 | −437.424 | 8.462 |
| 2800 | 61.956 | 358.498 | 305.145 | 149.389 | −919.154 | −419.617 | 7.828 |
| 2900 | 61.983 | 360.673 | 307.022 | 155.586 | −920.997 | −401.744 | 7.236 |
| 3000 | 62.007 | 362.774 | 308.846 | 161.785 | −922.828 | −383.807 | 6.683 |
| 3100 | 62.029 | 364.808 | 310.619 | 167.987 | −924.648 | −365.810 | 6.164 |
| 3200 | 62.049 | 366.778 | 312.343 | 174.191 | −926.456 | −347.754 | 5.676 |
| 3300 | 62.067 | 368.687 | 314.022 | 180.397 | −928.253 | −329.641 | 5.218 |
| 3400 | 62.084 | 370.540 | 315.657 | 186.605 | −930.039 | −311.475 | 4.785 |
| 3500 | 62.099 | 372.340 | 317.251 | 192.814 | −931.814 | −293.256 | 4.377 |
| 3600 | 62.113 | 374.090 | 318.805 | 199.024 | −933.581 | −274.986 | 3.990 |
| 3700 | 62.126 | 375.792 | 320.323 | 205.236 | −935.339 | −256.668 | 3.624 |
| 3800 | 62.138 | 377.449 | 321.804 | 211.449 | −937.090 | −238.302 | 3.276 |
| 3900 | 62.149 | 379.063 | 323.252 | 217.664 | −938.835 | −219.890 | 2.945 |
| 4000 | 62.159 | 380.637 | 324.667 | 223.879 | −940.577 | −201.433 | 2.630 |
| 4100 | 62.169 | 382.172 | 326.051 | 230.096 | −942.316 | −182.933 | 2.331 |
| 4200 | 62.178 | 383.670 | 327.405 | 236.313 | −944.055 | −164.391 | 2.044 |
| 4300 | 62.186 | 385.133 | 328.730 | 242.531 | −945.796 | −145.807 | 1.771 |
| 4400 | 62.193 | 386.563 | 330.029 | 248.750 | −947.520 | −127.184 | 1.510 |
| 4500 | 62.201 | 387.960 | 331.301 | 254.970 | −949.261 | −108.520 | 1.260 |
| 4600 | 62.207 | 389.328 | 332.547 | 261.190 | −951.010 | −89.818 | 1.020 |
| 4700 | 62.214 | 390.666 | 333.770 | 267.411 | −952.769 | −71.077 | 0.790 |
| 4800 | 62.220 | 391.975 | 334.969 | 273.633 | −954.538 | −52.299 | 0.569 |
| 4900 | 62.225 | 393.258 | 336.145 | 279.855 | −956.321 | −33.484 | 0.357 |
| 5000 | 62.230 | 394.516 | 337.300 | 286.078 | −958.119 | −14.633 | 0.153 |
| 5100 | 62.235 | 395.748 | 338.434 | 292.301 | −959.930 | 4.254 | −0.044 |
| 5200 | 62.240 | 396.956 | 339.548 | 298.525 | −961.765 | 23.178 | −0.233 |
| 5300 | 62.244 | 398.142 | 340.642 | 304.749 | −963.622 | 42.137 | −0.415 |
| 5400 | 62.249 | 399.306 | 341.718 | 310.974 | −965.505 | 61.131 | −0.591 |
| 5500 | 62.252 | 400.448 | 342.775 | 317.199 | −967.414 | 80.160 | −0.761 |
| 5600 | 62.256 | 401.570 | 343.815 | 323.424 | −969.354 | 99.225 | −0.926 |
| 5700 | 62.260 | 402.672 | 344.838 | 329.650 | −971.325 | 118.324 | −1.084 |
| 5800 | 62.263 | 403.754 | 345.845 | 335.876 | −973.331 | 137.458 | −1.238 |
| 5900 | 62.266 | 404.819 | 346.835 | 342.103 | −975.373 | 156.627 | −1.387 |
| 6000 | 62.269 | 405.865 | 347.810 | 348.330 | −977.454 | 175.831 | −1.531 |

PREVIOUS: December 1968 (1 atm) CURRENT December 1968 (1 bar)

### Enthalpy of Formation

Due to lack of thermal data, the enthalpy of formation for $LiF_2^-$ (g) is arbitrarily selected from the following three estimated values. For the reaction (1) $LiF(g) + F^-(g) = LiF_2(g)$, we expect the enthalpy change would be between 0 to −31 K cal·mol$^{-1}$. Comparison with the other molecules like $CO_2$, BOF, $BeF_2$, etc. having 16 valence electrons leads us to assume *that the isoelectronic molecule* $LiF_2^-$ should also be quite stable. This indicates that reaction (1) is favorable or $\Delta_r H°(298.15\ K)$ is negative. However, the LiF–F$^-$ bond strength is expected to be weaker than half of the two ionic bonds between $Li^+$ and $F^-$ in $Li_2F_2$ molecule (refer to $Li_2F_2(g)$ table for the molecular structure). In other words, the $\Delta_r H°(298.15\ K)$ value of reaction (1) is less negative than half of the enthalpy of dimerization (−62.4 K cal·mol$^{-1}$). Incorporating $\Delta_r H°(298.15\ K) = 0$ and −31 K cal·mol$^{-1}$, respectively, for reaction (1), with $\Delta_f H°(298.15\ K) = -81.45$ and −62.2 kcal·mol$^{-1}$ for LiF(g) and $F^-$ (g), we derived the corresponding values for $\Delta_f H°(LiF_2^-, g, 298.15\ K)$ as −144 and −175 K cal·mol$^{-1}$, which are the upper and lower limits.

The electron affinities of Li and F atoms are reported as 0.7 and 3.448 eV, respectively, by Beckett and Cassidy.[1] From this data we estimate that the electron affinity of $LiF_2(g)$ should be closer to that of F atom than to that of Li Assuming $\Delta_r H°(298.15\ K)$ = electron affinity of F atom = 83.5 kcal·mol$^{-1}$ for the reaction $LiF_2^-(g) = LiF_2(g) + e^-(g)$, we obtain the enthalpy of formation for $LiF_2^-$ (g) as 177.3 kcal·mol$^{-1}$. The $\Delta_f H°(LiF_2, g, 298.15\ K)$ used for calculation is derived from an estimated $\Delta_r H°(298.15\ K) = 169.9$ kcal·mol$^{-1}$ for the decomposition of LiF dimer of $Li_2F_2(g) = LiF_2(g) + Li(g)$ as the sum of two enthalpy changes, namely, half of the enthalpy of dissociation of the dimer and the enthalpy of dissociation of the monomer.

The third estimated value for the enthalpy of formation of $LiF_2^-$ (g) is calculated as follows. Based on the two enthalpies of reaction, i.e. $\Delta_r H°(298.15\ K) = 62.4$ kcal·mol$^{-1}$ for $Li_2F_2(g) = LiF(g)$, and $\Delta_r H°(298.15\ K) = 183.5$ kcal·mol$^{-1}$ for $LiF(g) = Li^+(g) + F^-(g)$, we assume the enthalpy change of the reaction $Li_2F_2(g) = LiF_2^-(g) + Li^+(g)$ to be 1/2(62.4) + 183.5 = 214.7 kcal·mol$^{-1}$. In other words, we consider the $LiF_2^-$ (g) molecule is formed by breaking half of the dimer dissociation bonds and one monomer dissociation bond to produce two ions. Using $\Delta_f H°(298.15\ K) = -225.33$ and 164.24 K cal·mol$^{-1}$ for $Li_2F_2(g)$ and $Li^+(g)$, we evaluate $\Delta_f H°(LiF_2^-, g, 298.15\ K) = -174.9$ kcal·mol$^{-1}$.

From the above three estimated values, we tentatively choose $\Delta_f H°(LiF_2^-, g, 298.15\ K)$ as −170 ± 15 K cal·mol$^{-1}$.

### Heat Capacity and Entropy

According to Walsh,[3] molecules with not more than 16 valence electrons are linear in their ground states Since $LiF_2^-$ (g) has 16 valence electrons, we assume its molecular structure is linear. The Li–F bond distance is estimated by comparison with that of LiF(g) reported by Wharton *et al.*[2] The vibrational frequencies are estimated from those of the isoelectronic gaseous molecules, $CO_2$ and $BeF_2$.

### References

[1] C. W. Beckett and E. C. Cassidy, U. S Nat. Bur. Stand. Report 8628, (1965).
[2] L. Wharton, W. Klemperer, L. P. Gold, R. Strauch, J. J. Gallagher, and V. E. Derr, J. Chem. Phys. 38, 1203 (1963).
[3] A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).

$\Delta_fH^\circ$(0 K) = −938.070 ± 16.7 kJ·mol$^{-1}$
$S^\circ$(298.15 K) = 258.627 ± 8.4 J·K$^{-1}$·mol$^{-1}$ $\Delta_fH^\circ$(298.15 K) = −942.781 ± 16.7 kJ·mol$^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|
| [570](1) | 301.5(1) |
| [570](1) | 571.5(1) |
| [490](1) | 658.0(1) |

Ground State Quantum Weight: [1] $\sigma$ = 4
Point Group: $D_{2h}$
Bond Distances: Li–F = 1.68Å: F–F = 2.67 Å
Bond Angles: Li–F–Li = 74.76°: F–Li–F = 105.24°
Product of the Moments of Inertia: $I_AI_BI_C$ = 3.678682 × 10$^{-115}$ g$^3$·cm$^6$

## Enthalpy of Formation

$\Delta_fH^\circ$(Li$_2$F$_2$, g, 298.15 K) is calculated based on the adopted value $\Delta_rH^\circ$(1000) = 61.4 kcal·mol$^{-1}$ for the reaction Li$_2$F$_2$(g) = 2LiF(g) which is consistent with the literature values listed in the table below. Due to lack of Knowledge of the fragmentation patterns, the relative ionization cross sections of the ionic species formed in the mass spectrometer, and the molecular constants of the LiF polymers, the evaluation of equilibrium constants used to calculate $\Delta_rH^\circ$ involves considerable uncertainty. In order to solve this problem more research work seems necessary.

| Source | $\Delta_rH^\circ$(1000 K), kcal·mol$^{-1}$ | Method |
|---|---|---|
| Berkowitz *et al.*[1] | 61.6 ± 2 | mass spectrometry with a double–oven apparatus |
| Buchler and Stauffer[2] | 61.3 ± 3 | mass spectrometry with a two–piece Ni Knudsen cell |
| Eisenstadt *et al.*[3] | 61.2 | molecular–beam velocity–selector |
| Hildenbrand *et al.*[4] | 60.4 ± 3 | torsion effusion |
| Akishin *et al.*[5] | 59.5 ± 3 | mass spectrometry with a double effusion chamber |
| Porter and Schoonmaker[6] | 65.0 * | mass spectrometry with a Mo Knudsen cell |

*derived from reported vapor pressures of LiF(g) and Li$_2$F$_2$(g) at 1073 K.

## Heat Capacity and Entropy

The molecular structure of Li$_2$F$_2$(g) was determined as $D_{2h}$ by Bushler *et al.*,[12] using electric deflection and mass spectrometric detection. Akishin and Rambidi[7] studied the structure of Li$_2$F$_2$(g) by electron deflection with sector microphotometry and assigned the bond distances of Li–F and F–F which are adopted. Evidence for a matrix stabilized linear structure of Li$_2$F$_2$ has been obtained by extending the spectral measurements for matrix isolated lithium fluoride into the far infrared region by Redington[8] and Abramowitz *et al.*[9]

Klemperer and Norris[10] observed two infrared active vibrational frequencies, 640 and 460 cm$^{-1}$, and assigned them as $\nu_5(B_{2u})$ and $\nu_6(B_{3u})$ The infrared absorption spectra of lithium fluoride monomer and dimer isolated in solid inert gas matrices were investigated by Linevsky,[11] Snelson and Pitzer,[13] and Schlick and Schnepp.[14] Redington[8] obtained infrared spectra of LiF species suspended in solid Ne, O$_2$, CO, and CH$_4$ at liquid helium temperature. The observed solvent shifts for LiF and Li$_2$F$_2$ spectra exhibit several regularities. The vibrational frequencies used for calculation are those reported by Snelson[1] who re–examined the spectrum of LiF species over the range 200–4000 cm$^{-1}$, using sample purity of 99.3%. The saturated vapor was isolated at 900°C and the superheated unsaturated vapor at 1200°C. A variety of deposition rates and matrix dilutions was tried. Based on the frequencies assigned to the isotopic species, the vibrational frequencies of the natural isotopic Li$_2$F$_2$(g) are calculated. It appears that the vibrational frequencies calculated on the basis of the potential function for an ionic model by Berkowitz[1] are too low.

The three principal moments of inertia are: $I_A$ = 2.3980 × 10$^{-39}$, $I_B$ = 11.2447 × 10$^{-39}$ and $I_C$ = 13.6427 × 10$^{-39}$ g·cm$^2$.

## References

[1] J. Berkowitz, H. A. Tasman, and W. A. Chupka, J. Chem. Phys. 36, 2170 (1962).
[2] A. Buchler and J. L. Stauffer, "Thermodynamics," Vol. I, International Atomic Energy Agency, Vienna, (1966).
[3] M. Eisenstadt, G M. Rothberg, and P. Kusch, J Chem. Phys. 29, 797 (1958).
[4] D. L. Hildenbrand, W. F. Hall, F. Ju, and N. D Potter, J. Chem. Phys. 40, 2882 (1964).
[5] P. A. Akishin, L. N Gorokhov, and L. N. Sidorov, Russ. J. Phys. Chem. 33, 648 (1959).
[6] R. F. Porter and R C. Schoonmaker, J. Chem. Phys. 29, 1070 (1958).
[7] P. A. Akishin and N. G. Rambidi, Z. Physik. Chem. 213, 111 (1960).
[8] R. L. Redington, J. Chem. Phys. 44, 1238 (1966).
[9] S. Abramowitz, N. Acquista, and I. W. Levin, U.S. Nat. Bur. Stand. Report 9601, (July 1, 1967).

Continued on page 1215

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p^\circ$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_fH^\circ$ | $\Delta_fG^\circ$ | log K$_f$ |
| 0 | 0. | 0. | INFINITE | −13.359 | −938.070 | −938.070 | INFINITE |
| 100 | 36.231 | 206.434 | 306.175 | −9.974 | −938.582 | −940.720 | 491.382 |
| 200 | 51.023 | 235.802 | 264.055 | −5.651 | −940.871 | −941.971 | 246.017 |
| 250 | 57.938 | 247.958 | 259.639 | −2.920 | −941.900 | −942.124 | 196.846 |
| 298.15 | 63.131 | 258.627 | 258.627 | 0. | −942.781 | −942.086 | 165.049 |
| 300 | 63.304 | 259.018 | 258.629 | 0.117 | −942.813 | −942.081 | 164.031 |
| 350 | 67.331 | 269.094 | 259.415 | 3.388 | −943.657 | −941.892 | 140.570 |
| 400 | 70.346 | 278.291 | 261.208 | 6.833 | −944.517 | −941.582 | 122.958 |
| 450 | 72.626 | 286.715 | 263.581 | 10.410 | −945.454 | −941.160 | 109.247 |
| 500 | 74.375 | 294.461 | 266.287 | 14.087 | −952.495 | −940.014 | 98.203 |
| 600 | 76.816 | 308.254 | 272.161 | 21.656 | −954.366 | −937.337 | 81.602 |
| 700 | 78.383 | 320.222 | 278.191 | 29.421 | −956.002 | −934.367 | 69.723 |
| 800 | 79 442 | 330.762 | 284.117 | 37.316 | −957.510 | −931.173 | 60.799 |
| 900 | 80.187 | 340.164 | 289.831 | 45.299 | −958.962 | −927.793 | 53.848 |
| 1000 | 80.730 | 348.642 | 295.296 | 53.347 | −960.377 | −924.254 | 48.278 |
| 1100 | 81.138 | 356.357 | 300.501 | 61.441 | −961.765 | −920.574 | 43.714 |
| 1200 | 81.451 | 363.430 | 305.455 | 69.571 | −963.133 | −916.769 | 39.906 |
| 1300 | 81.696 | 369.960 | 310.169 | 77.729 | −964.489 | −912.850 | 36.679 |
| 1400 | 81.892 | 376.022 | 314.659 | 85.909 | −965.832 | −908.827 | 33.909 |
| 1500 | 82.051 | 381.677 | 318.940 | 94.106 | −967.160 | −904 709 | 31.505 |
| 1600 | 82.182 | 386.977 | 323.028 | 102.318 | −968.476 | −900.503 | 29.398 |
| 1700 | 82.290 | 391.963 | 326.938 | 110.542 | −1260.252 | −881.862 | 27.096 |
| 1800 | 82.382 | 396.669 | 330.683 | 118.775 | −1260.039 | −859.610 | 24.945 |
| 1900 | 82.459 | 401.125 | 334.274 | 127.018 | −1259.832 | −837.370 | 23.021 |
| 2000 | 82.525 | 405.357 | 337.723 | 135.267 | −1259.631 | −815.140 | 21.289 |
| 2100 | 82.582 | 409.385 | 341.041 | 143.522 | −1259.436 | −792.921 | 19 723 |
| 2200 | 82.632 | 413.227 | 344.235 | 151.783 | −1259.245 | −770.710 | 18.299 |
| 2300 | 82.675 | 416.902 | 347.315 | 160.049 | −1259.058 | −748.508 | 16.999 |
| 2400 | 82.713 | 420.421 | 350.288 | 168.318 | −1258.875 | −726.314 | 15.808 |
| 2500 | 82.747 | 423.798 | 353.162 | 176.591 | −1258.694 | −704 128 | 14.712 |
| 2600 | 82.777 | 427.044 | 355.941 | 184.867 | −1258.516 | −681.949 | 13.701 |
| 2700 | 82.803 | 430.169 | 358.633 | 193.146 | −1258.341 | −659.776 | 12.764 |
| 2800 | 82.827 | 433.180 | 361.242 | 201.428 | −1258.169 | −637.610 | 11.895 |
| 2900 | 82.848 | 436.087 | 363.773 | 209.712 | −1258.002 | −615.450 | 11.085 |
| 3000 | 82.868 | 438.896 | 366.231 | 217.997 | −1257.839 | −593.296 | 10.330 |
| 3100 | 82.885 | 441.614 | 368.619 | 226.285 | −1257.683 | −571.148 | 9.624 |
| 3200 | 82.901 | 444.246 | 370.941 | 234.574 | −1257.534 | −549.004 | 8.962 |
| 3300 | 82.916 | 446.797 | 373.201 | 242.865 | −1257.395 | −526.864 | 8.340 |
| 3400 | 82.929 | 449.272 | 375.403 | 251.158 | −1257.268 | −504.729 | 7 754 |
| 3500 | 82.941 | 451.676 | 377.548 | 259.451 | −1257.155 | −482.597 | 7.202 |
| 3600 | 82.952 | 454.013 | 379.639 | 267.746 | −1257.059 | −460.468 | 6.681 |
| 3700 | 82.962 | 456.286 | 381.680 | 276.041 | −1256.981 | −438.342 | 6.188 |
| 3800 | 82.972 | 458.499 | 383.673 | 284.338 | −1256.925 | −416.218 | 5.721 |
| 3900 | 82.980 | 460.654 | 385.619 | 292.636 | −1256.893 | −394.094 | 5.278 |
| 4000 | 82.988 | 462.755 | 387.521 | 300.934 | −1256.890 | −371.971 | 4.857 |
| 4100 | 82.996 | 464.804 | 389.382 | 309.233 | −1256.917 | −349.848 | 4.457 |
| 4200 | 83.003 | 466.804 | 391.201 | 317.533 | −1256.978 | −327.723 | 4.076 |
| 4300 | 83.009 | 468.758 | 392.982 | 325.834 | −1257.077 | −305.597 | 3.712 |
| 4400 | 83.015 | 470.666 | 394.726 | 334.135 | −1257.175 | −283.472 | 3.365 |
| 4500 | 83.021 | 472.532 | 396.434 | 342 437 | −1257.340 | −261.340 | 3.034 |
| 4600 | 83.026 | 474.356 | 398.109 | 350.739 | −1257.556 | −239.205 | 2.716 |
| 4700 | 83.031 | 476.142 | 399.750 | 359.042 | −1257.820 | −217.064 | 2.412 |
| 4800 | 83.036 | 477.890 | 401.360 | 367.346 | −1258.138 | −194.917 | 2.121 |
| 4900 | 83.040 | 479.602 | 402.939 | 375.649 | −1258.512 | −172.763 | 1.842 |
| 5000 | 83.044 | 481.280 | 404.489 | 383.954 | −1258.946 | −150.600 | 1.573 |
| 5100 | 83.048 | 482.925 | 406.011 | 392.258 | −1259.434 | −128.430 | 1.315 |
| 5200 | 83.052 | 484.537 | 407.506 | 400.563 | −1259.998 | −106.248 | 1.067 |
| 5300 | 83.055 | 486 119 | 408.974 | 408.869 | −1260.634 | −84.054 | 0.828 |
| 5400 | 83.059 | 487.672 | 410.417 | 417.174 | −1261.346 | −61.848 | 0.598 |
| 5500 | 83.062 | 489.196 | 411.836 | 425.480 | −1262.138 | −39.628 | 0.376 |
| 5600 | 83.065 | 490.693 | 413.231 | 433.787 | −1263.014 | −17.393 | 0.162 |
| 5700 | 83.067 | 492.163 | 414.603 | 442.093 | −1263.977 | 4.859 | −0.045 |
| 5800 | 83.070 | 493.607 | 415.952 | 450.400 | −1265.032 | 27.128 | −0.244 |
| 5900 | 83.072 | 495.028 | 417.281 | 458.707 | −1266.182 | 49.417 | −0.438 |
| 6000 | 83.075 | 496.424 | 418.588 | 467.015 | −1267.431 | 71.725 | −0.624 |

PREVIOUS· December 1968 (1 atm) CURRENT December 1968 (1 bar)

## Magnesium Fluoride ($MgF_2$) CRYSTAL $M_r$ = 62.301806 Magnesium Fluoride ($MgF_2$) $F_2Mg_1(cr)$

$S°(298.15\ K) = 57.255 \pm 0.21\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 1536 \pm 5\ K$

$\Delta_f H°(0\ K) = -1120.332 \pm 1.3\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -1124.241 \pm 1.3\ kJ{\cdot}mol^{-1}$
$\Delta_{fus} H° = 58.702 \pm 0.4\ kJ{\cdot}mol^{-1}$

### Enthalpy of Formation

Rudzitis *et al* [1] used fluorine bomb calorimetry to study the heat of combustion of a highly pure (99 91 mole %) sample of magnesium. Six combustion experiments were performed, and the sole combustion product was identified as $MgF_2$ by x-ray diffraction. Values for the completeness of combustion ranged from 98 4 to 99.99% Corrections for the unburned magnesium were based on analysis performed by hydrogen evolution. This study gave $\Delta_f H°(MgF_2, cr, 298.15\ K) = -268.7 \pm 0\ 3\ kcal\ mol^{-1}(-1124\ 241 \pm 1.3\ kJ\ mol^{-1})$ which is adopted. The quoted uncertainty is twice the combined standard deviation arising from the scatter in the six results and from the analytical and calibration data.

More uncertain values for $\Delta_f H°$ derived indirectly from reaction calorimetry,[2,3] high temperature equilibria,[4] and emf's of solid electrolyte galvanic cells[5,6] are tabulated below. The original data are reanalyzed with the use of the most recent auxiliary data. These sources are included in the table.

| Source | Method | Reaction | T/K | $\Delta_r H°$(298.15 K) kcal·mol⁻¹ | Drift cal K⁻¹·mol⁻¹ | $\Delta_f H°$(298.15 K) kcal·mol⁻¹ |
|---|---|---|---|---|---|---|
| 2 | Reaction Calorimetry | $Mg(OH)_2(cr)+2(HF4.5H_2O)=MgF_2(cr)+H_2O(l)$ | 346.9 | −30.85[b] | | 268.4±1.0 |
| 3 | Reaction Calorimetry | $Mg(cr)+2(HF8OH_2O)=MgF_2(cr)+H_2(g)$ | 293 | 109 46±0 7[b] | | −263.1±1.0 |
| 4 | Equilibria | $MgF_2(cr)+H_2O(g)=MgO(cr)+2HF(g)$ | 1173–1373 | 51.58±0.9[a] | 4.6±0.3 | −268.0±1.5 |
| 5 | emf | $AlF_3(cr)+1.5Mg(cr)=Al(cr)+1.5MgF_2(cr)$ | 720–860 | 41.5±0.2[a] | −1.5 | −268.3±1.6 |
| 6 | emf | $AlF_3(cr)+1.5Mg(cr)=Al(cr)+1.5MgF_2(cr)$ | 750–900 | −40.6±0.2[a] | 1.8 | −267.7±1.8 |

[a] 3rd Law Values
[b] $\Delta_f H°$(HF, aq) consistent with JANAF value for HF(g); also, $\phi_c$(HF, aq) taken from reference 9.

Auxiliary $\Delta_f H°$(298 15 K) values (kcal·mol⁻¹)· $Mg(OH)_2(cr)$, −221.0 ± 0 5,[7] HF4 5 $H_2O$, −76.6 ± 0.1,[c] $H_2O(l)$, −68.315;[8] $HF8OH_2O$, −76.8 ± 0 1;[c] $H_2O(g)$, −57 7979;[7] MgO(cr), −143 7 + 0.15,[7] HF(g), −65 14 ± 0 2,[7] $AlF_3(cr)$, −361.0 ± 0 3[7] With the exception of the older calorimetric measurements of Wartenberg,[3] these results are in reasonable agreement with the directly measured $\Delta_f H°$ value.[1]

### Heat Capacity and Entropy

Todd[10] measured the low temperature heat capacities (54.2−296.5 K) by adiabatic calorimetry. These $C_p°$ data extrapolate to 14.71 cal·K⁻¹·mol⁻¹ at 298 15 K. Integration of these $C_p°$'s gives $S°(298.15\ K) = 13\ 68\ cal\ K^{-1}\ mol^{-1}$ when combined with $S°(51\ K) = 0.539\ cal{\cdot}K^{-1}\ mol^{-1}$. The latter value is calculated from a combination of Debye and Einstein functions which fits all the experimental $C_p°$ data with an average deviation of ±1.0%.

Relative enthalpies $H°(T,298\ 15)$ have been measured (411.3−1516 K) by the "drop" method[11] on a portion of the same sample used for the $C_p°$ study [10] Gravimetric analysis for Mg as $MgSO_4$ indicated a $MgF_2$ purity of 99 87 wt%. However, premelting effects which appear in the experimental enthalpies about 80° below the melting point suggest that the sample was probably somewhat less pure. Insufficient information is reported to attempt to correct for the impurities. High temperature heat capacities (300–2000 K) are derived from the measured enthalpies[11] by curve fitting with orthogonal polynomials. The curve is constrained to join smoothly with the low-temperature $C_p°$ data near 298.15 K Three enthalpy points which appear to involve premelting are not included in the fit Also, we omit the enthalpy point at 411.3 K which shows an usually large positive deviation (+2.9%) from the adopted curve The maximum deviation of the seven enthalpy points used in the fit is −0.5% and occurs at 1032 7 K. The older heat capacity measurements (288–1278 K) reported by Krestovnikov and Karentnikov[12] are considered less reliable and are not included in our evaluation.

### Fusion Data

$T_{fus}$ is the value measured by drop calorimetry.[11] Melting point determinations (1529 and 1534 K) on two commercially available materials which had been further purified by hydrofluorination[13] suggest an uncertainty in the adopted $T_{fus}$ value (1536 K) of ±5 K. Other literature values include 1525 K[14] and 1528 K.[15]

$\Delta_{fus}H°$ is calculated as the difference between JANAF enthalpies for the liquid and crystal at $T_{fus}$. Other reported values for $\Delta_{fus}H°$ are 13.9[11] and 13.15 kcal mol⁻¹.[14]

### Sublimation Data

Refer to the ideal gas table for details.

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −9.914 | −1120.332 | −1120.332 | INFINITE |
| 100 | 21.722 | 10.686 | 102.413 | −9.173 | −1123.140 | −1106.221 | 577.830 |
| 200 | 48.817 | 35.056 | 62.549 | −5.499 | −1124 402 | −1088.654 | 284.327 |
| 298.15 | 61.547 | 57.255 | 57.255 | 0. | −1124.241 | −1071.109 | 187.654 |
| 300 | 61.689 | 57.636 | 57.256 | 0.114 | −1124.231 | −1070.779 | 186.439 |
| 400 | 68.484 | 76.377 | 59.765 | 6.645 | −1123.475 | −1053.065 | 137.516 |
| 500 | 72.634 | 92.132 | 64.706 | 13.713 | −1122 439 | −1035.579 | 108.186 |
| 600 | 75.320 | 105.624 | 70.429 | 21.117 | −1121.275 | −1018.315 | 88.652 |
| 700 | 77.178 | 117.381 | 76.315 | 28.746 | −1120.070 | −1001.250 | 74.714 |
| 800 | 78.555 | 127.780 | 82.110 | 36.535 | −1118.878 | −984.358 | 64.272 |
| 900 | 79.626 | 137.096 | 87.711 | 44.446 | −1117.740 | −967.612 | 56.159 |
| 1000 | 80.496 | 145.532 | 93.078 | 52.453 | −1125.279 | −950.276 | 49.637 |
| 1100 | 81.237 | 153.239 | 98.202 | 60.541 | −1124.342 | −932.821 | 44.296 |
| 1200 | 81.877 | 160.336 | 103.088 | 68.697 | −1123.363 | −915.452 | 39.849 |
| 1300 | 82.454 | 166.912 | 107.748 | 76.914 | −1122.346 | −898.167 | 36.089 |
| 1400 | 82.977 | 173.042 | 112.195 | 85.186 | −1248.705 | −877.795 | 32.751 |
| 1500 | 83.467 | 178.784 | 116 445 | 93.508 | −1246.272 | −851.386 | 29.648 |
| 1536.000 | 83.635 | 180.766 | 117.929 | 96.516 | ---- CRYSTAL <--> LIQUID ---- | | |
| 1600 | 83.923 | 184.186 | 120.512 | 101.878 | −1243.809 | −825.141 | 26.938 |
| 1700 | 84.358 | 189.286 | 124.409 | 110.292 | −1241.319 | −799.050 | 24.552 |
| 1800 | 84.776 | 194.120 | 128 148 | 118.749 | −1238.801 | −773.107 | 22.435 |
| 1900 | 85.178 | 198.715 | 131.743 | 127.247 | −1236.254 | −747.304 | 20.545 |
| 2000 | 85.567 | 203.094 | 135.201 | 135 784 | −1233.676 | −721.636 | 18.847 |

PREVIOUS March 1966 CURRENT: June 1975

Continued on page 1215

## Magnesium Fluoride ($MgF_2$) LIQUID $M_r$ = 62.301806 Magnesium Fluoride ($MgF_2$) $F_2Mg_1(l)$

$S°(298.15\ K) = [89.967]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = [-1072.356]\ kJ{\cdot}mol^{-1}$

$T_{fus} = 1536 \pm 5\ K$ $\Delta_{fus}H° = 8.702 \pm 0.4\ kJ{\cdot}mol^{-1}$

### Enthalpy of Formation

$\Delta_fH°(MgF_2, l, 298.15\ K)$ is calculated from $\Delta_fH°(MgF_2, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1536\ K)–H°(298\ 15\ K)$, between the crystal and liquid.

### Heat Capacity and Entropy

Naylor[1] has measured relative enthalpies (1539–1760 K) for the liquid by drop calorimetry. These results give a $C_p°(l)$ equal to 22.687 cal $K^{-1}{\cdot}mol^{-1}$. This value is used in the temperature range 1000–3000 K. Below 1000 K, the assumed glass transition temperature, $C_p°$ is assumed to be that of the crystal. $S°(298\ 15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

### Fusion Data

Refer to the crystal table for details.

### Vaporization Data

$T_{vap} = 2536\ K$ is the temperature at which $\Delta_rG°$ for the process $MgF\ (l) = MgF_2\ (g)$ is zero. $\Delta_{vap}H° = 274.052\ kJ\ mol^{-1}$ is the difference between the $\Delta_fH°$ values for the gas and liquid at $T_{vap}$. Several methods[2-6] predict an insignificant amount of dimer (–1%) in the saturated vapor below 2000 K.

### References

[1] B. F. Naylor, J. Amer. Chem. Soc. 67, 150 (1945).
[2] J. Berkowitz and J R. Marquart, J. Chem. Phys. 37, 1853 (1962).
[3] R. R. Hammer and J. A. Pask, J. Amer. Ceram. Soc. 47, 264 (1964).
[4] M. A. Greenbaum, H. C.Ko, M. Wong, and M. Farber, J. Phys Chem. 68, 965 (1964).
[5] D L. Hildenbrand, W F. Hall, F. Ju, and N. D Potter, J Chem Phys. 40, 2882 (1964).
[6] J W. Green, G D Blue, T. C. Ehlert and J. L. Margrave, J. Chem. Phys. 41, 2245 (1964).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | $J{\cdot}K^{-1}mol^{-1}$ | | | $kJ{\cdot}mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 61.547 | 89.967 | 89.967 | 0. | -1072.356 | -1028.977 | 180.272 |
| 300 | 61.689 | 90.348 | 89.968 | 0.114 | -1072.345 | -1028.707 | 179.114 |
| 400 | 68.484 | 109.088 | 92.477 | 6.645 | -1071.589 | -1014.265 | 132.449 |
| 500 | 72.634 | 124.843 | 97.418 | 13.713 | -1070.553 | -1000.049 | 104.474 |
| 600 | 75.320 | 138.336 | 103.140 | 21.117 | -1069.390 | -986.057 | 85.844 |
| 700 | 77.178 | 150.092 | 109.026 | 28.746 | -1068.184 | -972.263 | 72.551 |
| 800 | 78.555 | 160.491 | 114.822 | 36.535 | -1066.993 | -958.642 | 62.593 |
| 900 | 79.626 | 169.807 | 120.423 | 44.446 | -1065.855 | -945 167 | 54.856 |
| 1000 | 80.496 | 178.244 | 125.790 | 52.454 | -1073.393 | -931.102 | 48.636 |
| 1000.000 | 80.496 | 178.244 | 125.790 | 52.454 | GLASS <--> LIQUID | | |
| 1000.000 | 94.922 | 178.244 | 125.790 | 52.454 | TRANSITION | | |
| 1100 | 94.922 | 187.291 | 130.976 | 61.946 | -1071.052 | -916.987 | 43.544 |
| 1200 | 94.922 | 195.550 | 136.018 | 71.438 | -1068.736 | -903.083 | 39.310 |
| 1300 | 94.922 | 203.148 | 140.894 | 80.931 | -1066.444 | -889.372 | 35.735 |
| 1400 | 94.922 | 210.182 | 145.595 | 90.423 | -1191.583 | -872.669 | 32.560 |
| 1500 | 94.922 | 216.731 | 150.121 | 99.915 | -1187.980 | -850.015 | 29.600 |
| 1536.000 | 94.922 | 218.983 | 151.709 | 103.332 | --- CRYSTAL <--> LIQUID --- | | |
| 1600 | 94.922 | 222.858 | 154.478 | 109 407 | -1184.395 | -827 601 | 27.018 |
| 1700 | 94.922 | 228.612 | 158.671 | 118.900 | -1180.826 | -805.411 | 24 747 |
| 1800 | 94.922 | 234.038 | 162.709 | 128.392 | -1177.273 | -783.430 | 22.735 |
| 1900 | 94.922 | 239.170 | 166.599 | 137.884 | -1173.731 | -761.647 | 20.939 |
| 2000 | 94.922 | 244 039 | 170.351 | 147.376 | -1170.199 | -740.049 | 19.328 |
| 2100 | 94.922 | 248.670 | 173.971 | 156.869 | -1166.672 | -718.629 | 17.875 |
| 2200 | 94.922 | 253.086 | 177.467 | 166.361 | -1163.149 | -697.376 | 16.558 |
| 2300 | 94.922 | 257.305 | 180.848 | 175.853 | -1159 625 | -676.283 | 15.359 |
| 2400 | 94.922 | 261.345 | 184.118 | 185.345 | -1156.097 | -655.344 | 14.263 |
| 2500 | 94.922 | 265.220 | 187.285 | 194.838 | -1152.561 | -634.552 | 13.258 |
| 2600 | 94.922 | 268.943 | 190.355 | 204.330 | -1149.014 | -613.902 | 12.333 |
| 2700 | 94.922 | 272.526 | 193.332 | 213.822 | -1145.455 | -593.388 | 11.480 |
| 2800 | 94.922 | 275.978 | 196.223 | 223.314 | -1141.879 | -573.006 | 10.690 |
| 2900 | 94.922 | 279.309 | 199.030 | 232.807 | -1138.285 | -552.753 | 9.956 |
| 3000 | 94.922 | 282.527 | 201.760 | 242.299 | -1134.673 | -532.624 | 9.274 |

PREVIOUS: March 1966 CURRENT: June 1975

## Magnesium Fluoride ($MgF_2$) CRYSTAL-LIQUID

0 to 1536 K crystal
above 1536 K liquid

Refer to the individual tables for details.

## $M_r = 62.301806$ Magnesium Fluoride ($MgF_2$) $F_2Mg_1(cr,l)$

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p^\circ$ = 0.1 MPa

|  | J·K⁻¹mol⁻¹ |  |  | kJ·mol⁻¹ |  |  |  |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_fH^\circ$ | $\Delta_fG^\circ$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −9.914 | −1120.332 | −1120.332 | INFINITE |
| 100 | 21.722 | 10 686 | 102 413 | −9.173 | −1123.140 | −1106.221 | 577.830 |
| 200 | 48.817 | 35.056 | 62.549 | −5.499 | −1124.402 | −1088.654 | 284.327 |
| 298.15 | 61.547 | 57.255 | 57.255 | 0. | −1124.241 | −1071 109 | 187.654 |
| 300 | 61.689 | 57.636 | 57.256 | 0.114 | −1124.231 | −1070.779 | 186.439 |
| 400 | 68.484 | 76.377 | 59.765 | 6.645 | −1123 475 | −1053.065 | 137.516 |
| 500 | 72.634 | 92.132 | 64.706 | 13.713 | −1122 439 | −1035.579 | 108.186 |
| 600 | 75.320 | 105 624 | 70.429 | 21 117 | −1121.275 | −1018.315 | 88.652 |
| 700 | 77.178 | 117.381 | 76.315 | 28.746 | −1120.070 | −1001.250 | 74.714 |
| 800 | 78.555 | 127.780 | 82.110 | 36.535 | −1118.878 | −984.358 | 64.272 |
| 900 | 79 626 | 137 096 | 87.711 | 44.446 | −1117.740 | −967.612 | 56.159 |
| 1000 | 80.496 | 145.532 | 93.078 | 52.453 | −1125.279 | −950.276 | 49.637 |
| 1100 | 81.237 | 153.239 | 98 202 | 60.541 | −1124.342 | −932.821 | 44.296 |
| 1200 | 81 877 | 160.336 | 103.088 | 68.697 | −1123.363 | −915.452 | 39.849 |
| 1300 | 82 454 | 166.912 | 107.748 | 76.914 | −1122.346 | −898 167 | 36.089 |
| 1400 | 82.977 | 173.042 | 112 195 | 85 186 | −1248.705 | −877.795 | 32.751 |
| 1500 | 83.467 | 178 784 | 116.445 | 93.508 | −1246.272 | −851.386 | 29.648 |
| 1536.000 | 83.635 | 180.766 | 117.929 | 96.516 | CRYSTAL <--> LIQUID TRANSITION |  |  |
| 1536.000 | 94 922 | 218 983 | 117.929 | 155.218 |  |  |  |
| 1600 | 94.922 | 222.858 | 122.050 | 161.293 | −1184.395 | −827.601 | 27.018 |
| 1700 | 94.922 | 228.612 | 128.150 | 170.785 | −1180.826 | −805.411 | 24.747 |
| 1800 | 94.922 | 234.038 | 133.884 | 180.277 | −1177.273 | −783.430 | 22.735 |
| 1900 | 94.922 | 239.170 | 139.291 | 189.769 | −1173.731 | −761.647 | 20.939 |
| 2000 | 94.922 | 244.039 | 144 408 | 199.262 | −1170.199 | −740.049 | 19.328 |
| 2100 | 94.922 | 248.670 | 149.264 | 208.754 | −1166.672 | −718.629 | 17.875 |
| 2200 | 94.922 | 253.086 | 153.883 | 218.246 | −1163.149 | −697.376 | 16.558 |
| 2300 | 94.922 | 257.305 | 158 289 | 227.738 | −1159.625 | −676.283 | 15.359 |
| 2400 | 94.922 | 261.345 | 162.499 | 237.231 | −1156.097 | −655.344 | 14.263 |
| 2500 | 94.922 | 265.220 | 166.531 | 246.723 | −1152.561 | −634.552 | 13.258 |
| 2600 | 94.922 | 268.943 | 170.399 | 256.215 | −1149.014 | −613.902 | 12.333 |
| 2700 | 94.922 | 272.526 | 174.115 | 265.707 | −1145.454 | −593.388 | 11.480 |
| 2800 | 94.922 | 275.978 | 177.692 | 275.200 | −1141.879 | −573.006 | 10.690 |
| 2900 | 94.922 | 279.309 | 181.139 | 284.692 | −1138.285 | −552.753 | 9 956 |
| 3000 | 94.922 | 282.527 | 184.465 | 294.184 | −1134.673 | −532.624 | 9.274 |

PREVIOUS: CURRENT June 1975

# Magnesium Fluoride (MgF$_2$) IDEAL GAS $M_r = 62.301806$ Magnesium Fluoride (MgF$_2$) F$_2$Mg$_1$(g)

$\Delta_f H°(0\ K) = -724.994 \pm 3.3$ (or $\pm 16.7$) kJ·mol$^{-1}$

$S°(298.15\ K) = 256.508 \pm 2.1$ (or $\pm 12.6$) J·K$^{-1}$·mol$^{-1}$ $\Delta_f H°(298.15\ K) = -726.761 \pm 3.3$ (or 16.7) kJ·mol$^{-1}$

| Vibrational Frequencies and Degeneracies<br>υ, cm$^{-1}$ | υ, cm$^{-1}$ | υ, cm$^{-1}$ |
|---|---|---|
| 508 (1) | 215 (1) | 875 (1) |

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: $C_{2v}$
Bond Distance: Mg–F = 1.77 ± 0.02 Å
Bond Angle. F–Mg–F = 158°
Product of the Principal Moments of Inertia: $I_A I_B I_C = 1.033673 \times 10^{-115}$ g$^3$·cm$^6$

## Enthalpy of Formation

$\Delta_{sub}H°(298.15\ K)$ is added to $\Delta_f H°(MgF_2, cr, 298.15\ K)$ to give $\Delta_f H°(g, 298.15\ K) = 173.7 \pm 0.8$ kcal·mol$^{-1}$ $\Delta_{sub}H°(298.15\ K)$ is selected from the results of a 3rd law analysis of twenty sets[19] of vapor pressure data for MgF$_2$(cr, l). These measurements cover an extended temperature range (~1200°) and include the use of manometric.[1,4] Knudsen effusion,[2,5,6] torsion effusion[5-8] and mass spectrometric[3,9] methods. The amount of dimer present in the saturated vapor is predicted not to exceed 1% below 2000 K by several methods.[3,6,7-9]

| Source | | Reaction | Method | T/K | Data Points | $\Delta_r H°$ kcal·mol$^{-1}$ 2nd law | $\Delta_r H°$ kcal·mol$^{-1}$ 3rd law | Drift cal K$^{-1}$·mol$^{-1}$ | $-\Delta_f H°$(298.15 K) kcal·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| [1] | | A | Manometric | 1934–2129 | 6 | 89.2 | 82.5±1.0 | −3.3±3.4 | 173.8±1.5 |
| [2] | Set 1 | B | Knudsen Effusion | 1337–1480 | 8 | 93.7 | 94.6±0.7 | 0.6±2.6 | 174.1±1.0 |
| | 2 | B | " | 1440–1530 | 4 | 91.3 | 95.0±0.4 | 2.5±2.9 | 173.7±0.7 |
| | 3 | B | " | 1284–1357 | 6 | 100.3 | 94.8±0.3 | −4.1±1.9 | 173.9±0.6 |
| [3] | | B | Mass Spec | 1450 | 1 | 91.4[a] | 93.9 | 174.8 | |
| [4] | Set 1 | A | Manometric | 2155–2327 | Equation | 82.9 | 82.40±0.03 | −0.2 | 173.9±0.5 |
| | 2 | A | Manometric | 2087–2357 | Equation | 84.8 | 82.53±0.2 | −1.0 | 173.8±0.7 |
| [5,6] | Set 1 | B | Knudsen Effusion | 1451–1533 | 6 | 98.7 | 95.3±0.5 | −2.3±3.5 | 173.4±0.8 |
| | 2 | A | " | 1568–1613 | 4 | 81.9 | 82.9±0.2 | 0.6±4.2 | |
| | 3 | B | Torsion Effusion | 1413–1518 | 11[b] | 92.9 | 95.3±0.6 | 1.7±2.3 | 173.4±0.9 |
| | 4 | A | " | 1539–1614 | 11[c] | 80.6 | 82.8±0.3 | 1.4±1.6 | 173.5±0.8 |
| [7] | Set 1 | B | " | 1273–1433 | 21 | 72.7 | 90.6±1.4 | 13.2±1.0 | 178.1±1.7 |
| | 2 | B | " | 1373–1513 | 18[b] | 76.6 | 91.0±1.0 | 10.0±0.8 | 177.7±1.3 |
| [8] | Set 1 | B | " | 1340–1500 | Equation | 97.7 | 95.8±0.2 | −1.4 | 172.9±0.5 |
| | 2 | B | " | 1348–1482 | " | 98.3 | 96.0±0.2 | −1.6 | 172.7±0.5 |
| | 3 | B | " | 1324–1465 | " | 96.7 | 95.7±0.1 | −0.7 | 173.0±0.4 |
| | 4 | B | " | 1376–1517 | " | 98.9 | 95.6±0.3 | −2.2 | 173.1±0.7 |
| | 5 | B | " | 1345–1515 | " | 97.9 | 95.7±0.2 | −1.5 | 173.0±0.5 |
| | 6 | B | " | 1341–1520 | " | 96.9 | 95.6±0.1 | −1.0 | 173.1±0.4 |
| [9] | | B | Mass Spec | 1241–1492 | Equation | 93.9 | 95.4±0.2 | 1.1 | 173.3±0.5 |

Reactions: (A) $MgF_2(l) = Mg\ F_2(g)$; (B) $MgF_2(cr) = MgF_2(g)$.

[a] 2nd law value by slope method. [b] One point rejected due to failure of a statistical test.

[c] Two points rejected due to failure of a statistical test.

These data are in agreement on $\Delta_{sub}H°(298.15\ K) = 95.0 \pm 0.5$ kcal·mol$^{-1}$. We adopt this value but assign an alternate uncertainty to $\Delta_f H°$ to include the possibility that MgF$_2$ is linear (refer below).

## Heat Capacity and Entropy

Considerable confusion exists as to whether MgF$_2$ is bent or linear. Electron diffraction,[11] electric deflection,[12] matrix isolation Raman[23] and infrared[13,22,23] spectral studies, and MO calculatons[14-16,24] predict a linear configuration. Other matrix isolation IR studies[17,18] and MO calculations[19,24] favor the nonlinear structure. Isotopic shifts[18] in the matrix frequencies suggest that the most probable value of the apex angle

Continued on page 1215

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ (J·K$^{-1}$mol$^{-1}$) | $S°$ (J·K$^{-1}$mol$^{-1}$) | $-[G°-H°(T_r)]/T$ (J·K$^{-1}$mol$^{-1}$) | $H°-H°(T_r)$ (kJ·mol$^{-1}$) | $\Delta_f H°$ (kJ·mol$^{-1}$) | $\Delta_f G°$ (kJ·mol$^{-1}$) | log $K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0. | 0. | INFINITE | −12.056 | −724.994 | −724.994 | INFINITE |
| 100 | 37.519 | 210.143 | 296.182 | −8.604 | −725.091 | −728.117 | 380.330 |
| 200 | 43.734 | 238.149 | 260.788 | −4.528 | −725.951 | −730.821 | 190.871 |
| 250 | 46.242 | 248.185 | 257.291 | −2.277 | −726.373 | −731.990 | 152.941 |
| 298.15 | 48.259 | 256.508 | 256.508 | 0. | −726.761 | −733.036 | 128.425 |
| 300 | 48.329 | 256.806 | 256.509 | 0.089 | −726.775 | −733.075 | 127.640 |
| 350 | 50.021 | 264.388 | 257.103 | 2.550 | −727.166 | −734.094 | 109.558 |
| 400 | 51.375 | 271.159 | 258.445 | 5.086 | −727.553 | −735.057 | 95.989 |
| 450 | 52.455 | 277.275 | 260.203 | 7.683 | −727.944 | −735.972 | 85.429 |
| 500 | 53.320 | 282.848 | 262.193 | 10.328 | −728.344 | −736.842 | 76.977 |
| 600 | 54.583 | 292.689 | 266.477 | 15.727 | −729.185 | −738.464 | 64.289 |
| 700 | 55.431 | 301.171 | 270.842 | 21.231 | −730.106 | −739.939 | 55.215 |
| 800 | 56.020 | 308.613 | 275.107 | 26.805 | −731.129 | −741.275 | 48.400 |
| 900 | 56.444 | 315.237 | 279.205 | 32.429 | −732.277 | −742.476 | 43.092 |
| 1000 | 56.758 | 321.201 | 283.111 | 38.090 | −742.162 | −742.829 | 38.801 |
| 1100 | 56.996 | 326.623 | 286.824 | 43.778 | −743.625 | −742.825 | 35.274 |
| 1200 | 57.180 | 331.590 | 290.351 | 49.487 | −745.093 | −742.687 | 32.328 |
| 1300 | 57.326 | 336.173 | 293.702 | 55.213 | −746.567 | −742.427 | 29.831 |
| 1400 | 57.442 | 340.426 | 296.889 | 60.952 | −875.459 | −738.886 | 27.568 |
| 1500 | 57.538 | 344.392 | 299.925 | 66.701 | −875.599 | −729.126 | 25.390 |
| 1600 | 57.616 | 348.108 | 302.822 | 72.459 | −875.749 | −719.356 | 23.485 |
| 1700 | 57.681 | 351.603 | 305.589 | 78.224 | −875.908 | −709.577 | 21.803 |
| 1800 | 57.736 | 354.902 | 308.238 | 83.994 | −876.075 | −699.788 | 20.307 |
| 1900 | 57.783 | 358.025 | 310.777 | 89.771 | −876.250 | −689.990 | 18.969 |
| 2000 | 57.823 | 360.990 | 313.214 | 95.551 | −876.429 | −680.182 | 17.765 |
| 2100 | 57.858 | 363.812 | 315.557 | 101.335 | −876.611 | −670.365 | 16.674 |
| 2200 | 57.888 | 366.504 | 317.812 | 107.122 | −876.793 | −660.539 | 15.683 |
| 2300 | 57.914 | 369.078 | 319.985 | 112.912 | −876.971 | −650.706 | 14.778 |
| 2400 | 57.937 | 371.543 | 322.083 | 118.705 | −877.142 | −640.864 | 13.948 |
| 2500 | 57.958 | 373.909 | 324.109 | 124.500 | −877.304 | −631.016 | 13.184 |
| 2600 | 57.976 | 376.182 | 326.068 | 130.297 | −877.453 | −621.162 | 12.479 |
| 2700 | 57.992 | 378.370 | 327.965 | 136.095 | −877.587 | −611.302 | 11.826 |
| 2800 | 58.007 | 380.480 | 329.803 | 141.895 | −877.704 | −601.437 | 11.220 |
| 2900 | 58.020 | 382.516 | 331.586 | 147.696 | −877.801 | −591.569 | 10.655 |
| 3000 | 58.032 | 384.483 | 333.316 | 153.499 | −877.878 | −581.697 | 10.128 |
| 3100 | 58.042 | 386.386 | 334.998 | 159.302 | −877.934 | −571.824 | 9.635 |
| 3200 | 58.052 | 388.229 | 336.633 | 165.107 | −877.968 | −561.948 | 9.173 |
| 3300 | 58.061 | 390.015 | 338.223 | 170.913 | −877.980 | −552.072 | 8.739 |
| 3400 | 58.069 | 391.749 | 339.772 | 176.719 | −877.971 | −542.197 | 8.330 |
| 3500 | 58.076 | 393.432 | 341.281 | 182.527 | −877.942 | −532.321 | 7.944 |
| 3600 | 58.083 | 395.068 | 342.753 | 188.335 | −877.894 | −522.447 | 7.581 |
| 3700 | 58.089 | 396.660 | 344.188 | 194.143 | −877.829 | −512.574 | 7.236 |
| 3800 | 58.095 | 398.209 | 345.590 | 199.952 | −877.748 | −502.704 | 6.910 |
| 3900 | 58.100 | 399.718 | 346.958 | 205.762 | −877.655 | −492.835 | 6.601 |
| 4000 | 58.105 | 401.189 | 348.296 | 211.572 | −877.550 | −482.969 | 6.307 |
| 4100 | 58.110 | 402.624 | 349.603 | 217.383 | −877.437 | −473.106 | 6.027 |
| 4200 | 58.114 | 404.024 | 350.883 | 223.194 | −877.318 | −463.246 | 5.761 |
| 4300 | 58.118 | 405.392 | 352.134 | 229.006 | −877.196 | −453.389 | 5.508 |
| 4400 | 58.122 | 406.728 | 353.360 | 234.818 | −877.075 | −443.534 | 5.265 |
| 4500 | 58.125 | 408.034 | 354.561 | 240.630 | −876.955 | −433.682 | 5.034 |
| 4600 | 58.129 | 409.312 | 355.737 | 246.443 | −876.842 | −423.833 | 4.813 |
| 4700 | 58.132 | 410.562 | 356.890 | 252.256 | −876.737 | −413.986 | 4.601 |
| 4800 | 58.134 | 411.786 | 358.021 | 258.069 | −876.643 | −404.141 | 4.398 |
| 4900 | 58.137 | 412.984 | 359.131 | 263.883 | −876.564 | −394.298 | 4.203 |
| 5000 | 58.140 | 414.159 | 360.219 | 269.697 | −876.501 | −384.457 | 4.016 |
| 5100 | 58.142 | 415.310 | 361.288 | 275.511 | −876.458 | −374.616 | 3.837 |
| 5200 | 58.144 | 416.439 | 362.338 | 281.325 | −876.438 | −364.776 | 3.664 |
| 5300 | 58.146 | 417.547 | 363.369 | 287.140 | −876.441 | −354.937 | 3.498 |
| 5400 | 58.148 | 418.634 | 364.383 | 292.955 | −876.471 | −345.097 | 3.338 |
| 5500 | 58.150 | 419.701 | 365.379 | 298.769 | −876.531 | −335.256 | 3.184 |
| 5600 | 58.152 | 420.748 | 366.358 | 304.585 | −876.622 | −325.414 | 3.035 |
| 5700 | 58.154 | 421.778 | 367.322 | 310.400 | −876.747 | −315.570 | 2.892 |
| 5800 | 58.155 | 422.789 | 368.269 | 316.215 | −876.907 | −305.724 | 2.753 |
| 5900 | 58.157 | 423.783 | 369.202 | 322.031 | −877.105 | −295.874 | 2.619 |
| 6000 | 58.158 | 424.761 | 370.120 | 327.847 | −877.343 | −286.021 | 2.490 |

PREVIOUS: June 1975 (1 atm) CURRENT: June 1975 (1 bar)

## Magnesium Fluoride, Ion ($MgF_2^+$) IDEAL GAS $M_r = 62.301257$ Magnesium Fluoride, Ion ($MgF_2^+$) $F_2Mg_1^+(g)$

$\Delta_f H°(0\ K) = 587.193 \pm 20.9$ (or $\pm 37.7$) kJ mol$^{-1}$
$S°(298.15\ K) = [258.145 \pm 12.6]$ J·K$^{-1}$·mol$^{-1}$ $\Delta_f H°(298.15\ K) = 591.982 \pm 20.9$ (or $\pm 37.7$) kJ·mol$^{-1}$

Electronic Levels and Quantum Weights

| State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|
| $^2\Pi$ | 0 | 4 |
| $^2\Pi$ | [20000] | 4 |
| $^2\Sigma$ | [25000] | 2 |

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ |
|---|
| [500](1) |
| [200](2) |
| [800](1) |

Point Group. [$D_{\infty h}$] $\sigma = 2$
Bond Distance. Mg–F = [1.95] Å
Bond Angle. F–Mg–F = [180]°
Rotational Constant: $B_0 = [0.116677]$ cm$^{-1}$

### Enthalpy of Formation

The $MgF_2^+$ ion has been identified as an important species in the vapor mass spectra of the $MgF_2$,[1-3] $MgF_2$–Tl–Pd[4] and $MgF_2$–Cu[5] systems. The observed appearance potentials (AP) for this ion are tabulated below.

| Source | Year | AP, eV |
|---|---|---|
| Berkowitz and Marquart[1] | 1962 | 13.5±0.4 |
| Green *et al.*[2] | 1964 | 13.6 |
| Murad *et al.*[4] | 1966 | 14.0±0.5 |
| Hildenbrand[5] | 1968 | 13.5 |
| Hildenbrand[3] | 1968 | 13.3±0.3 |

These results show the normal scatter expected for such measurements; the largest deviation is 0.7 eV. We adopt an average value of 13.6±0.2 eV (313.62±4.6 kcal·mol$^{-1}$), and we assume that this value refers to the direct ionization process $MgF_2(g) + e^- = MgF_2^+(g) + 2e^-$ occurring at 0 K. Combining the selected AP value with $\Delta_f H°(MgF_2,g) = -173.3 \pm 0.8$ kcal·mol$^{-1}$,[6] we obtain $\Delta_f H°(MgF_2^+$, g, 0 K$) = 140.3 \pm 5$ kcal·mol$^{-1}$. The $\Delta_f H°$ value at 298.15 K is 141.5 kcal·mol$^{-1}$. An alternate uncertainty of ±9 kcal·mol$^{-1}$ is included to cover the possibility that the $MgF_2$ molecule is linear.[6]

### Heat Capacity and Entropy

A comparison of the atomization energies, $\Delta_a H°(0\ K)$ in kcal·mol$^{-1}$, for $MgF_2(245)$[6] and $MgF_2^+$ (107.7) suggests weaker bonding in the ion relative to the neutral molecule. One might therefore expect that the fundamental frequencies of $MgF_2^+$ would be somewhat less than those for $MgF_2$. We assume a slight decrease in the three vibrational frequencies of $MgF_2$.[6] $MgF_2^+$ (fifteen valence electrons) is isoelectronic with the molecules $BO_2$, $N_3$, NCO, and $N_2O^+$. By analogy with the ground states[6] for these isoelectronic molecules, we assume that the ground state for $MgF_2^+$ is $^2\Pi$. We also include two excited states ($^2\Pi$ and $^2\Sigma$) which would be expected to exist based on those observed for $BO_2$.[6]

According to the diagram of Walsh,[7] $MgF_2^+$ is predicted to be linear. This prediction is supported by the fact that several other fifteen valence electron molecules ($BO_2$, NCO, $N_2O^+$, and $N_3$) are now known to be linear in their ground states. We adopt a linear configuration. Due to the weaker bonding in $MgF_2^+$ relative to $MgF_2$, it is reasonable to assume that $r_e(MgF_2^+) > r_e(MgF_2)$. We assume a 10% increase in the bond length for $MgF_2$.[6]

### References

[1] J. Berkowitz and J. R. Marquart, J. Chem. Phys. 37, 1853 (1962).
[2] J. W. Green, G. D. Blue, T. C. Ehlert, and J. L. Margrave, J. Chem. Phys. 41, 2245 (1964).
[3] D. L. Hildenbrand, J. Chem. Phys. 48, 3657 (1968).
[4] E. Murad, D. L. Hildenbrand, and R. P. Main, J. Chem. Phys. 45, 263 (1966).
[5] D. L. Hildenbrand, J. Chem. Phys. 48, 2457 (1968).
[6] JANAF Thermochemical Tables: $MgF_2(g)$, 6–30–75; $BO_2(g)$, 6–30–68; CNO(g), $N_2O^+(g)$ and $N_3(g)$, 12–31–70.
[7] A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0 | 0. | INFINITE | -12.414 | 587.193 | | |
| 100 | 38.135 | 208.753 | 300.902 | -9.215 | | | |
| 200 | 47.129 | 238.250 | 262 789 | -4.908 | | | |
| 250 | 50.159 | 249.106 | 258.996 | -2.473 | | | |
| 298.15 | 52.449 | 258.145 | 258.145 | 0. | 591.982 | 578.963 | -101.432 |
| 300 | 52.526 | 258.469 | 258 146 | 0.097 | 592.013 | 578.883 | -100.792 |
| 350 | 54.358 | 266.710 | 258.792 | 2.771 | 592.876 | 576.626 | -86.057 |
| 400 | 55 774 | 274.065 | 260.250 | 5.526 | 593.746 | 574.245 | -74.989 |
| 450 | 56.875 | 280.700 | 262.160 | 8.343 | 594.615 | 571.756 | -66.368 |
| 500 | 57.738 | 286.739 | 264.320 | 11.210 | 595.476 | 569.169 | -59.461 |
| 600 | 58 973 | 297.384 | 268.967 | 17.050 | 597.154 | 563.749 | -49.079 |
| 700 | 59.786 | 306.539 | 273.696 | 22.990 | 598.749 | 558.054 | -41.643 |
| 800 | 60.344 | 314.561 | 278.313 | 28.998 | 600.239 | 552.138 | -36.051 |
| 900 | 60.742 | 321.693 | 282.745 | 35 054 | 601.600 | 546.042 | -31.691 |
| 1000 | 61.034 | 328.109 | 286.966 | 41.143 | 594.222 | 540.515 | -28.234 |
| 1100 | 61.255 | 333.937 | 290.975 | 47.258 | 595.265 | 535.094 | -25.409 |
| 1200 | 61.425 | 339.274 | 294.780 | 53.393 | 596.301 | 529.578 | -23.052 |
| 1300 | 61.559 | 344.196 | 298.395 | 59.542 | 597.329 | 523 976 | -21.054 |
| 1400 | 61.666 | 348.763 | 301.831 | 65.703 | 470.938 | 521.462 | -19.456 |
| 1500 | 61.753 | 353.020 | 305 104 | 71.875 | 473.299 | 524.989 | -18.282 |
| 1600 | 61.825 | 357.008 | 308.224 | 78.054 | 475.649 | 528.358 | -17.249 |
| 1700 | 61.885 | 360.758 | 311.205 | 84.239 | 477.989 | 531.580 | -16.333 |
| 1800 | 61.936 | 364.297 | 314.058 | 90.430 | 480.320 | 534.666 | -15.516 |
| 1900 | 61.979 | 367 647 | 316.791 | 96.626 | 482.644 | 537.621 | -14.780 |
| 2000 | 62.016 | 370.827 | 319.414 | 102.826 | 484.963 | 540.455 | -14.115 |
| 2100 | 62.048 | 373.853 | 321.935 | 109.029 | 487.278 | 543.172 | -13.511 |
| 2200 | 62.077 | 376.740 | 324.361 | 115.235 | 489.595 | 545.780 | -12.958 |
| 2300 | 62.103 | 379.500 | 326.698 | 121.444 | 491.914 | 548.282 | -12.452 |
| 2400 | 62.126 | 382.144 | 328.954 | 127.656 | 494.240 | 550.683 | -11.985 |
| 2500 | 62.149 | 384.680 | 331.133 | 133.870 | 496.576 | 552.987 | -11.554 |
| 2600 | 62.170 | 387.118 | 333.239 | 140.086 | 498.925 | 555.197 | -11.154 |
| 2700 | 62.192 | 389.465 | 335.279 | 146.304 | 501.289 | 557.316 | -10.782 |
| 2800 | 62.214 | 391 727 | 337.254 | 152.524 | 503.671 | 559.348 | -10.435 |
| 2900 | 62.236 | 393.911 | 339.171 | 158.746 | 506.074 | 561.294 | -10.110 |
| 3000 | 62.260 | 396.021 | 341.031 | 164.971 | 508.497 | 563.157 | -9.805 |
| 3100 | 62.286 | 398.063 | 342.838 | 171 199 | 510.944 | 564.938 | -9.519 |
| 3200 | 62.313 | 400.041 | 344.595 | 177.428 | 513 414 | 566.641 | -9.249 |
| 3300 | 62.343 | 401.959 | 346.304 | 183.661 | 515.907 | 568.266 | -8.995 |
| 3400 | 62.376 | 403.820 | 347.968 | 189.897 | 518.424 | 569.815 | -8.754 |
| 3500 | 62.411 | 405.629 | 349.590 | 196.137 | 520.964 | 571.289 | -8.526 |
| 3600 | 62.449 | 407.388 | 351.171 | 202.380 | 523.525 | 572.691 | -8.310 |
| 3700 | 62.491 | 409 099 | 352.714 | 208.627 | 526.108 | 574.021 | -8.104 |
| 3800 | 62.536 | 410.767 | 354.220 | 214.878 | 528.709 | 575.281 | -7.908 |
| 3900 | 62.584 | 412.392 | 355.691 | 221.134 | 531.328 | 576.473 | -7.721 |
| 4000 | 62.636 | 413.977 | 357.128 | 227.395 | 533.962 | 577 597 | -7.543 |
| 4100 | 62.691 | 415.524 | 358.534 | 233.661 | 536.609 | 578.655 | -7.372 |
| 4200 | 62.749 | 417.035 | 359.908 | 239.933 | 539.267 | 579.648 | -7.209 |
| 4300 | 62.811 | 418.513 | 361.254 | 246.211 | 541.934 | 580.578 | -7.053 |
| 4400 | 62.876 | 419.957 | 362.572 | 252.495 | 544.606 | 581.446 | -6.903 |
| 4500 | 62.945 | 421.371 | 363.863 | 258.786 | 547.283 | 582.253 | -6.759 |
| 4600 | 63.016 | 422.755 | 365.128 | 265 084 | 549.960 | 583.001 | -6.620 |
| 4700 | 63 090 | 424 111 | 366.369 | 271.390 | 552.636 | 583.690 | -6.487 |
| 4800 | 63.167 | 425 440 | 367.586 | 277.703 | 555.308 | 584.323 | -6.359 |
| 4900 | 63.247 | 426.744 | 368.780 | 284.023 | 557 973 | 584.900 | -6.235 |
| 5000 | 63.329 | 428.022 | 369.952 | 290.352 | 560.629 | 585.422 | -6.116 |
| 5100 | 63.413 | 429.277 | 371 103 | 296.689 | 563.274 | 585.892 | -6.001 |
| 5200 | 63.499 | 430.509 | 372.234 | 303.035 | 565.904 | 586.310 | -5.890 |
| 5300 | 63.587 | 431 720 | 373.345 | 309.389 | 568.520 | 586.677 | -5.782 |
| 5400 | 63.677 | 432.909 | 374.437 | 315.752 | 571.116 | 586.995 | -5.678 |
| 5500 | 63.767 | 434 078 | 375.510 | 322.124 | 573.692 | 587.265 | -5.577 |
| 5600 | 63.859 | 435.228 | 376.567 | 328.506 | 576.246 | 587.489 | -5.480 |
| 5700 | 63.953 | 436.359 | 377.606 | 334.896 | 578.775 | 587 667 | -5.385 |
| 5800 | 64.046 | 437.472 | 378.628 | 341.296 | 581.278 | 587.801 | -5.294 |
| 5900 | 64.141 | 438.568 | 379.635 | 347 706 | 583.752 | 587.893 | -5.205 |
| 6000 | 64.235 | 439.647 | 380 626 | 354.124 | 586.196 | 587.942 | -5.118 |

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

## Molybdenum Fluoride ($MoF_2$) IDEAL GAS $M_r$ = 133.936806 Molybdenum Fluoride ($MoF_2$) $F_2Mo_1(g)$

$\Delta_{at}H°(0\ K) = 974.035 \pm 25.1\ kJ\cdot mol^{-1}$
$S°(298\ 15\ K) = [271.932 \pm 8.4]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_fH°(0\ K) = [-162\ 853 \pm 16.7]\ kJ\cdot mol^{-1}$
$\Delta_fH°(298.15\ K) = [-162.758 \pm 16.7]\ kJ\cdot mol^{-1}$

| Electronic Levels and Quantum Weights<br>$\epsilon_i$, $cm^{-1}$ | $g_i$ |
|---|---|
| 0 | [3] |
| [450] | [5] |

| Vibrational Frequencies and Degeneracies<br>$\nu$, $cm^{-1}$ |
|---|
| [700](1) |
| [150](2) |
| [700](1) |

Point Group: $[D_{\infty h}]$ $\sigma = [2]$
Bond Distance: Mo–F = [1.82] Å
Bond Angle: F–Mo–F = [180]°
Rotational Constant: $B_0 = [0.133939]\ cm^{-1}$

### Enthalpy of Formation

The adopted enthalpy of formation at 298.15 K is that derived by Brewer[1] from the high temperature mass spectrometric measurements of equilibria among gaseous fluorides by Hildenbrand (1818–2242 K).[2] *The value of $\Delta_fH°(0\ K)$ combined with JANAF data[3] for Mo(g) and* F(g) gives $\Delta_{at}H°(0\ K) = 232.8 \pm 6\ kcal\cdot mol^{-1}$ and an average Mo–F bond energy of $\Delta_{at}H°(0\ K)/2 = 116\ 4 \pm 3\ kcal\cdot mol^{-1}$.

### Heat Capacity and Entropy

We use the vibrational frequencies of 700(2) and 150(2) $cm^{-1}$ estimated by Hildenbrand[2] and adopted by Brewer [1] Brewer[1] assumed a linear molecule with a Mo–F distance of 1.82 Å as in $MoF_6$(g). No electronic level data are available for the dihalides of molybdenum. Brewer[1] uses g = 3 for the ground state and one excited level at 450 $cm^{-1}$ with g = 5 Additional electronic contributions are expected, but the electronic contribution was kept small[1] to be as consistent as possible with the smaller entropy values derived for MoF(g) and $MoF_2$(g) from the 2nd law treatment of Hildenbrand's equilibria data.[2]

This table is based on the critical analysis of data existing in 1978 by Brewer.[1]

### References

[1] L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication, (Sept. 1978), of preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.
[2] D L. Hildenbrand, J. Chem. Phys. 65, 614 (1976).
[3] JANAF Thermochemical Tables. Mo(g), 3–31–78, F(g), 9–30–65.

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | $J\cdot K^{-1}mol^{-1}$ | | | $kJ\cdot mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | -13.505 | -162.853 | -162.853 | INFINITE |
| 100 | 41.502 | 217.787 | 318.908 | -10.112 | -162.858 | -166.897 | 87.178 |
| 200 | 52.007 | 250.046 | 277.031 | -5.397 | -162.914 | -170.897 | 44.634 |
| 250 | 55.223 | 262.022 | 272.864 | -2.711 | -162.848 | -172.900 | 36.125 |
| 298.15 | 57.221 | 271.932 | 271.932 | 0. | -162.758 | -174.844 | 30.632 |
| 300 | 57.282 | 272.286 | 271.933 | 0.106 | -162 754 | -174.919 | 30.456 |
| 350 | 58.594 | 281.222 | 272.636 | 3.005 | -162.657 | -176.954 | 26.409 |
| 400 | 59.454 | 289.106 | 274.212 | 5.958 | -162.577 | -179.002 | 23.375 |
| 450 | 60.042 | 296.145 | 276.265 | 8.946 | -162.521 | -181.059 | 21.017 |
| 500 | 60.460 | 302.494 | 278.575 | 11.959 | -162.490 | -183.121 | 19.131 |
| 600 | 61 005 | 313.569 | 283.511 | 18.035 | -162.504 | -187.247 | 16.301 |
| 700 | 61.337 | 323.000 | 288.496 | 24.153 | -162.610 | -191.364 | 14.280 |
| 800 | 61.557 | 331.206 | 293.333 | 30.298 | -162.796 | -195.460 | 12.762 |
| 900 | 61.711 | 338.466 | 297 952 | 36.462 | -163.052 | -199.528 | 11.580 |
| 1000 | 61.824 | 344.974 | 302.334 | 42.639 | -163.378 | -203.564 | 10.633 |
| 1100 | 61.909 | 350.870 | 306.483 | 48.826 | -163.774 | -207.564 | 9.856 |
| 1200 | 61 976 | 356.260 | 310.410 | 55.021 | -164.244 | -211.525 | 9.207 |
| 1300 | 62.028 | 361.223 | 314.130 | 61.221 | -164.794 | -215.444 | 8.657 |
| 1400 | 62.071 | 365.821 | 317.660 | 67.426 | -165.429 | -219.316 | 8.183 |
| 1500 | 62.105 | 370 105 | 321.015 | 73.635 | -166.156 | -223.141 | 7.770 |
| 1600 | 62.134 | 374.114 | 324.210 | 79.847 | -166.980 | -226.913 | 7.408 |
| 1700 | 62.158 | 377.882 | 327.257 | 86 061 | -167.906 | -230 631 | 7.086 |
| 1800 | 62.178 | 381.435 | 330.169 | 92.278 | -168.940 | -234.292 | 6.799 |
| 1900 | 62.196 | 384.797 | 332.957 | 98 497 | -170.088 | -237.892 | 6.540 |
| 2000 | 62.211 | 387.988 | 335.629 | 104.717 | -171.355 | -241.428 | 6.305 |
| 2100 | 62.224 | 391.024 | 338 195 | 110.939 | -172.747 | -244.898 | 6.092 |
| 2200 | 62.235 | 393.918 | 340.663 | 117.162 | -174.269 | -248.299 | 5 895 |
| 2300 | 62.245 | 396.685 | 343.039 | 123.386 | -175.928 | -251.627 | 5.715 |
| 2400 | 62.254 | 399.335 | 345.330 | 129.611 | -177.729 | -254.880 | 5.547 |
| 2500 | 62.262 | 401.876 | 347.541 | 135.837 | -179.682 | -258.055 | 5.392 |
| 2600 | 62.269 | 404.318 | 349.678 | 142.063 | -181.803 | -261.149 | 5.247 |
| 2700 | 62.275 | 406.668 | 351.746 | 148.291 | -184.129 | -264 157 | 5 110 |
| 2800 | 62.281 | 408.933 | 353.748 | 154.518 | -186.720 | -267.075 | 4.982 |
| 2900 | 62.286 | 411.119 | 355.689 | 160.747 | -225.538 | -269.845 | 4.860 |
| 3000 | 62.290 | 413.230 | 357.572 | 166.975 | -226.856 | -271.350 | 4.725 |
| 3100 | 62.294 | 415.273 | 359.401 | 173.205 | -228.147 | -272.812 | 4.597 |
| 3200 | 62.298 | 417.251 | 361 178 | 179.434 | -229.409 | -274.232 | 4.476 |
| 3300 | 62.302 | 419.168 | 362.906 | 185.664 | -230.640 | -275.614 | 4.363 |
| 3400 | 62.305 | 421.028 | 364.588 | 191.895 | -231.840 | -276.959 | 4.255 |
| 3500 | 62.308 | 422.834 | 366.227 | 198 125 | -233.007 | -278.269 | 4.153 |
| 3600 | 62.310 | 424.589 | 367.824 | 204.356 | -234.140 | -279.546 | 4.056 |
| 3700 | 62.313 | 426.297 | 369.381 | 210.587 | -235.239 | -280.792 | 3.964 |
| 3800 | 62.315 | 427.958 | 370.901 | 216.819 | -236.304 | -282.009 | 3.876 |
| 3900 | 62.317 | 429.577 | 372.385 | 223.050 | -237.334 | -283.198 | 3.793 |
| 4000 | 62.319 | 431.155 | 373.834 | 229.282 | -238.330 | -284.361 | 3.713 |
| 4100 | 62.321 | 432.694 | 375.251 | 235.514 | -239.292 | -285.500 | 3.637 |
| 4200 | 62.323 | 434.195 | 376.637 | 241.747 | -240.220 | -286.615 | 3.565 |
| 4300 | 62.324 | 435.662 | 377.992 | 247.979 | -241.115 | -287.710 | 3.495 |
| 4400 | 62.326 | 437.095 | 379.319 | 254.211 | -241.977 | -288.783 | 3.428 |
| 4500 | 62.327 | 438.495 | 380.619 | 260.444 | -242.806 | -289.837 | 3.364 |
| 4600 | 62.329 | 439.865 | 381.892 | 266.677 | -243.604 | -290.874 | 3.303 |
| 4700 | 62.330 | 441.206 | 383.140 | 272.910 | -244.371 | -291.893 | 3.244 |
| 4800 | 62.331 | 442.518 | 384.363 | 279.143 | -245.108 | -292.896 | 3.187 |
| 4900 | 62.332 | 443.803 | 385.563 | 285.376 | -245.815 | -293.885 | 3.133 |
| 5000 | 62.333 | 445.063 | 386.741 | 291.609 | -837.878 | -289.127 | 3.020 |
| 5100 | 62.334 | 446.297 | 387.896 | 297.843 | -840.208 | -278.130 | 2.849 |
| 5200 | 62.335 | 447.507 | 389.031 | 304 076 | -842.657 | -267.084 | 2.683 |
| 5300 | 62.336 | 448.695 | 390.146 | 310.310 | -845.224 | -255.991 | 2.523 |
| 5400 | 62.337 | 449.860 | 391.241 | 316.543 | -847.907 | -244.849 | 2.368 |
| 5500 | 62.337 | 451.004 | 392.317 | 322.777 | -850.706 | -233.656 | 2.219 |
| 5600 | 62.338 | 452.127 | 393.375 | 329.011 | -853.618 | -222.410 | 2.075 |
| 5700 | 62.339 | 453.230 | 394.416 | 335.244 | -856.641 | -211.113 | 1.935 |
| 5800 | 62.339 | 454.315 | 395.439 | 341.478 | -859.774 | -199.761 | 1.799 |
| 5900 | 62.340 | 455.380 | 396.446 | 347.712 | -863.012 | -188.353 | 1.668 |
| 6000 | 62.341 | 456.428 | 397.437 | 353.946 | -866.358 | -176.891 | 1.540 |

PREVIOUS: December 1978 (1 atm) CURRENT December 1978 (1 bar)

## Difluoroamidogen (NF$_2$) IDEAL GAS $M_r$ = 52.003506

$S°(298.15\ K) = 249.950\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = 44.8 \pm 8\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = 42.3 \pm 8\ kJ{\cdot}mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, cm$^{-1}$ |
|---|
| 1074(1) |
| 573(1) |
| 931(1) |

Ground State Quantum Weight: 2 $\sigma = 2$
Point Group: $C_{2v}$
Bond Distance: N–F = 1.37 Å
Bond Angle: F–N–F = 104.2°
Product of the Moments of Inertia: $I_A I_B I_C = 7.61262 \times 10^{-116}\ g^3{\cdot}cm^6$

### Enthalpy of Formation

Colburn and Johnson[1] reported the study of the dissociation reaction $N_2F_4(g) = 2\ NF_2(l)$ by two independent methods (a) measurement of the pressure variation with temperature at constant volume and (b) a spectrophotometric method based on the temperature dependence of the ultraviolet absorption of NF$_2$ radical. The authors gave a more detailed account of their data in a later publication.[2] The contents of these articles indicate that 2 NF$_2$(l) should read 2 NF$_2$(g) in the above reaction. The first method gave a value of 19.85 kcal·mol$^{-1}$ for the enthalpy of dissociation in the temperature range 373 to 423 K which corresponds to 19.87 kcal·mol$^{-1}$ at 298 15 K. From their $\Delta H$ and $\Delta S$ data, $\Delta G$ was calculated and used in a 3rd law evaluation of the enthalpy of dissociation. The $\Delta_r H°(298.15\ K)$ so calculated showed an increasing trend with increasing temperature; the average value was 22.87 kcal·mol$^{-1}$ which is not in agreement with their value of 19.87 kcal·mol$^{-1}$. The spectrophotometric value of 21.7 kcal·mol$^{-1}$ at 298.15 K was obtained from the integrated Van't Hoff equation.

Piette, Johnson, Booman and Colburn[3] studied the temperature dependence of the EPR spectrum of the NF$_2$ radical. They obtained a 2nd law value of 19.3 kcal·mol$^{-1}$ for the enthalpy of dissociation. This value, however, depends upon the degree of dissociation of N$_2$F$_4$ which they calculated from the (dP/dT) measurements of Colburn and Johnson.[1] Any error in the (dP/dT) measurements would manifest itself in like manner here.

Doorenbos and Loy[4] investigated the ESR spectrum of the N$_2$F$_4$–NF$_2$ equilibrium from which they calculated a 2nd law value of 19.8 kcal mol$^{-1}$ for the enthalpy of dissociation. They report that at 25°C and 13 atm, N$_2$F$_4$ is 0.022% dissociated in the vapor phase. A 3rd law calculation using this datum and the relationship $K_p = (4\alpha^2/1-\alpha^2)P_T$, where $\alpha$ is the degree of dissociation of N$_2$F$_4$ and $P_T$ is the total pressure, gave a heat of dissociation of 21.79 kcal·mol$^{-1}$ at 298 15 K, this is not in agreement with their 2nd law value.

Herron and Diebler[5] report thermal dissociation data for N$_2$F$_4$. From their data they calculated a 2nd law value of 21.5 kcal·mol$^{-1}$ for the heat of dissociation of N$_2$F$_4$. A 2nd and 3rd law evaluation of their data was performed. It is found that if the k factor, relating their measured ion abundances to partial pressure, is taken as $4.72 \times 10^{-8}$, a 3rd law is obtained that shows slight scatter but no temperature dependence. Excluding those points that showed scatter, the 3rd law heat of dissociation at 298.15 K is 22.27 kcal·mol$^{-1}$. A 2nd law plot gives a heat value of 22.23 kcal·mol$^{-1}$ at an average temperature of 400 K or 22.25 kcal·mol$^{-1}$ at 298.15 K. Those points that deviated from the chosen straight line in the 2nd law plot shows corresponding deviations in the 3rd law calculation. Those points lying on the 2nd law slope give a constant 3rd law value.

The enthalpy of dissociation for $N_2F_4(g) = 2\ NF_2(g)$ is taken to be 22.26 kcal·mol$^{-1}$. Utilizing the enthalpy of formation of N$_2$F$_4$(g), the enthalpy of formation of the difluoroamino radical becomes 10.1 ± 2.0 kcal·mol$^{-1}$. All values for the enthalpy of dissociation fall within the limits of error assigned to the enthalpy of formation of NF$_2$.

### Heat Capacity and Entropy

Refer to table on tetrafluorohydrazine, N$_2$F$_4$(g), for discussion.

### References

[1] C. B. Colburn and F. A. Johnson, J. Chem. Phys. 33, 1869 (1960).
[2] C. B. Colburn and F. A. Johnson, J. Am. Chem. Soc. 83, 3043 (1961).
[3] L. H. Piette, F. A Johnson, K. A. Booman and C B. Colburn, J. Chem. Phys. 35, 1481 (1961).
[4] H. E. Doorenbos and B. R. Loy, J. Chem. Phys. 39, 2393 (1963).
[5] J. T. Herron and V. H. Dibeler, J. Res. Nat. Bur. Stand. 65A, 405 (1961).

## Difluoroamidogen (NF$_2$) F$_2$N$_1$(g)

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0 | INFINITE | −10.575 | 44.844 | 44.844 | INFINITE |
| 100 | 33.409 | 210.747 | 283.220 | −7.247 | 43.813 | 47.766 | −24.950 |
| 200 | 36.304 | 234.591 | 253.546 | −3.791 | 42.885 | 52.096 | −13.606 |
| 250 | 38.656 | 242.940 | 250.612 | −1.918 | 42.528 | 54.441 | −11.375 |
| 298.15 | 41.005 | 249.950 | 249.950 | 0. | 42.258 | 56.762 | −9.944 |
| 300 | 41.093 | 250.204 | 249.951 | 0.076 | 42.249 | 56.852 | −9.899 |
| 350 | 43.377 | 256.713 | 250.460 | 2.189 | 42.045 | 59.302 | −8.850 |
| 400 | 45.399 | 262.640 | 251.617 | 4.409 | 41.905 | 61.778 | −8.067 |
| 450 | 47.136 | 268.091 | 253.149 | 6.724 | 41.820 | 64.268 | −7.460 |
| 500 | 48.604 | 273.135 | 254.898 | 9.118 | 41.779 | 66.765 | −6.975 |
| 600 | 50.874 | 282.209 | 258.711 | 14.099 | 41.794 | 71.762 | −6.247 |
| 700 | 52.481 | 290.179 | 262.649 | 19.271 | 41.893 | 76.750 | −5.727 |
| 800 | 53.639 | 297.267 | 266.542 | 24.580 | 42.038 | 81.720 | −5.336 |
| 900 | 54.491 | 303.636 | 270.315 | 29.989 | 42.204 | 86.670 | −5.030 |
| 1000 | 55.132 | 309.412 | 273.941 | 35.471 | 42.377 | 91.602 | −4 785 |
| 1100 | 55.625 | 314.691 | 277.409 | 41.010 | 42.547 | 96.516 | −4.583 |
| 1200 | 56.010 | 319.548 | 280.721 | 46.593 | 42.709 | 101.415 | −4.414 |
| 1300 | 56.316 | 324.044 | 283.883 | 52.210 | 42.860 | 106.301 | −4.271 |
| 1400 | 56.563 | 328.227 | 286.902 | 57.854 | 42.997 | 111.176 | −4.148 |
| 1500 | 56.766 | 332.136 | 289.789 | 63.521 | 43.119 | 116.041 | −4.041 |
| 1600 | 56 933 | 335.805 | 292.552 | 69.206 | 43.226 | 120.899 | −3.947 |
| 1700 | 57.073 | 339.261 | 295.199 | 74.907 | 43.319 | 125.751 | −3.864 |
| 1800 | 57.191 | 342.527 | 297.738 | 80.620 | 43.398 | 130.598 | −3.790 |
| 1900 | 57.292 | 345.622 | 300.177 | 86.344 | 43.465 | 135.440 | −3.724 |
| 2000 | 57.379 | 348.563 | 302.524 | 92.078 | 43.523 | 140.279 | −3.664 |
| 2100 | 57.453 | 351.364 | 304.783 | 97.820 | 43.575 | 145 116 | −3.610 |
| 2200 | 57.519 | 354.038 | 306.962 | 103.568 | 43.625 | 149.950 | −3.560 |
| 2300 | 57.576 | 356.596 | 309.065 | 109.323 | 43.675 | 154.782 | −3.515 |
| 2400 | 57.626 | 359.048 | 311.097 | 115.083 | 43.729 | 159.611 | −3 474 |
| 2500 | 57.670 | 361.401 | 313.062 | 120.848 | 43.791 | 164.439 | −3.436 |
| 2600 | 57.710 | 363.664 | 314.965 | 126.617 | 43.864 | 169.263 | −3.401 |
| 2700 | 57.745 | 365.843 | 316.809 | 132.390 | 43.953 | 174.085 | −3.368 |
| 2800 | 57.776 | 367.943 | 318.598 | 138.166 | 44.059 | 178.902 | −3.337 |
| 2900 | 57.805 | 369.971 | 320.335 | 143.945 | 44.187 | 183.716 | −3.309 |
| 3000 | 57.831 | 371.931 | 322.022 | 149.727 | 44.337 | 188.525 | −3.283 |
| 3100 | 57.854 | 373.828 | 323.663 | 155.511 | 44.514 | 193.328 | −3.258 |
| 3200 | 57.875 | 375.665 | 325.260 | 161.297 | 44.718 | 198.125 | −3.234 |
| 3300 | 57.894 | 377.446 | 326.814 | 167.086 | 44.951 | 202.916 | −3.212 |
| 3400 | 57.912 | 379.175 | 328.329 | 172.876 | 45.215 | 207.699 | −3.191 |
| 3500 | 57.928 | 380.854 | 329.806 | 178.668 | 45.510 | 212.474 | −3 171 |
| 3600 | 57.943 | 382.486 | 331.246 | 184.462 | 45.838 | 217.240 | −3.152 |
| 3700 | 57.957 | 384.074 | 332.653 | 190.257 | 46.199 | 221.996 | −3.134 |
| 3800 | 57.969 | 385.619 | 334.027 | 196.053 | 46.592 | 226.742 | −3.117 |
| 3900 | 57.981 | 387.125 | 335.369 | 201.851 | 47.019 | 231.477 | −3.100 |
| 4000 | 57.992 | 388.593 | 336.681 | 207.649 | 47.479 | 236.201 | −3.084 |
| 4100 | 58.002 | 390.026 | 337.965 | 213.449 | 47.972 | 240.913 | −3.069 |
| 4200 | 58.011 | 391.423 | 339.221 | 219.249 | 48.497 | 245.613 | −3.055 |
| 4300 | 58.020 | 392.788 | 340.451 | 225.051 | 49.055 | 250.299 | −3.041 |
| 4400 | 58.028 | 394.122 | 341.656 | 230.853 | 49.644 | 254.973 | −3.027 |
| 4500 | 58.035 | 395.427 | 342.836 | 236.656 | 50.265 | 259.632 | −3.014 |
| 4600 | 58.042 | 396.702 | 343.993 | 242.460 | 50.916 | 264.278 | −3.001 |
| 4700 | 58.049 | 397.950 | 345.128 | 248.265 | 51.597 | 268.909 | −2.989 |
| 4800 | 58.055 | 399.173 | 346.241 | 254.070 | 52.306 | 273.525 | −2.977 |
| 4900 | 58.061 | 400.370 | 347.334 | 259.876 | 53.045 | 278.126 | −2.965 |
| 5000 | 58.067 | 401.543 | 348.406 | 265.682 | 53.810 | 282.712 | −2.953 |
| 5100 | 58.072 | 402.693 | 349.460 | 271.489 | 54.602 | 287.282 | −2.942 |
| 5200 | 58.077 | 403.820 | 350.494 | 277.297 | 55.420 | 291.837 | −2.932 |
| 5300 | 58.081 | 404.927 | 351.511 | 283.105 | 56.264 | 296.375 | −2.921 |
| 5400 | 58.086 | 406.012 | 352.510 | 288.913 | 57.131 | 300.897 | −2.911 |
| 5500 | 58.090 | 407.078 | 353.493 | 294.722 | 58.022 | 305.403 | −2.900 |
| 5600 | 58.094 | 408.125 | 354.459 | 300.531 | 58.936 | 309.893 | −2.891 |
| 5700 | 58.097 | 409 153 | 355.409 | 306.341 | 59.872 | 314.366 | −2.881 |
| 5800 | 58.101 | 410.164 | 356.345 | 312.150 | 60.829 | 318.822 | −2.871 |
| 5900 | 58.104 | 411.157 | 357.265 | 317.961 | 61.805 | 323.263 | −2.862 |
| 6000 | 58.108 | 412.134 | 358.172 | 323.771 | 62.802 | 327.685 | −2.853 |

PREVIOUS: March 1964 (1 atm)    CURRENT: March 1964 (1 bar)

Difluoroamidogen (NF$_2$) F$_2$N$_1$(g)

## Nitrogen Fluoride, Cis ($N_2F_2$) IDEAL GAS $M_r = 66.010206$ Nitrogen Fluoride, Cis (FNNF) $F_2N_2(g)$

$\Delta_fH°(0\ K) = 74.711 \pm 5.0\ kJ\cdot mol^{-1}$
$S°(298.15\ K) = 259.810\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = 68.618 \pm 5.0\ kJ\cdot mol^{-1}$

| Electronic Levels and Quantum Weights<br>$\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ |
|---|---|
| 896(1) | 952(1) |
| 1524(1) | 573(1) |
| 552(1) | 737(1) |

Ground State Quantum Weight: = 1 $\sigma = 2$
Point Group: $C_{2v}$
Bond Distances: N–F = 1.384 Å; N–N = 1.214 Å
Bond Angle: F–N–N = 114.5 ± 0.5°
Product of the Moments of Inertia: $I_AI_BI_C = 6.590443 \times 10^{-115}\ g^3\cdot cm^6$

### Enthalpy of Formation

The enthalpy of formation was derived from the heat of reaction $N_2F_2(g) + 8/3\ NH_3(g) = 2\ NH_4F(cr) + 4/3\ N_2(g)$ which was measured calorimetrically by Armstrong and Marantz.[1] There are two isomers, the trans and the active form of difluoridiazine. The enthalpy of formation were determined to be 19.4 and 16.4 kcal·mol$^{-1}$ for the trans and the active isomers, respectively. The active form of $N_2F_2$ has been interpreted here as the cis isomer which will be discussed later. The enthalpy of isomerization has also been reported as 3.0 kcal·mol$^{-1}$ by Armstrong and Marantz. The value, $\Delta_fH°$(cis $N_2F_2$, g, 298.15 K) = 16.4 kcal·mol$^{-1}$, is adopted in the tabulation.

Pankratov *et al.*[2] have measured the enthalpy of reaction $N_2F_2(g) + 3\ KI = 2\ KF + N_2 + KI_3$ in acidic solution (pH = 3), and reported $\Delta_fH°$(active $N_2F_2$, g, 298.15 K) = 25.3 ± 2.0 kcal·mol$^{-1}$.

The "heat of isomerization" has been reported as 27.5 ± 5.0 kcal·mol$^{-1}$ by Colburn *et al.*[9] The derivation of this value is unknown. The authors observed three values of the equilibrium constant for the isomerization reaction. Third law analysis of their data gives $\Delta_rH°$(298.15 K) = 2.52 ± 0.05 kcal·mol$^{-1}$ for the reaction *cis* $N_2F_2(g) \rightarrow$ trans $N_2F_2(g)$ which is in good agreement with Armstrong and Sidney's data.

### Heat Capacity and Entropy

Although the infrared spectrum[7,8] of the active form of $N_2F_2(g)$ has been interpreted as favoring the 1,1–di–flurodiazine over the *cis* configuration,[3,4] NMR[5] and microwave[6] studies definitely indicate the latter. The vibrational frequencies[7] previously assigned to the 1,1–difluorodiazine have been adopted here for the *cis* isomer. The selected bond distances and angle were taken from the isotopic nitrogen microwave studies.[6] The principal moments of inertia were: $I_A = 4.2469 \times 10^{-39}$, $I_B = 10.5134 \times 10^{-39}$, and $I_C = 14.7603 \times 10^{-39}\ g\cdot cm^2$.

Refer to the trans–$N_2F_2(g)$ table for the comparison of the different physical properties between *trans* and *cis* isomers.

### References

[1] G. T. Armstrong and S. Marantz, J. Chem. Phys. 38, 169 (1963).
[2] A. V. Pankratov, A. N. Zercheninov, O. G. Talakin, O. M. Sokolov, and N. A. Knyazeva, Zh. Fiz. Khim. 37, 1399 (1963).
[3] R. Ettinger, F. A. Johnson and C. B. Colburn, J. Chem. Phys. 34, 2187 (1961).
[4] J. T. Herron and V. H. Dibeler, J. Res. Nat. Bur. Stand. 65A, 405 (1961).
[5] J. H. Noggle, J. D. Baldeschwieler, and C. B. Colburn, J. Chem. Phsy. 37, 182 (1962).
[6] R. L. Kuczkowski and E. B. Wilson, Jr., J. Chem. Phys. 39, 1030 (1963).
[7] R. H. Sanborn, J. Chem. Phys. 33, 1855 (1960).
[8] R. H. Sanborn, J. Chem. Phys. 34, 2188 (1961).
[9] C. B. Colburn, F. A. Johnson, A. Kennedy, K. McCallum, L. C. Metzger and C. O. Parker, J. Amer. Chem. Soc. 81, 6397 (1959).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ (J·K$^{-1}$mol$^{-1}$) | $S°$ (J·K$^{-1}$mol$^{-1}$) | $-[G°-H°(T_r)]/T$ (J·K$^{-1}$mol$^{-1}$) | $H°-H°(T_r)$ (kJ·mol$^{-1}$) | $\Delta_fH°$ (kJ·mol$^{-1}$) | $\Delta_fG°$ (kJ·mol$^{-1}$) | log $K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0. | 0. | INFINITE | −11.402 | 74.711 | 74.711 | INFINITE |
| 100 | 33.621 | 216.960 | 297.678 | −8.072 | 72.232 | 83.554 | −43.644 |
| 200 | 40.350 | 241.888 | 264.073 | −4.437 | 70.027 | 95.777 | −25.014 |
| 250 | 45.327 | 251.424 | 260.607 | −2.296 | 69.210 | 102.313 | −21.377 |
| 298.15 | 49.961 | 259.810 | 259.810 | 0. | 68.618 | 108.745 | −19.052 |
| 300 | 50.131 | 260.119 | 259.811 | 0.093 | 68.598 | 108.994 | −18.978 |
| 350 | 54.432 | 268.177 | 260.437 | 2.709 | 68.169 | 115.763 | −17.277 |
| 400 | 58.158 | 275.695 | 261.880 | 5.526 | 67.895 | 122.583 | −16.008 |
| 450 | 61.339 | 282.734 | 263.810 | 8.516 | 67.752 | 129.429 | −15.024 |
| 500 | 64.039 | 289.340 | 266.036 | 11.652 | 67.716 | 136.284 | −14.238 |
| 600 | 68.275 | 301.411 | 270.946 | 18.279 | 67.887 | 149.987 | −13.057 |
| 700 | 71.349 | 312.179 | 276.081 | 25.268 | 68.281 | 163.641 | −12.211 |
| 800 | 73.616 | 321.862 | 281.209 | 32.522 | 68.816 | 177.229 | −11.572 |
| 900 | 75.317 | 330.635 | 286.221 | 39.973 | 69.436 | 190.744 | −11.070 |
| 1000 | 76.619 | 338.641 | 291.069 | 47.572 | 70.106 | 204.187 | −10.666 |
| 1100 | 77.631 | 345.993 | 295.732 | 55.287 | 70.803 | 217.561 | −10.331 |
| 1200 | 78.432 | 352.784 | 300.207 | 63.092 | 71.513 | 230.872 | −10.050 |
| 1300 | 79.074 | 359.088 | 304.497 | 70.968 | 72.226 | 244.123 | −9.809 |
| 1400 | 79.596 | 364.968 | 308.609 | 78.902 | 72.936 | 257.319 | −9.601 |
| 1500 | 80.026 | 370.474 | 312.551 | 86.884 | 73.639 | 270.464 | −9.418 |
| 1600 | 80.383 | 375.651 | 316.335 | 94.905 | 74.333 | 283.564 | −9.257 |
| 1700 | 80.683 | 380.533 | 319.969 | 102.959 | 75.016 | 296.620 | −9.114 |
| 1800 | 80.938 | 385.152 | 323.463 | 111.040 | 75.688 | 309.636 | −8.985 |
| 1900 | 81.155 | 389.534 | 326.826 | 119.145 | 76.351 | 322.614 | −8.869 |
| 2000 | 81.342 | 393.702 | 330.067 | 127.270 | 77.007 | 335.559 | −8.764 |
| 2100 | 81.505 | 397.675 | 333.192 | 135.413 | 77.657 | 348.470 | −8.668 |
| 2200 | 81.646 | 401.470 | 336.210 | 143.571 | 78.306 | 361.351 | −8.580 |
| 2300 | 81.770 | 405.102 | 339.127 | 151.742 | 78.955 | 374.202 | −8.498 |
| 2400 | 81.879 | 408.584 | 341.949 | 159.924 | 79.609 | 387.025 | −8.423 |
| 2500 | 81.976 | 411.929 | 344.682 | 168.117 | 80.271 | 399.820 | −8.354 |
| 2600 | 82.062 | 415.146 | 347.331 | 176.319 | 80.944 | 412.589 | −8.289 |
| 2700 | 82.140 | 418.244 | 349.900 | 184.529 | 81.632 | 425.332 | −8.229 |
| 2800 | 82.209 | 421.233 | 352.394 | 192.747 | 82.338 | 438.049 | −8.172 |
| 2900 | 82.271 | 424.119 | 354.818 | 200.971 | 83.064 | 450.740 | −8.119 |
| 3000 | 82.327 | 426.909 | 357.175 | 209.201 | 83.813 | 463.405 | −8.069 |
| 3100 | 82.378 | 429.609 | 359.468 | 217.436 | 84.588 | 476.046 | −8.021 |
| 3200 | 82.425 | 432.225 | 361.701 | 225.676 | 85.389 | 488.661 | −7.977 |
| 3300 | 82.467 | 434.762 | 363.877 | 233.921 | 86.219 | 501.250 | −7.934 |
| 3400 | 82.506 | 437.225 | 365.998 | 242.170 | 87.079 | 513.814 | −7.894 |
| 3500 | 82.542 | 439.617 | 368.068 | 250.422 | 87.970 | 526.352 | −7.855 |
| 3600 | 82.574 | 441.942 | 370.088 | 258.678 | 88.893 | 538.865 | −7.819 |
| 3700 | 82.604 | 444.205 | 372.060 | 266.937 | 89.847 | 551.351 | −7.784 |
| 3800 | 82.632 | 446.409 | 373.988 | 275.199 | 90.834 | 563.810 | −7.750 |
| 3900 | 82.658 | 448.555 | 375.873 | 283.463 | 91.854 | 576.244 | −7.718 |
| 4000 | 82.681 | 450.648 | 377.716 | 291.730 | 92.905 | 588.651 | −7.687 |
| 4100 | 82.704 | 452.690 | 379.520 | 299.999 | 93.989 | 601.031 | −7.657 |
| 4200 | 82.724 | 454.683 | 381.286 | 308.271 | 95.105 | 613.385 | −7.629 |
| 4300 | 82.743 | 456.630 | 383.015 | 316.544 | 96.252 | 625.711 | −7.601 |
| 4400 | 82.761 | 458.533 | 384.710 | 324.819 | 97.430 | 638.011 | −7.574 |
| 4500 | 82.778 | 460.393 | 386.371 | 333.096 | 98.639 | 650.283 | −7.548 |
| 4600 | 82.794 | 462.212 | 388.000 | 341.375 | 99.877 | 662.528 | −7.523 |
| 4700 | 82.808 | 463.993 | 389.598 | 349.655 | 101.144 | 674.746 | −7.499 |
| 4800 | 82.822 | 465.737 | 391.166 | 357.936 | 102.438 | 686.937 | −7.475 |
| 4900 | 82.835 | 467.444 | 392.706 | 366.219 | 103.760 | 699.100 | −7.453 |
| 5000 | 82.847 | 469.118 | 394.217 | 374.503 | 105.109 | 711.236 | −7.430 |
| 5100 | 82.859 | 470.759 | 395.702 | 382.789 | 106.483 | 723.345 | −7.409 |
| 5200 | 82.869 | 472.368 | 397.161 | 391.075 | 107.882 | 735.427 | −7.387 |
| 5300 | 82.880 | 473.946 | 398.595 | 399.362 | 109.305 | 747.482 | −7.367 |
| 5400 | 82.889 | 475.496 | 400.005 | 407.651 | 110.751 | 759.509 | −7.347 |
| 5500 | 82.898 | 477.017 | 401.391 | 415.940 | 112.220 | 771.510 | −7.327 |
| 5600 | 82.907 | 478.511 | 402.755 | 424.231 | 113.710 | 783.484 | −7.308 |
| 5700 | 82.915 | 479.978 | 404.097 | 432.522 | 115.220 | 795.430 | −7.289 |
| 5800 | 82.923 | 481.420 | 405.418 | 440.814 | 116.750 | 807.350 | −7.271 |
| 5900 | 82.930 | 482.838 | 406.718 | 449.106 | 118.299 | 819.244 | −7.253 |
| 6000 | 82.937 | 484.232 | 407.998 | 457.400 | 119.865 | 831.111 | −7.235 |

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

## Nitrogen Fluoride, Trans ($N_2F_2$) IDEAL GAS $M_r$ = 66.010206 Nitrogen Fluoride, Trans (FNNF) $F_2N_2(g)$

$S°(298.15 K) = 262.660 J·K^{-1}·mol^{-1}$

$\Delta_fH°(0 K) = 86.436 \pm 5.0 kJ·mol^{-1}$
$\Delta_fH°(298.15 K) = 81.170 \pm 5.0 kJ·mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ |
|---|---|
| 1010(1) | 989(1) |
| 1636(1) | 421(1) |
| 592(1) | 360(1) |

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group. $C_{2h}$
Bond Distances: N–F = 1.44 Å; N–N = 1.25 Å
Bond Angle: F–N–N = 115°
Product of the Moments of Inertia: $I_AI_BI_C = 4.328461 \times 10^{-115} g^3·cm^6$

### Enthalpy of Formation

Armstrong and Marantz[1] have measured calorimetrically the enthalpy of reaction $N_2F_2(g) + 8/3\ NH_3(g) = 2\ NH_4F(cr) + 4/3\ N_2(g)$, and reported $\Delta_fH°$(*trans* $N_2F_2$, g, 298.15 K) = 19.4 ± 1 2 kcal·mol$^{-1}$ which is adopted in this tabulation.

### Heat Capacity and Entropy

The bond distances and bond angle were obtained from Bauer[2] by electron diffraction. The fundamental vibrational frequencies were obtained from Sanborn[3] by infrared spectroscopy The three principal moments of inertia are $I_A = 0.9191 \times 10^{-39}$, $I_B = 21.2461 \times 10^{-39}$, and $I_C = 22.1652 \times 10^{-39} g·cm^2$.

As pointed out by Ettinger *et al*.,[4] the *trans* $N_2F_2$ is the less active isomer which is different from the active isomer by its (1) vapor pressure (2) boiling point (3) heat of vaporization (4) critical temperature (5) melting point (6) mass spectral cracking pattern (7) NMR spectrum (8) infrared spectrum (9) heat of isomerization (10) reactivity with mercury and glass.

### References

[1] G. T. Armstrong and S. Marantz, J. Chem. Phys. 38, 169 (1963).
[2] S. H. Bauer, J. Amer. Chem. Soc 69, 3104 (1947).
[3] R. H. Sanborn, J. Chem. Phys. 33, (1955).
[4] R. Ettinger, F. A. Johnson and C. B. Colburn, J. Chem. Phys. 34, 2187 (1961).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ (J·K⁻¹mol⁻¹) | S° (J·K⁻¹mol⁻¹) | $-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹) | $H°-H°(T_r)$ (kJ·mol⁻¹) | $\Delta_fH°$ (kJ·mol⁻¹) | $\Delta_fG°$ (kJ·mol⁻¹) | log $K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0. | 0. | INFINITE | −12.229 | 86.436 | 86.436 | INFINITE |
| 100 | 35.368 | 215.607 | 304.259 | −8.865 | 83.990 | 95.448 | −49.857 |
| 200 | 45.076 | 243.033 | 267.293 | −4.852 | 82.164 | 107.685 | −28.124 |
| 250 | 49.593 | 253.586 | 263.519 | −2.483 | 81.575 | 114.137 | −23.848 |
| 298.15 | 53.466 | 262.660 | 262.660 | 0. | 81.170 | 120.448 | −21.102 |
| 300 | 53.606 | 262.991 | 262.661 | 0.099 | 81.157 | 120.691 | −21.014 |
| 350 | 57.134 | 271.525 | 263.326 | 2.870 | 80.881 | 127.304 | −18.999 |
| 400 | 60.214 | 279.360 | 264.848 | 5.805 | 80.726 | 133.948 | −17.492 |
| 450 | 62.886 | 286.610 | 266.868 | 8.884 | 80.673 | 140.605 | −16.321 |
| 500 | 65.199 | 293.359 | 269.183 | 12.088 | 80.704 | 147.263 | −15.384 |
| 600 | 68.922 | 305.591 | 274.254 | 18.803 | 80.962 | 160.554 | −13.977 |
| 700 | 71.707 | 316.435 | 279.520 | 25.841 | 81.406 | 173.786 | −12.968 |
| 800 | 73.810 | 326.154 | 284.752 | 33.121 | 81.967 | 186.946 | −12.206 |
| 900 | 75.417 | 334.944 | 289.849 | 40.586 | 82.601 | 200.031 | −11.610 |
| 1000 | 76.663 | 342.958 | 294.765 | 48.193 | 83.278 | 213.043 | −11.128 |
| 1100 | 77.643 | 350.312 | 299.485 | 55.910 | 83.978 | 225.986 | −10.731 |
| 1200 | 78.424 | 357.103 | 304.007 | 63 715 | 84.688 | 238.864 | −10.397 |
| 1300 | 79.055 | 363.406 | 308.337 | 71.590 | 85.400 | 251.683 | −10.113 |
| 1400 | 79.571 | 369.284 | 312.482 | 79.522 | 86.108 | 264 448 | −9.867 |
| 1500 | 79 998 | 374.789 | 316 455 | 87.501 | 86.808 | 277.162 | −9.652 |
| 1600 | 80.354 | 379.963 | 320.264 | 95.519 | 87.499 | 289.829 | −9.462 |
| 1700 | 80.654 | 384.844 | 323.920 | 103.570 | 88.179 | 302.454 | −9.293 |
| 1800 | 80.908 | 389.462 | 327.435 | 111.649 | 88.848 | 315.039 | −9.142 |
| 1900 | 81.127 | 393.842 | 330.815 | 119.751 | 89.508 | 327.587 | −9.006 |
| 2000 | 81.315 | 398.008 | 334.072 | 127.873 | 90.161 | 340.101 | −8.883 |
| 2100 | 81.478 | 401.980 | 337.212 | 136.013 | 90.809 | 352.582 | −8.770 |
| 2200 | 81.621 | 405 773 | 340.242 | 144.168 | 91.455 | 365.032 | −8.667 |
| 2300 | 81.746 | 409.404 | 343.171 | 152.336 | 92.102 | 377.453 | −8.572 |
| 2400 | 81.857 | 412.886 | 346.004 | 160.517 | 92.753 | 389.846 | −8.485 |
| 2500 | 81.955 | 416.229 | 348.746 | 168.707 | 93.413 | 402.211 | −8.404 |
| 2600 | 82.042 | 419.445 | 351.404 | 176.907 | 94.084 | 414.550 | −8.328 |
| 2700 | 82.120 | 422.543 | 353.982 | 185.115 | 94.770 | 426.862 | −8.258 |
| 2800 | 82.191 | 425.531 | 356.484 | 193.331 | 95.474 | 439.149 | −8.192 |
| 2900 | 82.254 | 428.416 | 358.915 | 201.553 | 96.199 | 451.411 | −8.131 |
| 3000 | 82.311 | 431.206 | 361.279 | 209.782 | 96.946 | 463.647 | −8.073 |
| 3100 | 82.363 | 433.906 | 363.578 | 218.015 | 97.719 | 475.857 | −8.018 |
| 3200 | 82.410 | 436.521 | 365.817 | 226.254 | 98.519 | 488.042 | −7.966 |
| 3300 | 82.453 | 439.058 | 367.998 | 234.497 | 99.348 | 500.202 | −7.918 |
| 3400 | 82.493 | 441.520 | 370.125 | 242.745 | 100.206 | 512.337 | −7.871 |
| 3500 | 82.529 | 443.912 | 372.199 | 250.996 | 101.096 | 524.445 | −7.827 |
| 3600 | 82.562 | 446.237 | 374.223 | 259.250 | 102.017 | 536.528 | −7.785 |
| 3700 | 82.593 | 448.500 | 376.200 | 267.508 | 102.971 | 548.585 | −7.745 |
| 3800 | 82.621 | 450.703 | 378.132 | 275.769 | 103.956 | 560.615 | −7.706 |
| 3900 | 82.647 | 452.849 | 380.020 | 284.032 | 104.975 | 572.619 | −7.669 |
| 4000 | 82.671 | 454.942 | 381.867 | 292.298 | 106.026 | 584.597 | −7.634 |
| 4100 | 82.694 | 456.984 | 383.675 | 300.566 | 107.108 | 596.548 | −7.600 |
| 4200 | 82.715 | 458.977 | 385.444 | 308.837 | 108.223 | 608.472 | −7.567 |
| 4300 | 82.734 | 460.923 | 387.177 | 317.109 | 109.370 | 620.369 | −7.536 |
| 4400 | 82.753 | 462.825 | 388.875 | 325.384 | 110.547 | 632.239 | −7.506 |
| 4500 | 82.770 | 464.685 | 390.539 | 333.660 | 111.754 | 644.083 | −7.476 |
| 4600 | 82.786 | 466.505 | 392.170 | 341.938 | 112.992 | 655.898 | −7.448 |
| 4700 | 82.801 | 468.285 | 393.771 | 350.217 | 114.258 | 667.687 | −7.421 |
| 4800 | 82.815 | 470.029 | 395.342 | 358.498 | 115.552 | 679.449 | −7.394 |
| 4900 | 82.828 | 471.736 | 396.883 | 366.780 | 116.873 | 691.183 | −7.368 |
| 5000 | 82.840 | 473.410 | 398.397 | 375.063 | 118.221 | 702.890 | −7.343 |
| 5100 | 82.852 | 475.050 | 399.884 | 383.348 | 119.594 | 714.570 | −7.319 |
| 5200 | 82.863 | 476.659 | 401.345 | 391.634 | 120.992 | 726.222 | −7.295 |
| 5300 | 82.874 | 478.238 | 402.781 | 399.921 | 122.415 | 737.848 | −7.272 |
| 5400 | 82.883 | 479.787 | 404.193 | 408.208 | 123.860 | 749.446 | −7.249 |
| 5500 | 82.893 | 481.308 | 405.581 | 416.497 | 125.328 | 761.017 | −7.228 |
| 5600 | 82.902 | 482.802 | 406.947 | 424.787 | 126.818 | 772.562 | −7.206 |
| 5700 | 82.910 | 484.269 | 408.290 | 433.078 | 128.328 | 784.080 | −7.185 |
| 5800 | 82.918 | 485.711 | 409.613 | 441.369 | 129.857 | 795.571 | −7.165 |
| 5900 | 82 926 | 487 128 | 410.915 | 449.661 | 131.406 | 807.036 | −7.145 |
| 6000 | 82 933 | 488.522 | 412.197 | 457.954 | 132.972 | 818.474 | −7.125 |

PREVIOUS· December 1965 (1 atm) CURRENT December 1965 (1 bar)

Nitrogen Fluoride, Trans (FNNF) $F_2N_2(g)$

## Sodium Fluoride, Ion ($NaF_2^-$) IDEAL GAS $M_r = 60.987125$ Sodium Fluoride, Ion ($NaF_2^-$) $F_2Na_1^-(g)$

$S°(298.15\ K) = [250.672 \pm 8.4]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -661.011 \pm 41.8\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -669.440 \pm 41.8\ kJ\cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ |
|---|
| [400](1) |
| [170](2) |
| [650](1) |

Ground State Quantum Weight: [1] $\sigma = [2]$
Point Group: $[D_{\infty h}]$
Bond Distance. Na–F = [1 93] Å
Bond Angle. F–Na–F = [180]°
Rotational Constant: $B_0 = [0.119105]\ cm^{-1}$

### Enthalpy of Formation

The enthalpy of formation for $NaF_2^-(g)$ is estimated from three calculated values. The methods of calculation are described as follows. The first reaction we take into consideration is $NaF(g) + F^-(g) = NaF_2\ (g)$. In a manner analogous to $LiF_2$ (g) molecule (see $LiF_2^-(g)$ table for details), we assume $NaF_2^-(g)$ is stable and $\Delta_r H°(298.15\ K)$ for the reaction $NaF(g) + F^-(g) = NaF_2^-(g)$ is somewhere between 0 to $1/2(-64) = -32\ kcal\cdot mol^{-1}$ where the value $-56\ kcal\cdot mol^{-1}$ is the enthalpy of dimerization. Based on $\Delta_r H°(298.15\ K) = 0$ and $-28\ kcal\cdot mol^{-1}$, respectively, with JANAF $\Delta_f H°(298.15\ K)$ values for the species involved, we obtain $\Delta_f H°(NaF_2^-, g, 298.15\ K) = -132$ and $-164\ kcal\cdot mol^{-1}$ as the upper and lower limits.

The enthalpy of formation, based on the reaction $NaF_2^-(g) = NaF_2(g) + e^-(g)$, is $-165\ 8\ kcal\cdot mol^{-1}$, using $\Delta_r H°(298.15\ K)$ and $\Delta_f H°(NaF_2, g, 298.15\ K)$ estimated as 83.5 and $-82.3\ kcal\cdot mol^{-1}$, respectively. The $\Delta_r H°(298.15\ K)$ value is obtained from an assumption that the enthalpy change for removing an electron from $NaF_2^-(g)$ is comparable to that from $F^-(g)$. Due to the fact that the Na atom has smaller electronegativity (0.9) than that of the F atom (4.0), we expect that there is less possibility that the electron will associate with Na atom in the $NaF_2^-$ molecule. Therefore, we adopt EA(F,g), reported by Pritchard,[1] or $\Delta_r H°(298\ 15\ K) = 83.5\ kcal\cdot mol^{-1}$ for the reaction $F^-(g) = F(g) + e^-(g)$ as the $\Delta_r H°(298.15\ K)$ for $NaF_2^-\ (g) = NaF_2(g) + e^-(g)$. The value of $\Delta_f H°(298.15\ K)$ for $NaF_2(g)$ is calculated using the enthalpy change for the reaction $Na_2F_2(g) = NaF_2(g) + Na(g)$ as $145.8\ kcal\cdot mol^{-1}$ which is derived from the sum of two enthalpy changes, namely, half of the $\Delta_r H°(298.15\ K)$ value for the dimer dissociation reaction $Na_2F_2(g) = 2NaF(g)$, and the $\Delta_r H°(298.15\ K)$ for the monomer dissociation reaction $NaF(g) = Na(g) + F(g)$.

Employing $\Delta_r H°(298.15\ K) = 63.5\ kcal\cdot mol^{-1}$ for $Na_2F_2(g) = 2NaF(g)$ and $153.0\ kcal\cdot mol^{-1}$ for $NaF(g) = Na^+(g) + F^-(g)$, we estimate $\Delta_r H°(298.15\ K) = (1/2)(63.5) + 153.0 = 184.7\ kcal\cdot mol^{-1}$ for the reaction $Na_2F_2(g) = NaF_2(g) + Na^+(g)$, which leads to $\Delta_f H°(298.15\ K) = 163.4\ kcal\cdot mol^{-1}$ for $NaF_2$ (g). For all calculations the $\Delta_f H°(298.15\ K)$ values of the chemical species involved are taken from JANAF Thermochemical Tables.

$\Delta_f H°(NaF_2^-, g, 298.15\ K)$ is tentatively adopted as $-160 \pm 10\ kcal\cdot mol^{-1}$ ($-669\ 440 \pm 41.8\ kJ\cdot mol^{-1}$).

### Heat Capacity and Entropy

The molecular structure is assumed to be linear, according to the suggestion by Walsh[2] that molecules with not more than 16 valence electrons are linear in their ground state. The Na–F bond distance is estimated by comparison with that of NaF(g) reported by Veazey and Gordy.[3] The vibrational frequencies are estimated from those for the isoelectronic molecule $SiO_2(g)$.

### References

[1] H. O. Pritchard, Chem. Rev. 52, 529 (1953).
[2] A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).
[3] S. E. Veazey and W. Gordy, Phys. Rev. 138, A1303 (1965).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log K$_f$ |
| 0 | 0. | 0. | INFINITE | −13.040 | −661.011 | | |
| 100 | 40.374 | 198.472 | 295.762 | −9.729 | | | |
| 200 | 49.878 | 229.724 | 255.552 | −5.166 | | | |
| 250 | 52.805 | 241.186 | 251.564 | −2.595 | | | |
| 298.15 | 54.860 | 250.672 | 250.672 | 0. | −669.440 | −662.120 | 116.001 |
| 300 | 54.927 | 251.011 | 250.673 | 0.102 | −669.487 | −662.074 | 115.277 |
| 350 | 56.473 | 259.600 | 251.347 | 2.889 | −670 781 | −660.738 | 98.610 |
| 400 | 57.612 | 267.219 | 252.864 | 5.742 | −674.766 | −659.006 | 86.057 |
| 450 | 58.466 | 274.057 | 254 846 | 8.645 | −676.132 | −656.953 | 76.257 |
| 500 | 59.118 | 280.252 | 257.081 | 11.585 | −677.468 | −654.750 | 68.401 |
| 600 | 60.024 | 291.117 | 261.874 | 17.546 | −680.076 | −649.960 | 56.584 |
| 700 | 60.603 | 300.416 | 266.732 | 23.579 | −682.625 | −644.739 | 48.111 |
| 800 | 60.994 | 308.536 | 271.460 | 29.660 | −685.141 | −639.155 | 41.733 |
| 900 | 61 269 | 315.737 | 275 987 | 35.774 | −687.647 | −633.256 | 36.753 |
| 1000 | 61.469 | 322.203 | 280.291 | 41.912 | −690.166 | −627.078 | 32.755 |
| 1100 | 61.619 | 328.069 | 284.372 | 48.066 | −692.718 | −620 646 | 29.472 |
| 1200 | 61.735 | 333.436 | 288.240 | 54.234 | −792.085 | −611.540 | 26.620 |
| 1300 | 61.825 | 338.381 | 291.910 | 60.413 | −793.833 | −596.423 | 23.965 |
| 1400 | 61.897 | 342.965 | 295.395 | 66.599 | −795.595 | −581.172 | 21.684 |
| 1500 | 61.956 | 347.238 | 298.710 | 72.792 | −797.370 | −565.794 | 19.703 |
| 1600 | 62.004 | 351.238 | 301.869 | 78.990 | −799.158 | −550.298 | 17.965 |
| 1700 | 62.044 | 354.998 | 304.885 | 85.192 | −800.958 | −534.689 | 16.429 |
| 1800 | 62.077 | 358.545 | 307.769 | 91.398 | −802 769 | −518.974 | 15 060 |
| 1900 | 62.106 | 361.903 | 310.530 | 97.607 | −804.590 | −503.158 | 13.833 |
| 2000 | 62.130 | 365 089 | 313.179 | 103.819 | −806.418 | −487.246 | 12.726 |
| 2100 | 62.151 | 368 121 | 315.724 | 110.033 | −808.250 | −471.242 | 11.722 |
| 2200 | 62.170 | 371.012 | 318.172 | 116.250 | −810.085 | −455.151 | 10 807 |
| 2300 | 62.186 | 373.776 | 320.530 | 122.467 | −811.918 | −438.976 | 9.969 |
| 2400 | 62.200 | 376.423 | 322.804 | 128.687 | −813.748 | −422.722 | 9.200 |
| 2500 | 62.212 | 378.963 | 325.000 | 134.907 | −815.571 | −406.392 | 8.491 |
| 2600 | 62.223 | 381.403 | 327.122 | 141 129 | −817.385 | −389.989 | 7.835 |
| 2700 | 62.233 | 383.751 | 329.177 | 147.352 | −819 187 | −373.517 | 7.226 |
| 2800 | 62.241 | 386.015 | 331.166 | 153.575 | −820.976 | −356.978 | 6.659 |
| 2900 | 62.249 | 388.199 | 333.096 | 159.800 | −822.751 | −340.375 | 6.131 |
| 3000 | 62.256 | 390.309 | 334.968 | 166.025 | −824.509 | −323.711 | 5.636 |
| 3100 | 62.263 | 392.351 | 336.786 | 172.251 | −826.251 | −306.989 | 5.173 |
| 3200 | 62.269 | 394.328 | 338.554 | 178.478 | −827.975 | −290.211 | 4.737 |
| 3300 | 62.274 | 396.244 | 340.273 | 184.705 | −829.683 | −273.380 | 4.327 |
| 3400 | 62.279 | 398.103 | 341.947 | 190.933 | −831.374 | −256.497 | 3.941 |
| 3500 | 62.283 | 399.909 | 343.577 | 197.161 | −833.050 | −239.564 | 3.575 |
| 3600 | 62.287 | 401.663 | 345.166 | 203.389 | −834.711 | −222.584 | 3.230 |
| 3700 | 62.291 | 403.370 | 346.716 | 209.618 | −836.360 | −205.557 | 2.902 |
| 3800 | 62.295 | 405.031 | 348.229 | 215.847 | −837.998 | −188.487 | 2.591 |
| 3900 | 62.298 | 406.649 | 349.706 | 222.077 | −839.628 | −171.373 | 2.295 |
| 4000 | 62.301 | 408.227 | 351 150 | 228.307 | −841.252 | −154.218 | 2.014 |
| 4100 | 62.304 | 409.765 | 352.561 | 234.537 | −842.872 | −137.022 | 1.746 |
| 4200 | 62.306 | 411.266 | 353.941 | 240.768 | −844.490 | −119.786 | 1.490 |
| 4300 | 62.308 | 412.732 | 355.291 | 246.998 | −846.112 | −102.513 | 1.245 |
| 4400 | 62.311 | 414.165 | 356.613 | 253.229 | −847.699 | −85.204 | 1.012 |
| 4500 | 62.313 | 415.565 | 357.907 | 259.461 | −849.313 | −67.857 | 0.788 |
| 4600 | 62.315 | 416.935 | 359.176 | 265.692 | −850.946 | −50.474 | 0.573 |
| 4700 | 62.317 | 418.275 | 360 419 | 271.923 | −852.592 | −33.054 | 0.367 |
| 4800 | 62.318 | 419.587 | 361.638 | 278.155 | −854.255 | −15.600 | 0.170 |
| 4900 | 62.320 | 420.872 | 362.834 | 284.387 | −855.937 | 1.890 | −0.020 |
| 5000 | 62.321 | 422.131 | 364.007 | 290.619 | −857.635 | 19.413 | −0.203 |
| 5100 | 62.323 | 423.365 | 365 159 | 296.851 | −859.367 | 36.971 | −0.379 |
| 5200 | 62.324 | 424.575 | 366.290 | 303.084 | −861.128 | 54.564 | −0.548 |
| 5300 | 62.325 | 425.763 | 367.401 | 309.316 | −862.923 | 72.190 | −0.711 |
| 5400 | 62.327 | 426.928 | 368.493 | 315.549 | −864.755 | 89.851 | −0.869 |
| 5500 | 62.328 | 428.071 | 369.565 | 321.782 | −866.628 | 107.546 | −1.021 |
| 5600 | 62.329 | 429.194 | 370.620 | 328.014 | −868.543 | 125.275 | −1.169 |
| 5700 | 62.330 | 430.297 | 371.658 | 334.247 | −870.506 | 143.039 | −1.311 |
| 5800 | 62.331 | 431.381 | 372.678 | 340.480 | −872.517 | 160.838 | −1.449 |
| 5900 | 62.332 | 432.447 | 373.682 | 346.713 | −874.581 | 178.672 | −1.582 |
| 6000 | 62.333 | 433.495 | 374.670 | 352.947 | −876.542 | 196.523 | −1.711 |

PREVIOUS: December 1968 (1 atm) CURRENT· December 1968 (1 bar)

## Sodium Fluoride ((NaF)$_2$) IDEAL GAS $M_r$ = 83.976346

$\Delta_f H^\circ$(0 K) = [−839 955 ± 12.6] kJ·mol$^{-1}$
$S^\circ$(298 15 K) = [287.366 ± 16.7] J·K$^{-1}$·mol$^{-1}$ $\Delta_f H^\circ$(298.15 K) = [−846.423 ± 12.6] kJ·mol$^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|
| [420](1) | [200](1) |
| [400](1) | [425](1) |
| [350](1) | [500](1) |

Ground State Quantum Weight: [1] $\sigma$ = [4]
Point Group: [D$_{2h}$]
Bond Distance. Na–F = 2.02 Å
Bond Angle. Na–F–Na = [85]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [5.614743 × 10$^{-114}$] g$^3$·cm$^6$

### Enthalpy of Formation

Although the absolute values of the vapor pressure measurements are not used for evaluation, the ratios of the numbers of dimeric and monomeric NaF molecules that effuse from the oven at the temperatures 1115–1191 K determined by Eisenstadt *et al* [1] by use of the electron beam velocity selector method are used. Based on the reported equilibrium data, we evaluate the enthalpy change of the reaction (A) $Na_2F_2$(g) = 2 NaF(g) by the 2nd and 3rd law methods. The results are presented in the table below.

Porter and Schoonmaker[2] analyzed the vapor effusing from a Knudsen cell at 1121 K mass spectrometrically and derived the partial pressures of NaF(g) and $Na_2F_2$(g) at that temperature Using these reported partial pressures we calculate, by the 3rd law method, the value $\Delta_r H^\circ$(298.15 K) = 64.1 kcal·mol$^{-1}$ for reaction (A).

Sidorov *et al.*[3] studied the NaF–$ZrF_4$ system by the mass spectrometric method and derived the partial pressures of NaF(g) and $Na_2F_2$(g) as a function of composition and temperature. Employing the data points reported at 1074 and 1167 K we obtain the 3rd law value $\Delta_r H^\circ$(298.15 K) = 62.0±1.6 kcal·mol$^{-1}$ for the same reaction.

The $\Delta_f H^\circ$($Na_2F_2$, g, 298.15 K) is calculated based on the adopted 3rd law value $\Delta_r H^\circ$(298.15 K) = 63.5 kcal·mol$^{-1}$ for the reaction $Na_2F_2$(g) = 2 NaF(g), using $\Delta_f H^\circ$(NaF, g, 298.15 K) = −69 5 kcal·mol$^{-1}$. Brewer and Brackett[9] reported $\Delta_r H^\circ$(1000 K) = 56 9 kcal·mol$^{-1}$ for the above reaction. According to our tables the $\Delta_r H^\circ$(1000 K) value is 62.5 kcal mol$^{-1}$.

| Source | T/K | Data Points | $\Delta_r H^\circ$(298.15 K), kcal·mol$^{-1}$ 2nd law | 3rd law | Drift cal K$^{-1}$·mol$^{-1}$ | $\Delta_f H^\circ$(298.15 K) kcal·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| Eisenstadt *et al.*[1] | 1115–1191 | 6 | 58.1 ± 2.9 | 63.5 | 4.7 ± 2.5 | −202.4 |
| Porter and Schoonmaker[2] | 1121 | 1 | — | 64.1 | — | −203.0 |
| Sidorov *et al.*[3] | 1074–1167 | 8 | — | 62.0 ± 1.6 | — | −200.9 |

### Heat Capacity and Entropy

The $Na_2F_2$(g) molecule is assumed to have a rhombic structure with $D_{2h}$ ($\nu_h$) symmetry.[4 5] The Na–F bond distance is reported by Akishin and Rambidi,[5] who studied the molecular structure of alkali halide vapors by electron diffraction with sector microphotometry. The bond angle is estimated by comparison with those of the other alkali halides Berkowitz[4 6] has calculated the vibration frequencies of $Na_2F_2$ based on an ionic model. By comparison of the calculated frequencies of $Li_2F_2$[6] with those of the observed ones (see $Li_2F_2$(g) table for details), we re-estimate the vibrational frequencies for $Na_2F_2$(g) to be higher than the ones reported by Berkowitz.[6] Bauer *et al.*[7] used a pseudo electrostatic model, similar to the one suggested by O'Konski and Higuchi,[8] to calculate the entropies of dimerization for a number of gaseous alkali halides and estimated the six vibrational frequencies as 477, 318, 291, 477, 291 and 291 cm$^{-1}$. Bauer *et al.*[7] calculated $\Delta_{sub}H^\circ$(1146 K) = −32.5 cal K$^{-1}$·mol$^{-1}$ for the reaction 2 NaF(g) = $Na_2F_2$(g), *in reasonable agreement with the value* −33.5 cal K$^{-1}$·mol$^{-1}$ which is derived using JANAF $S^\circ$(1146 K) values for NaF(g) and $Na_2F_2$(g).

The three principal moments of inertia are: $I_A$ = 13.9948 × 10$^{-39}$, $I_B$ = 14.2197 × 10$^{-39}$, and $I_C$ = 28.2145 × 10$^{-39}$ g·cm$^2$.

### References

[1] M. Eisenstadt, G. M. Rothberg, and P Kusch, J. Chem. Phys. 29, 797 (1958).
[2] R. F. Porter and R. C. Schoonmaker, J. Chem. Phys. 29, 1070 (1958).
[3] L. N. Sidorov, P. A Akishin, V. I. Belousov, and V. V. Shol'ts, Russ. J Phys. Chem. 38, 641 (1964).
[4] J. Berkowitz, J. Chem. Phys. 29, 1386 (1958).
[5] P. A. Akishin and N. G. Rambidi, Z. Physik. Chem. 213, 111 (1960).
[6] J. Berkowitz, J. Chem. Phys. 32, 1519 (1960).
[7] S. H. Bauer, R. M. Diner and R. F. Porter, J. Chem. Phys. 29, 991 (1958).
[8] C. T. O'Konski and W. I. Higuchi, J. Chem. Phys. 23, 1175 (1955).
[9] L. Brewer and E. Brackett, Chem. Rev. 61, 425 (1961).

## Sodium Fluoride ((NaF)$_2$) $F_2Na_2$(g)

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p^\circ$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log K$_f$ |
| 0 | 0. | 0. | INFINITE | −15.250 | −839.955 | −839.955 | INFINITE |
| 100 | 41.612 | 225 792 | 342.904 | −11.711 | −842.002 | −842.782 | 440.224 |
| 200 | 60.880 | 260.954 | 293.579 | −6.525 | −844.657 | −842.438 | 220.022 |
| 250 | 66.886 | 275.228 | 288.512 | −3.321 | −845.604 | −841.771 | 175.878 |
| 298.15 | 70.821 | 287.366 | 287.366 | 0. | −846.423 | −840.957 | 147.332 |
| 300 | 70.945 | 287.805 | 287.368 | 0 131 | −846.454 | −840.923 | 146.418 |
| 350 | 73.732 | 298.963 | 288.243 | 3.752 | −847.327 | −839 934 | 125.353 |
| 400 | 75 698 | 308.945 | 290.218 | 7.491 | −853.557 | −838.401 | 109 484 |
| 450 | 77.125 | 317.947 | 292.807 | 11.313 | −854.527 | −836.448 | 97.092 |
| 500 | 78.187 | 326.131 | 295.736 | 15.197 | −855.419 | −834.391 | 87.168 |
| 600 | 79.625 | 340.524 | 302.034 | 23.094 | −857.028 | −830.030 | 72.261 |
| 700 | 80.524 | 352.871 | 308.436 | 31.105 | −858.473 | −825.415 | 61.593 |
| 800 | 81.120 | 363.665 | 314 679 | 39 189 | −859.817 | −820.599 | 53.580 |
| 900 | 81.536 | 373.245 | 320.664 | 47.323 | −861.111 | −815.619 | 47.337 |
| 1000 | 81.835 | 381.852 | 326.360 | 55.492 | −862.407 | −810.495 | 42.336 |
| 1100 | 82.059 | 389.662 | 331.765 | 63.687 | −863 748 | −805.240 | 38.238 |
| 1200 | 82.230 | 396.810 | 336.892 | 71.902 | −1058.700 | −794.979 | 34.605 |
| 1300 | 82.364 | 403.398 | 341.758 | 80.132 | −1058.397 | −773.014 | 31.060 |
| 1400 | 82 470 | 409.505 | 346.381 | 88.374 | −1058.103 | −751.073 | 28.023 |
| 1500 | 82.556 | 415.198 | 350.781 | 96.625 | −1057.819 | −729.152 | 25.391 |
| 1600 | 82.627 | 420.529 | 354.976 | 104.885 | −1057.546 | −707.250 | 23.089 |
| 1700 | 82.686 | 425.540 | 358.981 | 113.150 | −1057.283 | −685.365 | 21.059 |
| 1800 | 82.735 | 430.267 | 362.811 | 121.422 | −1057.030 | −663.494 | 19.254 |
| 1900 | 82.777 | 434.742 | 366.480 | 129.697 | −1056.785 | −641.638 | 17.640 |
| 2000 | 82.812 | 438.989 | 370.000 | 137.977 | −1056.547 | −619.794 | 16.187 |
| 2100 | 82.843 | 443.030 | 373.382 | 146.260 | −1056.313 | −597.963 | 14.874 |
| 2200 | 82.870 | 446.884 | 376.637 | 154.545 | −1056.081 | −576.142 | 13.679 |
| 2300 | 82.893 | 450.569 | 379.771 | 162.833 | −1055.850 | −554.331 | 12.589 |
| 2400 | 82.913 | 454.097 | 382.795 | 171.124 | −1055.617 | −532.531 | 11.590 |
| 2500 | 82.931 | 457.482 | 385.716 | 179.416 | −1055.380 | −510.741 | 10.671 |
| 2600 | 82.947 | 460.735 | 388.539 | 187.710 | −1055.138 | −488.960 | 9.823 |
| 2700 | 82.962 | 463.866 | 391.271 | 196.005 | −1054.890 | −467.189 | 9.038 |
| 2800 | 82.974 | 466.883 | 393.918 | 204.302 | −1054.634 | −445.427 | 8.310 |
| 2900 | 82.986 | 469.795 | 396.484 | 212.600 | −1054.370 | −423.674 | 7 631 |
| 3000 | 82.996 | 472.608 | 398.975 | 220.899 | −1054.100 | −401.930 | 6 998 |
| 3100 | 83.006 | 475.330 | 401.395 | 229 199 | −1053.823 | −380 196 | 6.406 |
| 3200 | 83 014 | 477.965 | 403.747 | 237.500 | −1053.542 | −358.471 | 5.851 |
| 3300 | 83.022 | 480.520 | 406.035 | 245.802 | −1053.256 | −336.754 | 5.330 |
| 3400 | 83.029 | 482.999 | 408.262 | 254.105 | −1052.970 | −315.046 | 4.840 |
| 3500 | 83.035 | 485.406 | 410.432 | 262.408 | −1052.686 | −293.347 | 4.378 |
| 3600 | 83.041 | 487 745 | 412.547 | 270.712 | −1052.406 | −271.655 | 3.942 |
| 3700 | 83.047 | 490.020 | 414.610 | 279.016 | −1052.136 | −249.971 | 3.529 |
| 3800 | 83.052 | 492.235 | 416.624 | 287.321 | −1051.878 | −228.295 | 3.138 |
| 3900 | 83.057 | 494.392 | 418.591 | 295.627 | −1051.637 | −206.625 | 2.767 |
| 4000 | 83.061 | 496.495 | 420.512 | 303.932 | −1051.419 | −184 961 | 2.415 |
| 4100 | 83.065 | 498.546 | 422.390 | 312.239 | −1051.229 | −163.302 | 2.080 |
| 4200 | 83.069 | 500.548 | 424.228 | 320.545 | −1051.067 | −141.647 | 1.762 |
| 4300 | 83.072 | 502.503 | 426.025 | 328.852 | −1050.948 | −119.996 | 1.458 |
| 4400 | 83.075 | 504.412 | 427.785 | 337.160 | −1050.788 | −98.354 | 1.168 |
| 4500 | 83.078 | 506.279 | 429.509 | 345.468 | −1050.719 | −76.710 | 0.890 |
| 4600 | 83.081 | 508.105 | 431.198 | 353.776 | −1050.717 | −55.065 | 0.625 |
| 4700 | 83 084 | 509.892 | 432.853 | 362.084 | −1050.772 | −33.420 | 0.371 |
| 4800 | 83.086 | 511.641 | 434.476 | 370.392 | −1050.891 | −11.773 | 0.128 |
| 4900 | 83.089 | 513.355 | 436.069 | 378.701 | −1051.079 | 9.877 | −0.105 |
| 5000 | 83.091 | 515.033 | 437.631 | 387.010 | −1051.328 | 31.530 | −0.329 |
| 5100 | 83.093 | 516.679 | 439.165 | 395.319 | −1051.670 | 53.191 | −0.545 |
| 5200 | 83.095 | 518.292 | 440.671 | 403.629 | −1052.100 | 74.859 | −0.752 |
| 5300 | 83.097 | 519.875 | 442.151 | 411.938 | −1052.623 | 96.536 | −0.951 |
| 5400 | 83.098 | 521.428 | 443.605 | 420.248 | −1053.246 | 118.224 | −1.144 |
| 5500 | 83.100 | 522.953 | 445.033 | 428.558 | −1053.975 | 139.924 | −1.329 |
| 5600 | 83.102 | 524.450 | 446.438 | 436.868 | −1054.814 | 161.639 | −1.508 |
| 5700 | 83.103 | 525.921 | 447.820 | 445.178 | −1055.770 | 183.369 | −1.680 |
| 5800 | 83 104 | 527.367 | 449.179 | 453.489 | −1056.847 | 205.118 | −1.847 |
| 5900 | 83.106 | 528 787 | 450.516 | 461.799 | −1058.051 | 226.886 | −2.009 |
| 6000 | 83.107 | 530 184 | 451.832 | 470.110 | −1059.069 | 248.639 | −2.165 |

PREVIOUS. December 1968 (1 atm) CURRENT: December 1968 (1 bar)

# Oxygen Fluoride (FOF) IDEAL GAS $M_r = 53.9962064$ Oxygen Fluoride (FOF) $F_2O_1(g)$

$\Delta_a H°(0\ K) = 375 \pm 2\ kJ{\cdot}mol^{-1}$
$S°(298.15\ K) = 247.46 \pm 0.4\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = 26.8 \pm 2\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = 24.5 \pm 2\ kJ{\cdot}mol^{-1}$

| Electronic Level and Quantum Weight | | |
|---|---|---|
| State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
| [$X^1A$] | 0.0 | 1 |

| Vibrational Frequencies and Degeneracies $\nu$, cm$^{-1}$ |
|---|
| 928(1) |
| 461(1) |
| 831(1) |

Point Group: $C_{2v}$ $\sigma = 2$
Bond Distance: F–O = 1.412 Å
Bond Angle: F–O–F = 103° 10′
Product of the Moments of Inertia: $I_A I_B I_C = 101.8236 \times 10^{-117}\ g^3{\cdot}cm^6$

## Enthalpy of Formation

King and Armstrong[1] have established the enthalpy of formation with a series of reactions in a flame calorimeter. They burned $OF_2$ in hydrogen to give HF aqueous; in addition they burned $F_2$ in hydrogen and $O_2$ in hydrogen so that the enthalpy of formation, 24.52 kJ·mol$^{-1}$, was directly obtainable. This value was in good agreement with the recalculated values of Wartenberg and Klinkott,[2] 23.85 ± 12.6 kJ·mol$^{-1}$, and of Ruff and Menzel,[3] 19.66 ± 8.45 kJ·mol$^{-1}$ but differed from that of Bisbee *et al.*,[4] −16.99 ± 8.4 kJ·mol$^{-1}$. There are several factors in the experiments of Bisbee *et al.* that might cause the enthalpy of formation to be too negative. We adopt the value of 24.52 kJ·mol$^{-1}$, reported by King and Armstrong.[1]

## Heat Capacity and Entropy

The structural parameters are those reported by Pierce *et al.*[5] for the average ground state molecule from the microwave spectrum. Earlier measurements of Hilton *et al.*[6] disagree but according to Pierce *et al.*,[7] the line assignments used by Hilton *et al.* are incorrect. The microwave study of Morino and Saito[8] yielded $r_e = 1.4053$ Å and an angle of 103°4′ which is in agreement with our adopted values. The principle moments of inertia (in g·cm$^2$) are: $I_A = 1.4392 \times 10^{-39}$, $I_B = 7.7225 \times 10^{-39}$, and $I_C = 9.1617 \times 10^{-39}$.

We adopt the vibrational frequencies reported by Jones *et al.*,[9] several other investigators reported similar values.[10-12] Nebgen *et al.*[13] obtained the harmonic frequencies and the anharmonic constants for the three vibrations.

There are numerous more recent studies focusing on Fermi resonance and Coriolis coupling but the results support our adopted values.

## References

[1] R.C. King and G.T. Armstrong, J. Res. Nat. Bur. Stand. 72A, 113 (1968).
[2] H. Wartenberg and G.Z. Klinkott, Z. Anorg. Chem. 193, 409 (1930).
[3] O. Ruff and W. Menzel, Z. Anorg. Chem. 190, 257 (1930).
[4] W.R. Bisbee, J.V. Hamilton, R. Rushworth, T.J. Houser, and J.M. Gerhauser, Advan. Chem. Ser. 54, 215 (1965).
[5] L. Pierce, N. DiCianni and R.H. Jackson, J. Chem. Phys. 38, 730 (1963).
[6] A.R. Hilton, A.W. Jache, J.B. Beal, W.D. Henderson and R.J. Robinson, J. Chem. Phys. 34 (1961).
[7] L. Pierce, R.H. Jackson and N. DiCianni, J. Chem. Phys. 35, 2240 (1961).
[8] Y. Morino and S. Saito, J. Mol. Spect. 19(4), 435–53 (1966).
[9] E.A. Jones, J.S. Kirby-Smith, P. J.H. Woltz and A.H. Nielsen, J. Chem. Phys. 19, 337 (1951).
[10] H.J. Bernstein and J. Powling, J. Chem. Phys. 18, 685 (1950).
[11] G. Hettner, R. Pohlman and H.J. Schumacher, Z. Physik. 96, 203 (1935).
[12] G.B.B.M. Sutherland and W.G. Penney, Proc. Roy. Soc. (London) 156A, 678 (1936).
[13] J.W. Nebgen, F.I. Metz and W.B. Rose, J. Mol. Spectrosc. 21, 99 (1966).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
|---|---|---|---|---|---|---|---|
| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
| 0 | .000 | .000 | INFINITE | −10.895 | 26.791 | 26.791 | INFINITE |
| 50 | 33.261 | 183.592 | 368.242 | −9.232 | 26.278 | 28.436 | −29.707 |
| 100 | 33.751 | 206.729 | 282.351 | −7.562 | 25.765 | 30.795 | −16.085 |
| 150 | 35.531 | 220.714 | 259.612 | −5.835 | 25.307 | 33.412 | −11.635 |
| 200 | 38.056 | 231.271 | 251.255 | −3.997 | 24.946 | 36.171 | −9.447 |
| 250 | 40.796 | 240.057 | 248.159 | −2.026 | 24.686 | 39.009 | −8.150 |
| 298.15 | 43.302 | 247.460 | 247.460 | .000 | 24.520 | 41.784 | −7.320 |
| 300 | 43.393 | 247.728 | 247.461 | .080 | 24.515 | 41.891 | −7.294 |
| 400 | 47.586 | 260.820 | 249.217 | 4.641 | 24.371 | 47.711 | −6.230 |
| 500 | 50.463 | 271.769 | 252.663 | 9.553 | 24.388 | 53.546 | −5.594 |
| 600 | 52.400 | 281.152 | 256.648 | 14.702 | 24.484 | 59.369 | −5.169 |
| 700 | 53.728 | 289.336 | 260.746 | 20.013 | 24.616 | 65.173 | −4.863 |
| 800 | 54.664 | 296.574 | 264.781 | 25.435 | 24.760 | 70.957 | −4.633 |
| 900 | 55.343 | 303.054 | 268.680 | 30.937 | 24.905 | 76.723 | −4.453 |
| 1000 | 55.847 | 308.912 | 272.415 | 36.498 | 25.045 | 82.473 | −4.308 |
| 1100 | 56.232 | 314.254 | 275.979 | 42.103 | 25.175 | 88.210 | −4.189 |
| 1200 | 56.531 | 319.160 | 279.376 | 47.741 | 25.294 | 93.935 | −4.089 |
| 1300 | 56.768 | 323.695 | 282.613 | 53.407 | 25.398 | 99.651 | −4.004 |
| 1400 | 56.958 | 327.909 | 285.699 | 59.093 | 25.487 | 105.359 | −3.931 |
| 1500 | 57.113 | 331.844 | 288.646 | 64.797 | 25.560 | 111.061 | −3.867 |
| 1600 | 57.241 | 335.534 | 291.462 | 70.515 | 25.616 | 116.759 | −3.812 |
| 1700 | 57.348 | 339.008 | 294.158 | 76.245 | 25.654 | 122.455 | −3.763 |
| 1800 | 57.438 | 342.288 | 296.742 | 81.984 | 25.676 | 128.148 | −3.719 |
| 1900 | 57.515 | 345.396 | 299.221 | 87.732 | 25.682 | 133.841 | −3.680 |
| 2000 | 57.580 | 348.348 | 301.605 | 93.487 | 25 674 | 139.534 | −3.644 |
| 2100 | 57.637 | 351.159 | 303.898 | 99.248 | 25.656 | 145.227 | −3.612 |
| 2200 | 57.687 | 353.841 | 306.108 | 105.014 | 25.628 | 150.922 | −3.583 |
| 2300 | 57 730 | 356.406 | 308.239 | 110.785 | 25.595 | 156.617 | −3.557 |
| 2400 | 57 768 | 358.864 | 310.298 | 116.560 | 25.561 | 162.314 | −3.533 |
| 2500 | 57.801 | 361.223 | 312.288 | 122.338 | 25.527 | 168.013 | −3.510 |
| 2600 | 57.831 | 363.491 | 314.214 | 128.120 | 25.498 | 173.713 | −3.490 |
| 2700 | 57.858 | 365.674 | 316.080 | 133.904 | 25.478 | 179.414 | −3.471 |
| 2800 | 57.882 | 367.778 | 317.889 | 139.691 | 25.468 | 185.116 | −3.453 |
| 2900 | 57 903 | 369.810 | 319.644 | 145.481 | 25.473 | 190.817 | −3.437 |
| 3000 | 57.923 | 371.773 | 321.349 | 151.272 | 25.495 | 196.519 | −3.422 |
| 3100 | 57.940 | 373.673 | 323.007 | 157.065 | 25.535 | 202.219 | −3.407 |
| 3200 | 57.956 | 375.513 | 324.619 | 162.860 | 25.597 | 207.917 | −3.394 |
| 3300 | 57.971 | 377.296 | 326.188 | 168.656 | 25.682 | 213.614 | −3.381 |
| 3400 | 57.984 | 379.027 | 327.717 | 174.454 | 25.792 | 219.307 | −3.369 |
| 3500 | 57.996 | 380.708 | 329.207 | 180.253 | 25.927 | 224.997 | −3.358 |
| 3600 | 58.007 | 382.342 | 330.660 | 186.053 | 26.090 | 230.682 | −3.347 |
| 3700 | 58.018 | 383.931 | 332.079 | 191.855 | 26.279 | 236.363 | −3.337 |
| 3800 | 58.027 | 385.479 | 333.464 | 197.657 | 26.496 | 242.038 | −3.327 |
| 3900 | 58.036 | 386.986 | 334.817 | 203.460 | 26.742 | 247.707 | −3.318 |
| 4000 | 58.044 | 388.456 | 336.140 | 209.264 | 27.016 | 253.369 | −3.309 |
| 4100 | 58.052 | 389.889 | 337.433 | 215.069 | 27.318 | 259.024 | −3.300 |
| 4200 | 58.059 | 391.288 | 338.699 | 220.874 | 27.649 | 264.672 | −3.292 |
| 4300 | 58.065 | 392.654 | 339.938 | 226.681 | 28.006 | 270.311 | −3.284 |
| 4400 | 58.071 | 393.989 | 341.151 | 232.487 | 28.392 | 275.942 | −3.276 |
| 4500 | 58.077 | 395.294 | 342.340 | 238.295 | 28.803 | 281.563 | −3.268 |
| 4600 | 58.082 | 396.571 | 343.505 | 244.103 | 29.241 | 287.175 | −3.261 |
| 4700 | 58.087 | 397.820 | 344.647 | 249.911 | 29.704 | 292.778 | −3.254 |
| 4800 | 58.092 | 399.043 | 345.768 | 255.720 | 30.192 | 298.370 | −3.247 |
| 4900 | 58.097 | 400.241 | 346.867 | 261.530 | 30.702 | 303.952 | −3.240 |
| 5000 | 58.101 | 401.415 | 347.947 | 267.339 | 31.236 | 309.523 | −3.234 |
| 5100 | 58.105 | 402.565 | 349.006 | 273.150 | 31.790 | 315.083 | −3.227 |
| 5200 | 58.108 | 403.694 | 350.047 | 278.960 | 32.366 | 320.632 | −3.221 |
| 5300 | 58.112 | 404.800 | 351.070 | 284.771 | 32.961 | 326.171 | −3.215 |
| 5400 | 58.115 | 405.887 | 352.075 | 290.583 | 33.573 | 331.697 | −3.209 |
| 5500 | 58.118 | 406.953 | 353.063 | 296.394 | 34.203 | 337.211 | −3.203 |
| 5600 | 58.121 | 408.000 | 354.035 | 302.206 | 34.849 | 342.716 | −3.197 |
| 5700 | 58.124 | 409.029 | 354.991 | 308.019 | 35.510 | 348.207 | −3.191 |
| 5800 | 58.127 | 410.040 | 355.931 | 313.831 | 36.184 | 353.687 | −3.185 |
| 5900 | 58.129 | 411.034 | 356.857 | 319.644 | 36.871 | 359.155 | −3.180 |
| 6000 | 58.131 | 412.011 | 357.768 | 325.457 | 37.568 | 364.612 | −3.174 |

PREVIOUS: December 1969 (1 bar) CURRENT: September 1995 (1 bar)

Oxygen Fluoride (FOF) $F_2O_1(g)$

## Thionyl Fluoride ($SOF_2$) IDEAL GAS $M_r = 86.056206$ Thionyl Fluoride ($OSF_2$) $F_2O_1S_1(g)$

$S°(298.15\ K) = 279.132\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = [-538.967 \pm 105]\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = [-543\ 920 \pm 105]\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|
| 1330 (1) | 377.8(1) |
| 808.2(1) | 747.0(1) |
| 530.4(1) | 392.5(1) |

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: $C_s$
Bond Distances: O–S = 1.412 Å; S–F = 1.585 Å
Bond Angles O–S–F = 106.82°; F–S–F = 92.82°
Product of the Moments of Inertia. $I_AI_BI_C = 1.655344 \times 10^{-114}\ g^3{\cdot}cm^6$

### Enthalpy of Formation

The increment in $\Delta_fH°$ at 298.15 K between gaseous $SOF_2$ and $SO_2F_2$ is estimated from increments for the four pairs a) S and SO, b) SO and $SO_2$, c) $SO_2$ and $SO_3$, and d) $SOCl_2$ and $SO_2Cl_2$. Based on $\Delta_fH° = -181\ 3$ kcal·mol$^{-1}$ for $SO_2F_2$[1], we derive a) −116, b) −109, c) −158, and d) −148 for $\Delta_fH°$ of $SOF_2(g)$. The derivation is based on $\Delta_fH°(SOCl_2$, g, 298.15 K).[1 2] Giving lesser weight to c) which involves $SO_3$, we adopt an average of $-130 \pm 25$ kcal·mol$^{-1}$.

### Heat Capacity and Entropy

The molecular structure is from the microwave study of Ferguson.[3] Principal moments of inertia are $I_A = 9.7369 \times 10^{-39}$, $I_B = 10.0399 \times 10^{-39}$, and $I_C = 16.9332 \times 10^{-39}\ g{\cdot}cm^2$. Vibrational frequencies are those assigned by Pace and Samuelson[4] from their gas phase infrared spectra. These authors also measured Raman spectra of liquid and gas and summarized earlier spectral studies. We adopt $\nu_1$ as the lower wave number of the Fermi resonance doublet at 1330 and 1340 cm$^{-1}$. Uncertainty is greatest for the overlapping bands near 378 and 392 cm$^{-1}$.

Pace and Turnbull[5] derived $S° = 63.56 \pm 0.15$ cal K$^{-1}$·mol$^{-1}$ for the ideal gas at $T_{vap} = 228\ 84$ K from calorimetric measurements of heat capacity (12 to 230 K), $\Delta_{fus}H°$, and $\Delta_{vap}H°$. Spectroscopic data of this table yield the corresponding value of $S° = 63.29$ which is 0.27 cal K$^{-1}$·mol$^{-1}$ smaller than observed. Pace and Turnbull attributed the minor discrepancy to bias in the measurements of $\Delta_{vap}H°$

### References

[1] JANAF Thermochemical Tables: $F_2O_2S(g)$, $Cl_2O_2S(g)$, OS(g), and S(g) 6–30–71, $O_2S(g)$ 6–30–61, $O_3S(g)$ 9–30–65.
[2] U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).
[3] R. C. Ferguson, J. Am. Chem. Soc. 76, 850 (1954).
[4] E L. Pace and H. V Salmuelson, J. Chem Phys. 44, 3682 (1966).
[5] E. L. Pace and B. F. Turnbull, J. Chem. Phys. 43, 1953 (1965).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −12.625 | −538.967 | −538.967 | INFINITE |
| 100 | 35.545 | 230.278 | 322.875 | −9.260 | −540.650 | −536.723 | 280.356 |
| 200 | 47.164 | 258.341 | 284.057 | −5.143 | −542.560 | −532.022 | 138 950 |
| 250 | 52.631 | 269.468 | 280.048 | −2.645 | −543.313 | −529.298 | 110.591 |
| 298.15 | 57.105 | 279.132 | 279.132 | 0. | −543.920 | −526.542 | 92.248 |
| 300 | 57.262 | 279.485 | 279.133 | 0.106 | −543.941 | −526.434 | 91 660 |
| 350 | 61.105 | 288.610 | 279.844 | 3.068 | −544.472 | −523 473 | 78.124 |
| 400 | 64 276 | 296.983 | 281.471 | 6.205 | −547.144 | −520.353 | 67.951 |
| 450 | 66.894 | 304.710 | 283.629 | 9 486 | −548.214 | −516.948 | 60.006 |
| 500 | 69.060 | 311.874 | 286.100 | 12.887 | −549.285 | −513.414 | 53.636 |
| 600 | 72.365 | 324.775 | 291.495 | 19.968 | −550.842 | −506.084 | 44.059 |
| 700 | 74 697 | 336.115 | 297.076 | 27.328 | −552.008 | −498.528 | 37.201 |
| 800 | 76.381 | 346.206 | 302.598 | 34.886 | −552.939 | −490.823 | 32.047 |
| 900 | 77.626 | 355.277 | 307.956 | 42.589 | −606.849 | −481.929 | 27.970 |
| 1000 | 78.568 | 363.507 | 313.106 | 50.401 | −606.315 | −468.077 | 24.450 |
| 1100 | 79.293 | 371.031 | 318.035 | 58.296 | −605.766 | −454.280 | 21.572 |
| 1200 | 79.863 | 377.956 | 322.743 | 66.255 | −605.214 | −440.533 | 19.176 |
| 1300 | 80.317 | 384.367 | 327.240 | 74.265 | −604.668 | −426.832 | 17.150 |
| 1400 | 80.685 | 390.333 | 331.536 | 82.315 | −604.132 | −413.172 | 15.416 |
| 1500 | 80.987 | 395.910 | 335.644 | 90.399 | −603.613 | −399.551 | 13.914 |
| 1600 | 81.237 | 401.145 | 339.576 | 98.511 | −603.112 | −385.963 | 12.600 |
| 1700 | 81.446 | 406 077 | 343.344 | 106.645 | −602.631 | −372.406 | 11 443 |
| 1800 | 81.623 | 410.737 | 346.960 | 114.799 | −602.172 | −358.877 | 10.414 |
| 1900 | 81 774 | 415.154 | 350.434 | 122.969 | −601.733 | −345.372 | 9.495 |
| 2000 | 81.904 | 419.352 | 353.776 | 131.153 | −601.312 | −331.891 | 8.668 |
| 2100 | 82.016 | 423.351 | 356.994 | 139.349 | −600.909 | −318.430 | 7.921 |
| 2200 | 82.114 | 427.169 | 360.098 | 147.556 | −600.518 | −304.987 | 7.241 |
| 2300 | 82.200 | 430.821 | 363.094 | 155 772 | −600.138 | −291.562 | 6.622 |
| 2400 | 82.276 | 434.321 | 365.989 | 163.996 | −599.764 | −278.154 | 6.054 |
| 2500 | 82.342 | 437.681 | 368.790 | 172.227 | −599.394 | −264.762 | 5.532 |
| 2600 | 82.402 | 440.912 | 371.502 | 180.464 | −599.023 | −251.384 | 5.050 |
| 2700 | 82 455 | 444.023 | 374.131 | 188.707 | −598.647 | −238.020 | 4 605 |
| 2800 | 82.503 | 447.022 | 376.681 | 196.955 | −598.264 | −224.670 | 4.191 |
| 2900 | 82.546 | 449.918 | 379.157 | 205.207 | −597.869 | −211.335 | 3.807 |
| 3000 | 82.584 | 452.717 | 381.563 | 213.464 | −597.461 | −198.013 | 3.448 |
| 3100 | 82.619 | 455.426 | 383.902 | 221.724 | −597.037 | −184.705 | 3.112 |
| 3200 | 82.651 | 458.049 | 386.178 | 229.988 | −596.594 | −171.411 | 2.798 |
| 3300 | 82.680 | 460.593 | 388.395 | 238.254 | −596.130 | −158.131 | 2.503 |
| 3400 | 82.707 | 463.062 | 390.555 | 246.524 | −595.645 | −144.865 | 2.226 |
| 3500 | 82.731 | 465.459 | 392.661 | 254.795 | −595.137 | −131.615 | 1 964 |
| 3600 | 82.754 | 467.790 | 394.715 | 263.070 | −594.606 | −118.378 | 1 718 |
| 3700 | 82 774 | 470.058 | 396.721 | 271.346 | −594.050 | −105.158 | 1.485 |
| 3800 | 82.793 | 472.266 | 398.680 | 279.625 | −593.469 | −91.952 | 1.264 |
| 3900 | 82.811 | 474.417 | 400.595 | 287.905 | −592.863 | −78.762 | 1.055 |
| 4000 | 82.827 | 476.513 | 402.467 | 296.187 | −592.233 | −65.588 | 0.856 |
| 4100 | 82.843 | 478.559 | 404.298 | 304.470 | −591.578 | −52.430 | 0.668 |
| 4200 | 82.857 | 480.555 | 406.090 | 312.755 | −590.900 | −39.288 | 0.489 |
| 4300 | 82.870 | 482.505 | 407.844 | 321.042 | −590.198 | −26.163 | 0.318 |
| 4400 | 82.882 | 484.410 | 409.563 | 329.329 | −589.474 | −13.054 | 0.155 |
| 4500 | 82.894 | 486.273 | 411.247 | 337.618 | −588.728 | 0.038 | −0.000 |
| 4600 | 82.904 | 488.095 | 412.898 | 345.908 | −587.961 | 13.113 | −0.149 |
| 4700 | 82 914 | 489.878 | 414.517 | 354.199 | −587.174 | 26.172 | −0.291 |
| 4800 | 82.924 | 491.624 | 416.105 | 362.491 | −586.369 | 39.213 | −0.427 |
| 4900 | 82.933 | 493.334 | 417.664 | 370.783 | −585.546 | 52.238 | −0.557 |
| 5000 | 82.941 | 495.009 | 419 194 | 379.077 | −584.706 | 65.245 | −0.682 |
| 5100 | 82.949 | 496.652 | 420.697 | 387.372 | −583.852 | 78.236 | −0.801 |
| 5200 | 82.956 | 498.263 | 422.173 | 395.667 | −582.983 | 91.210 | −0.916 |
| 5300 | 82.963 | 499.843 | 423.624 | 403.963 | −582.102 | 104.167 | −1.027 |
| 5400 | 82.970 | 501.394 | 425.049 | 412.259 | −581.209 | 117.107 | −1.133 |
| 5500 | 82.976 | 502.916 | 426.451 | 420.557 | −580.306 | 130.030 | −1.235 |
| 5600 | 82.982 | 504.411 | 427.830 | 428.855 | −579.394 | 142.937 | −1.333 |
| 5700 | 82.988 | 505.880 | 429.187 | 437.153 | −578.475 | 155.827 | −1.428 |
| 5800 | 82.993 | 507.324 | 430.521 | 445.452 | −577.549 | 168.702 | −1.519 |
| 5900 | 82.998 | 508 742 | 431.835 | 453.752 | −576.618 | 181.560 | −1.607 |
| 6000 | 83 003 | 510.137 | 433.129 | 462.052 | −575.683 | 194 403 | −1.692 |

PREVIOUS· June 1972 (1 atm) CURRENT June 1972 (1 bar)

Thionyl Fluoride ($OSF_2$) $F_2O_1S_1(g)$

$S°$(298 15 K) = [271.247] J·K$^{-1}$·mol$^{-1}$

$\Delta_f H°$(0 K) = [−962.125 ± 25.1] kJ·mol$^{-1}$
$\Delta_f H°$(298.15 K) = [−966.504 ± 25 1] kJ·mol$^{-1}$

| Vibrational Frequencies and Degeneracies | |
|---|---|
| $\nu$, cm | $\nu$, cm |
| [440](1) | [760](1) |
| [490](1) | [980](1) |
| [610](1) | [1420](1) |

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: [C$_{2v}$]
Bond Distances: Si–O = [1.60] Å; Si–F = [1.54] Å
Bond Angles: F–Si–O = [120]°; F–Si–F = [120]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [2.565383 × 10$^{-114}$] g$^3$·cm$^6$

## Enthalpy of Formation

$\Delta_f H°$(SiOF$_2$, g, 298 15 K) is estimated by comparison with those for SiF$_4$(g) and SiO$_2$(g).

## Heat Capacity and Entropy

The vibrational frequencies were estimated by comparison with those for COF$_2$(g) and TiOF(g) The vibrational frequencies for COF$_2$(g) and TiOF$_2$(g) were obtained from Lovell *et al.*[1] and Gordon,[2] respectively. The bond distances of Si–O and Si–F were assumed to be the same as those for SiO(g) and SiF$_4$(g), respectively. Point group, ground state multiplicity, and bond angles were estimated.

## References

[1] R J. Lovell, C. V. Stephenson, and E. A. Jones, J. Chem. Phys 22, 1953 (1954).
[2] J. S. Gordon, personal communication, (May 12, 1961).

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −12.006 | −962.125 | −962.125 | INFINITE |
| 100 | 34.330 | 225.460 | 312.100 | −8.664 | −963.409 | −959.869 | 501.384 |
| 200 | 43.808 | 251.839 | 275.855 | −4.803 | −965.111 | −955.667 | 249.595 |
| 250 | 49.127 | 262.195 | 272.106 | −2.478 | −965.867 | −953.217 | 199.164 |
| 298.15 | 53.689 | 271.247 | 271.247 | 0. | −966.504 | −950.721 | 166.562 |
| 300 | 53.851 | 271.579 | 271.248 | 0.099 | −966.527 | −950.623 | 165.518 |
| 350 | 57.899 | 280.193 | 271.919 | 2.896 | −967.092 | −947 927 | 141 470 |
| 400 | 61.320 | 288.154 | 273.457 | 5.879 | −967.574 | −945.155 | 123.425 |
| 450 | 64.198 | 295.548 | 275.506 | 9.019 | −967.983 | −942.327 | 109.383 |
| 500 | 66.615 | 302.441 | 277.858 | 12.291 | −968.334 | −939.457 | 98.144 |
| 600 | 70.366 | 314.937 | 283.019 | 19.151 | −968.904 | −933.626 | 81.279 |
| 700 | 73.058 | 325.997 | 288.384 | 26.329 | −969.352 | −927.709 | 69.227 |
| 800 | 75.027 | 335.888 | 293.715 | 33.738 | −969.730 | −921.734 | 60.183 |
| 900 | 76.497 | 344.814 | 298.905 | 41.318 | −970.069 | −915.714 | 53.147 |
| 1000 | 77.615 | 352.934 | 303.908 | 49.026 | −970.393 | −909.657 | 47.516 |
| 1100 | 78.481 | 360.374 | 308.708 | 56.833 | −970.717 | −903.568 | 42.907 |
| 1200 | 79.164 | 367.233 | 313.303 | 64.716 | −971.052 | −897.448 | 39.065 |
| 1300 | 79.710 | 373.592 | 317.699 | 72.661 | −971.409 | −891.301 | 35.813 |
| 1400 | 80.154 | 379.516 | 321.905 | 80.655 | −971.795 | −885.124 | 33.024 |
| 1500 | 80.518 | 385.058 | 325.932 | 88.689 | −972.216 | −878.919 | 30.607 |
| 1600 | 80.821 | 390.265 | 329.792 | 96.756 | −972.677 | −872.684 | 28.490 |
| 1700 | 81.074 | 395 172 | 333.495 | 104.851 | −1023.358 | −865 973 | 26.608 |
| 1800 | 81.289 | 399.813 | 337.052 | 112.970 | −1023.677 | −856.706 | 24.861 |
| 1900 | 81.473 | 404.213 | 340.472 | 121.108 | −1024.000 | −847.421 | 23.297 |
| 2000 | 81.630 | 408.396 | 343.764 | 129.264 | −1024.326 | −838.119 | 21.889 |
| 2100 | 81.767 | 412.382 | 346.938 | 137.434 | −1024.656 | −828.800 | 20.615 |
| 2200 | 81.886 | 416.189 | 349.999 | 145.616 | −1024.986 | −819.466 | 19.457 |
| 2300 | 81.991 | 419.831 | 352.957 | 153.810 | −1025.315 | −810.117 | 18.398 |
| 2400 | 82.083 | 423.323 | 355.817 | 162.014 | −1025.641 | −800.753 | 17.428 |
| 2500 | 82.164 | 426.675 | 358.584 | 170.227 | −1025.960 | −791.376 | 16.535 |
| 2600 | 82.237 | 429.899 | 361.266 | 178.447 | −1026.270 | −781.987 | 15.710 |
| 2700 | 82.301 | 433.004 | 363.866 | 186.674 | −1026.568 | −772.586 | 14.947 |
| 2800 | 82.360 | 435.998 | 366.389 | 194.907 | −1026.851 | −763.174 | 14.237 |
| 2900 | 82.412 | 438.889 | 368.839 | 203.145 | −1027.116 | −753.752 | 13.577 |
| 3000 | 82.459 | 441.684 | 371.221 | 211.389 | −1027.362 | −744.321 | 12.960 |
| 3100 | 82.502 | 444.388 | 373.538 | 219.637 | −1027.586 | −734.883 | 12.383 |
| 3200 | 82.541 | 447.008 | 375.793 | 227.889 | −1027.786 | −725.438 | 11.842 |
| 3300 | 82.577 | 449.549 | 377.990 | 236.145 | −1027.961 | −715.987 | 11.333 |
| 3400 | 82.609 | 452.014 | 380.131 | 244.405 | −1028.110 | −706.530 | 10.855 |
| 3500 | 82.639 | 454.410 | 382.219 | 252.667 | −1028.230 | −697.071 | 10.403 |
| 3600 | 82.666 | 456.738 | 384.257 | 260.932 | −1412.475 | −677.146 | 9.825 |
| 3700 | 82.692 | 459.003 | 386.246 | 269.200 | −1412.124 | −656.726 | 9.271 |
| 3800 | 82.715 | 461.209 | 388.190 | 277 471 | −1411.746 | −636.314 | 8.747 |
| 3900 | 82.736 | 463.358 | 390.090 | 285.743 | −1411.340 | −615.913 | 8.249 |
| 4000 | 82.756 | 465.453 | 391.948 | 294.018 | −1410.905 | −595.523 | 7.777 |
| 4100 | 82.775 | 467.496 | 393.766 | 302.294 | −1410.441 | −575.145 | 7.327 |
| 4200 | 82.792 | 469.491 | 395.545 | 310.573 | −1409.949 | −554.777 | 6.900 |
| 4300 | 82.808 | 471.440 | 397.288 | 318.853 | −1409.429 | −534.422 | 6.492 |
| 4400 | 82.823 | 473.343 | 398.995 | 327.134 | −1408.880 | −514.080 | 6.103 |
| 4500 | 82.837 | 475.205 | 400.668 | 335.417 | −1408.304 | −493.750 | 5.731 |
| 4600 | 82.850 | 477.026 | 402.308 | 343.702 | −1407.700 | −473.433 | 5.376 |
| 4700 | 82.863 | 478.808 | 403.917 | 351.987 | −1407.071 | −453.129 | 5.036 |
| 4800 | 82.874 | 480.552 | 405.495 | 360.274 | −1406.416 | −432.840 | 4.710 |
| 4900 | 82.885 | 482.261 | 407.044 | 368.562 | −1405.736 | −412.564 | 4.398 |
| 5000 | 82.895 | 483.936 | 408.566 | 376.851 | −1405.033 | −392.302 | 4.098 |
| 5100 | 82.905 | 485.577 | 410.060 | 385.141 | −1404.308 | −372.054 | 3.811 |
| 5200 | 82.914 | 487.187 | 411.527 | 393.432 | −1403.561 | −351.821 | 3.534 |
| 5300 | 82.922 | 488.767 | 412.970 | 401.724 | −1402.794 | −331.603 | 3.268 |
| 5400 | 82.931 | 490.317 | 414.388 | 410.017 | −1402.008 | −311.399 | 3.012 |
| 5500 | 82.938 | 491.839 | 415.782 | 418.310 | −1401.205 | −291.211 | 2.766 |
| 5600 | 82.946 | 493.333 | 417.154 | 426.604 | −1400.385 | −271.035 | 2.528 |
| 5700 | 82.952 | 494.801 | 418.503 | 434.899 | −1399.551 | −250.877 | 2.299 |
| 5800 | 82.959 | 496.244 | 419.831 | 443.195 | −1398.704 | −230.731 | 2.078 |
| 5900 | 82.965 | 497.662 | 421.138 | 451.491 | −1397.846 | −210.602 | 1.865 |
| 6000 | 82.971 | 499.057 | 422.425 | 459.788 | −1396.976 | −190.486 | 1.658 |

PREVIOUS: September 1963 (1 atm)    CURRENT· September 1963 (1 bar)

## Titanium Fluoride Oxide ($OTiF_2$) IDEAL GAS $M_r = 101.896205$ Titanium Fluoride Oxide ($OTiF_2$) $F_2O_1Ti_1(g)$

$S°(298.15\ K) = [284.678]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = [-920.454]\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [-924.873]\ kJ{\cdot}mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, $cm^{-1}$ | <br>$\nu$, $cm^{-1}$ |
|---|---|
| [553](1) | [715](1) |
| [888](1) | [300](1) |
| [350](1) | [452](1) |

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: [$C_{2v}$]
Bond Distances: Ti–O = [1.62] Å; Ti–F = [1.74] Å
Bond Angle: O–Ti–F = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [4.344131 \times 10^{-114}]\ g^3{\cdot}cm^6$

### Enthalpy of Formation

$\Delta_f H°(0\ K)$ was estimated as $-220\ kcal{\cdot}mol^{-1}$ by Gordon.[1] $\Delta_f H°(298\ 15\ K)$ was then calculated.

### Heat Capacity and Entropy

Molecular constants were estimated by Gordon.[1] The principal moments of inertia are: $I_A = 11.6652 \times 10^{-39}$, $I_B = 14.3272 \times 10^{-39}$, and $I_C = 25.9925 \times 10^{-39}\ g{\cdot}cm^2$.

### Reference

[1] J. S Gordon, Astrosystems, Inc., Caldwell Twp., N. J., personal communication, (January 10, 1963).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −13.577 | −920.454 | −920.454 | INFINITE |
| 100 | 37.517 | 231.211 | 332.858 | −10.165 | −921.961 | −918.554 | 479.803 |
| 200 | 52.117 | 261.723 | 290.111 | −5.678 | −923.776 | −914.396 | 238.816 |
| 250 | 58.147 | 274.024 | 285.687 | −2.916 | −924.409 | −911.974 | 190.547 |
| 298.15 | 62.779 | 284.678 | 284 678 | 0. | −924.873 | −909.535 | 159.347 |
| 300 | 62.936 | 285.067 | 284.679 | 0.116 | −924.889 | −909.440 | 158.348 |
| 350 | 66.665 | 295.060 | 285.460 | 3.360 | −925.259 | −906.835 | 135.338 |
| 400 | 69.558 | 304.159 | 287.237 | 6.769 | −925.555 | −904.182 | 118.074 |
| 450 | 71.812 | 312.488 | 289.587 | 10.305 | −925.801 | −901.495 | 104.643 |
| 500 | 73.585 | 320.149 | 292.265 | 13.942 | −926.017 | −898.782 | 93.895 |
| 600 | 76.128 | 333.807 | 298.079 | 21 437 | −926.401 | −893.299 | 77.769 |
| 700 | 77.806 | 345.676 | 304.049 | 29.139 | −926.765 | −887.753 | 66.245 |
| 800 | 78.961 | 356.146 | 309.920 | 36.981 | −927.126 | −882.155 | 57.599 |
| 900 | 79.784 | 365.496 | 315.585 | 44.920 | −927.535 | −876.510 | 50.871 |
| 1000 | 80.390 | 373.935 | 321.005 | 52.930 | −928.067 | −870.813 | 45.487 |
| 1100 | 80.848 | 381.620 | 326.171 | 60.993 | −928.793 | −865.055 | 41.078 |
| 1200 | 81.202 | 388.670 | 331.090 | 69.097 | −933.705 | −859.101 | 37.396 |
| 1300 | 81.480 | 395.181 | 335.773 | 77.231 | −934 112 | −852.868 | 34.269 |
| 1400 | 81.703 | 401.228 | 340.235 | 85.391 | −934.608 | −846.600 | 31.587 |
| 1500 | 81.885 | 406.871 | 344.491 | 93.571 | −935.210 | −840.294 | 29.262 |
| 1600 | 82.034 | 412.161 | 348.557 | 101.767 | −935.931 | −833.943 | 27.225 |
| 1700 | 82.159 | 417.138 | 352.446 | 109.977 | −936.785 | −827.544 | 25.427 |
| 1800 | 82.263 | 421.837 | 356.172 | 118.198 | −937.785 | −821.090 | 23.827 |
| 1900 | 82.352 | 426.288 | 359.746 | 126.429 | −938.944 | −814.576 | 22.394 |
| 2000 | 82.428 | 430.514 | 363.180 | 134.668 | −954.959 | −807.543 | 21.091 |
| 2100 | 82.494 | 434.537 | 366.483 | 142.914 | −957.216 | −800.117 | 19.902 |
| 2200 | 82.551 | 438.376 | 369.664 | 151.166 | −959.481 | −792.582 | 18.818 |
| 2300 | 82.601 | 442.047 | 372.732 | 159.424 | −961.751 | −784.945 | 17.827 |
| 2400 | 82.645 | 445.563 | 375.694 | 167.686 | −964.022 | −777.210 | 16.916 |
| 2500 | 82.684 | 448.938 | 378.556 | 175.953 | −966.291 | −769.379 | 16.075 |
| 2600 | 82.718 | 452.181 | 381.326 | 184.223 | −968.555 | −761.458 | 15.298 |
| 2700 | 82.749 | 455.304 | 384.009 | 192.496 | −970.811 | −753.449 | 14.576 |
| 2800 | 82.777 | 458.313 | 386.609 | 200 773 | −973.055 | −745.358 | 13.905 |
| 2900 | 82.801 | 461.219 | 389.132 | 209.052 | −975.284 | −737.187 | 13.278 |
| 3000 | 82.824 | 464.026 | 391.582 | 217.333 | −977.496 | −728.939 | 12.692 |
| 3100 | 82.844 | 466.742 | 393.963 | 225.616 | −979.689 | −720.617 | 12.142 |
| 3200 | 82.862 | 469.373 | 396.278 | 233.902 | −981.860 | −712.226 | 11.626 |
| 3300 | 82.879 | 471.923 | 398.532 | 242.189 | −984.008 | −703.766 | 11.140 |
| 3400 | 82.894 | 474.397 | 400.727 | 250 477 | −986.131 | −695.242 | 10.681 |
| 3500 | 82.908 | 476.800 | 402.867 | 258.768 | −988.229 | −686.656 | 10.248 |
| 3600 | 82.921 | 479.136 | 404.953 | 267.059 | −990.299 | −678.010 | 9.838 |
| 3700 | 82 933 | 481.408 | 406.989 | 275.352 | −1401 440 | −661.519 | 9.339 |
| 3800 | 82.944 | 483.620 | 408.976 | 283.646 | −1402.221 | −641.511 | 8.818 |
| 3900 | 82.954 | 485.775 | 410.918 | 291.941 | −1403.028 | −621.481 | 8.324 |
| 4000 | 82.963 | 487.875 | 412.816 | 300.236 | −1403.861 | −601.431 | 7.854 |
| 4100 | 82.972 | 489.924 | 414.672 | 308.533 | −1404.718 | −581.360 | 7.407 |
| 4200 | 82.980 | 491.923 | 416 487 | 316.831 | −1405.598 | −561.267 | 6.980 |
| 4300 | 82.988 | 493.876 | 418.264 | 325.129 | −1406.500 | −541.154 | 6.574 |
| 4400 | 82.995 | 495.784 | 420.005 | 333.428 | −1407.422 | −521.019 | 6.185 |
| 4500 | 83.001 | 497 649 | 421.709 | 341.728 | −1408.362 | −500.863 | 5.814 |
| 4600 | 83.007 | 499.473 | 423.380 | 350.029 | −1409.320 | −480.686 | 5.458 |
| 4700 | 83.013 | 501.259 | 425.018 | 358.330 | −1410.295 | −460.487 | 5.118 |
| 4800 | 83.018 | 503.006 | 426.625 | 366.631 | −1411.285 | −440.268 | 4.791 |
| 4900 | 83.024 | 504.718 | 428.201 | 374.933 | −1412.290 | −420.028 | 4.478 |
| 5000 | 83.028 | 506.396 | 429.748 | 383.236 | −1413.307 | −399.768 | 4.176 |
| 5100 | 83.033 | 508.040 | 431.267 | 391.539 | −1414.336 | −379.486 | 3.887 |
| 5200 | 83.037 | 509.652 | 432.759 | 399.842 | −1415.377 | −359.185 | 3.608 |
| 5300 | 83.041 | 511.234 | 434.225 | 408.146 | −1416.428 | −338.864 | 3.340 |
| 5400 | 83.045 | 512.786 | 435.666 | 416.451 | −1417.489 | −318.523 | 3.081 |
| 5500 | 83.048 | 514.310 | 437.082 | 424.755 | −1418.558 | −298.162 | 2.832 |
| 5600 | 83.052 | 515.806 | 438.474 | 433.060 | −1419.635 | −277.781 | 2.591 |
| 5700 | 83.055 | 517.276 | 439.844 | 441.366 | −1420.720 | −257.382 | 2.359 |
| 5800 | 83.058 | 518.721 | 441.191 | 449.671 | −1421.812 | −236.962 | 2.134 |
| 5900 | 83.061 | 520 141 | 442.518 | 457.977 | −1422.910 | −216.525 | 1.917 |
| 6000 | 83.064 | 521.537 | 443.823 | 466.283 | −1424.014 | −196.068 | 1.707 |

PREVIOUS: September 1963 (1 atm) CURRENT September 1963 (1 bar)

## Oxygen Fluoride (FOOF) IDEAL GAS $M_r = 69.9956064$ Oxygen Fluoride (FOOF) $F_2O_2(g)$

$S°(298.15 \text{ K}) = 277.2 \pm 0.2 \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_fH°(0 \text{ K}) = 22.9 \pm 2.0 \text{ kJ·mol}^{-1}$

$\Delta_fH°(298.15 \text{ K}) = 19.2 \pm 2.0 \text{ kJ·mol}^{-1}$

Electronic Level and Quantum Weight

| State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|
| | 0.0 | 1 |

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ | $\nu$,cm$^{-1}$ |
|---|---|
| 1210(1) | 202(1) |
| 630(1) | 614(1) |
| 360(1) | 466(1) |

Point Group: $C_s$ $\sigma = 1$

Bond Distances: F–O = 1.575 Å; O–O = 1.217 Å

Bond Angles: O–O–F = 109°30′; dihedral angle = 87°30′

Product of the Moments of Inertia: $I_AI_BI_C = 1.3348 \times 10^{-114}$ g$^3$·cm$^6$

### Enthalpy of Formation

A critical measurement for the calculation of the thermodynamic functions for both $O_2F$ and $O_2F_2$ is the standard enthalpy of formation of $O_2F_2$ by Kirshenbaum *et al.*[1] These authors made a calorimetric measurement at 190 K for decomposition of $O_2F_2$ into $O_2$ and $F_2$. Conversion of that measurement from 190 K to the standard enthalpy of formation at 298 K required knowledge of the difference in constant-volume heat capacity between the reactant ($O_2F_2$) and the products ($O_2$ and $F_2$). The authors assumed that difference to be zero over the entire range. With the published heat capacities for fluorine and oxygen, plus that for $O_2F_2$ reported here, we find that the average heat capacity difference over the 190 to 298 K temperature range to be 1.41 cal K$^{-1}$·mol$^{-1}$. The standard enthalpy of formation that Kirshenbaum *et al.*[1] reported was $\Delta_fH°(O_2F_2, 298.15 \text{ K}) = 19.8 \pm 1.3$ kJ·mol$^{-1}$. With the heat capacity correction suggested by Lyman,[2] it became $\Delta_fH°(O_2F_2, 298.15 \text{ K}) = 19.2 \pm 0.84$ kJ·mol$^{-1}$ as suggested by Lyman.[2]

The value adopted is that recommended by the evaluation of Lyman,[2] with an increased uncertainty.

### Heat Capacity and Entropy

The structure of this molecule is estimated to be a nonlinear chain with an O–O–F bond angle of 109°30′ and a dihedral angle 87°30′. The adopted bond lengths are $r$(F–O) = 1.575 Å and $r$(O–O) = 1.217 Å from the microwave study of Jackson.[3] The principle moments of inertia (in g·cm$^2$) are: $I_A = 4.1409\times10^{-39}$, $I_B = 1.6747\times10^{-38}$, $I_C = 1.9247\times10^{-38}$.

The vibrational frequencies are those recommended in the review by Jacox.[4] For $\nu_1 - \nu_5$ we adopt the gas phase results (rather than the matrix isolation matrix) of Kim and Campbell.[5] For $\nu_6$ we adopt the results of Spratley *et al.*[6] which were derived from oxygen matrix isolation studies. For $\nu_2$, $\nu_3$ and $\nu_5$, these matrix isolation studies agree within 6 cm$^{-1}$ of the gas phase results. The matrix isolation results of Arkell,[7] Gardiner *et al.*[8] and Jacox[4] are in support of these values.

### References

[1] A.D. Kirshenbaum, A.V. Grosse and J.G. Aston, J. Am. Chem. Soc. 81, 6398 (1959).
[2] J.L. Lyman, J. Phys. Chem. Ref. Data 18(2), 799 (1989).
[3] R.H. Jackson, J. Chem. Soc. 4585 (1962).
[4] M.E. Jacox, J. Phys. Chem. Ref. Data, Monograph No. 3, 1 (1994).
[5] K.C. Kim and G.M. Campbell, Appl. Spectrosc. 39(4), 625–8 (1985).
[6] R.D. Spratley, J.J. Turner and G.C. Pimentel, J. Chem. Phys. 44(5), 2063 (1966).
[7] A. Arkell, J. Am. Chem. Soc. 87, 4058 (1965).
[8] D.J. Gardiner, N.J. Lawrence and J.J. Turner, J. Chem. Soc. A, 400 (1971).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | .000 | .000 | INFINITE | −13.778 | 22.930 | 22.930 | INFINITE |
| 50 | 34.134 | 197.692 | 439.855 | −12.108 | 21.699 | 26.981 | −28.187 |
| 100 | 39.458 | 222.827 | 325.625 | −10.280 | 20.617 | 32.702 | −17.082 |
| 150 | 46.225 | 240.092 | 294.354 | −8.139 | 19.844 | 38.925 | −13.555 |
| 200 | 52.643 | 254.291 | 282.610 | −5.664 | 19.393 | 45.362 | −11.847 |
| 250 | 57.967 | 266.632 | 278.206 | −2.894 | 19.203 | 51.881 | −10.840 |
| 298.15 | 62.073 | 277.206 | 277.206 | .000 | 19.200 | 58.177 | −10.192 |
| 300 | 62.213 | 277.591 | 277.207 | .115 | 19.203 | 58.419 | −10.172 |
| 400 | 68.291 | 296.385 | 279.729 | 6.663 | 19.560 | 71.448 | −9.330 |
| 500 | 72.244 | 312.079 | 284.673 | 13.703 | 20.176 | 84.352 | −8.812 |
| 600 | 74.896 | 325.500 | 290.386 | 21.068 | 20.908 | 97.119 | −8.455 |
| 700 | 76.732 | 337.192 | 296.256 | 28.655 | 21.689 | 109.760 | −8.190 |
| 800 | 78.040 | 347.528 | 302.031 | 36.397 | 22.484 | 122.287 | −7.985 |
| 900 | 78.997 | 356.778 | 307.609 | 44.251 | 23.279 | 134.715 | −7.819 |
| 1000 | 79.716 | 365.140 | 312.951 | 52.189 | 24.064 | 147.054 | −7.681 |
| 1100 | 80.267 | 372.764 | 318.047 | 60.189 | 24.836 | 159.316 | −7.565 |
| 1200 | 80.697 | 379.768 | 322.903 | 68.238 | 25.590 | 171.508 | −7.466 |
| 1300 | 81.039 | 386.241 | 327.529 | 76.326 | 26.325 | 183.638 | −7.379 |
| 1400 | 81.316 | 392.257 | 331.940 | 84.444 | 27.039 | 195.712 | −7.302 |
| 1500 | 81.542 | 397.875 | 336.151 | 92.587 | 27.731 | 207.736 | −7.234 |
| 1600 | 81.729 | 403.144 | 340.175 | 100.751 | 28.398 | 219.714 | −7.173 |
| 1700 | 81.885 | 408.104 | 344.026 | 108.932 | 29.042 | 231.652 | −7.118 |
| 1800 | 82.017 | 412.788 | 347.717 | 117.127 | 29.662 | 243.552 | −7.068 |
| 1900 | 82.130 | 417.225 | 351.260 | 125.334 | 30.258 | 255.418 | −7.022 |
| 2000 | 82.226 | 421.441 | 354.664 | 133.552 | 30.832 | 267.254 | −6.980 |
| 2100 | 82.310 | 425.455 | 357.941 | 141.779 | 31.387 | 279.061 | −6.941 |
| 2200 | 82.383 | 429.285 | 361.097 | 150.014 | 31.924 | 290.843 | −6.905 |
| 2300 | 82.446 | 432.949 | 364.142 | 158.256 | 32.446 | 302.600 | −6.872 |
| 2400 | 82.502 | 436.459 | 367.083 | 166.503 | 32.958 | 314.334 | −6.841 |
| 2500 | 82.552 | 439.828 | 369.926 | 174.756 | 33.461 | 326.048 | −6.812 |
| 2600 | 82.596 | 443.066 | 372.677 | 183.013 | 33.960 | 337.742 | −6.785 |
| 2700 | 82.635 | 446.184 | 375.342 | 191.275 | 34.458 | 349.417 | −6.760 |
| 2800 | 82.671 | 449.190 | 377.926 | 199.540 | 34.958 | 361.073 | −6.736 |
| 2900 | 82.703 | 452.092 | 380.434 | 207.809 | 35.463 | 372.710 | −6.713 |
| 3000 | 82.731 | 454.896 | 382.869 | 216.081 | 35.977 | 384.331 | −6.692 |
| 3100 | 82.757 | 457.609 | 385.237 | 224.355 | 36.501 | 395.935 | −6.671 |
| 3200 | 82.781 | 460.237 | 387.540 | 232.632 | 37.038 | 407.520 | −6.652 |
| 3300 | 82.802 | 462.785 | 389.781 | 240.911 | 37.590 | 419.089 | −6.634 |
| 3400 | 82.822 | 465.257 | 391.965 | 249.192 | 38.160 | 430.641 | −6.616 |
| 3500 | 82.840 | 467.658 | 394.094 | 257.475 | 38.747 | 442.176 | −6.599 |
| 3600 | 82.857 | 469.992 | 396.170 | 265.760 | 39.354 | 453.695 | −6.583 |
| 3700 | 82.872 | 472.262 | 398.196 | 274.047 | 39.982 | 465.195 | −6.567 |
| 3800 | 82.886 | 474.473 | 400.174 | 282.335 | 40.631 | 476.679 | −6.552 |
| 3900 | 82.899 | 476.626 | 402.107 | 290.624 | 41.301 | 488.146 | −6.538 |
| 4000 | 82.911 | 478.725 | 403.996 | 298.914 | 41.994 | 499.594 | −6.524 |
| 4100 | 82.922 | 480.772 | 405.844 | 307.206 | 42.709 | 511.025 | −6.511 |
| 4200 | 82.933 | 482.771 | 407.652 | 315.499 | 43.446 | 522.439 | −6.497 |
| 4300 | 82.943 | 484.722 | 409.421 | 323.793 | 44.204 | 533.835 | −6.485 |
| 4400 | 82.952 | 486.629 | 411.155 | 332.087 | 44.984 | 545.212 | −6.472 |
| 4500 | 82.960 | 488.493 | 412.853 | 340.383 | 45.786 | 556.572 | −6.461 |
| 4600 | 82.968 | 490.317 | 414.517 | 348.679 | 46.607 | 567.913 | −6.449 |
| 4700 | 82.975 | 492.101 | 416.149 | 356.977 | 47.447 | 579.237 | −6.438 |
| 4800 | 82.982 | 493.848 | 417.749 | 365.274 | 48.306 | 590.543 | −6.426 |
| 4900 | 82.989 | 495.559 | 419.320 | 373.573 | 49.182 | 601.831 | −6.416 |
| 5000 | 82.995 | 497.236 | 420.861 | 381.872 | 50.074 | 613.101 | −6.405 |
| 5100 | 83.001 | 498.879 | 422.375 | 390.172 | 50.981 | 624.352 | −6.395 |
| 5200 | 83.006 | 500.491 | 423.862 | 398.472 | 51.902 | 635.585 | −6.385 |
| 5300 | 83.012 | 502.072 | 425.323 | 406.773 | 52.835 | 646.802 | −6.375 |
| 5400 | 83.016 | 503.624 | 426.758 | 415.075 | 53.779 | 657.999 | −6.365 |
| 5500 | 83.021 | 505.147 | 428.170 | 423.377 | 54.732 | 669.179 | −6.355 |
| 5600 | 83.025 | 506.643 | 429.558 | 431.679 | 55.693 | 680.343 | −6.346 |
| 5700 | 83.030 | 508.113 | 430.923 | 439.982 | 56.659 | 691.488 | −6.337 |
| 5800 | 83.033 | 509.557 | 432.267 | 448.285 | 57.630 | 702.618 | −6.328 |
| 5900 | 83.037 | 510.976 | 433.589 | 456.588 | 58.604 | 713.729 | −6.319 |
| 6000 | 83.041 | 512.372 | 434.890 | 464.892 | 59.578 | 724.825 | −6.310 |

PREVIOUS: CURRENT: September 1995 (1 bar)

**Sulfuryl Fluoride ($SO_2F_2$)** **IDEAL GAS** **$M_r$ = 102.055606** **Sulfuryl Fluoride ($SO_2F_2$)** **$F_2O_2S_1(g)$**

$S°(298.15\ K) = 283.623 \pm 0.4\ J{\cdot}K^{-1}\ mol^{-1}$

$\Delta_fH°(0\ K) = -750.138 \pm 8\ 4\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -758.559 \pm 8\ 4\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|
| 1269(1) | 1502(1) |
| 848(1) | 553(1) |
| 544(1) | 885(1) |
| 384(1) | 539(1) |
| 388(1) | |

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: $C_{2v}$
Bond Distances: S–O = 1 405 ± 0 003 Å, S–F = 1.530 ± 0.003 Å
Bond Angles: O–S–O = 123.97 ± 0.20°; F–S–F = 96.12 ± 0 17°
Product of the Moments of Inertia. $I_AI_BI_C = 4.490464 \times 10^{-114}\ g^3{\cdot}cm^6$

## Enthalpy of Formation

Ruh *et al.*[1] reported percent conversions for the reaction $SO_2(g) + Cl_2(g) + 2\ HF(g) \rightarrow SO_2F_2(g) + 2\ HCl(g)$ at 110 to 700°C and at pressures slightly above atmospheric. The data allow calculation of apparent values of $K_p$ from the assumption of exact stoichiometry. Two temperatures may be excluded, namely 110°C for failure to approach equilibrium and 597°C due to power failure. The remaining values (503 to 973 K) yield $\Delta_rH°$(3rd law) = −24.15 ± 2 and $\Delta_rH°$(2nd law) = −20.7 ± 1.6 kcal·mol$^{-1}$ at 298.15 K. The 3rd law values show a minor trend with temperature, corresponding to $\Delta_rS°$(2nd law) − $\Delta_rS°$(3rd law) = 5.4 ± 2.5 cal K$^{-1}$·mol$^{-1}$, but this inconsistency is small enough to suggest that there was reasonable approach to equilibrium. An example given in the text of the patent[1] reveals that the actual recovery of $SO_2$ was somewhat less than that predicted on the assumption of stoichiometry. Use of this actual recovery of $SO_2$ would make $\Delta_rH°$(3rd law) more negative by less than 0.4 kcal mol$^{-1}$. We adopt $\Delta_rH°$ = −24.15 kcal·mol$^{-1}$ and $\Delta_fH°$ = −181.3 ± 2 kcal·mol$^{-1}$ at 298.15 K.

Reese *et al.*[2] derived $\Delta_fH°$ = −205 kcal·mol$^{-1}$ *from electron impact studies They measured potentials of* 12.44 ± 0.1 *and* 19.9 ± 0.3 eV for the appearance of $SO_2^+$ from $SO_2$ and $SO_2F_2$, respectively. Combination of these values implies that $\Delta_fH°$ of $SO_2F_2$ should be about 1.0 eV more negative than the adopted value. This discrepancy could reasonably arise from neglect of the unknown excess energies of the products of the two reactions. Bond–energy comparisons tend to confirm this view. Average values of $D_0^\circ$(S–F) may be calculated from $\Delta_rH°/2$ for $SF_6 \rightarrow SF_4 + 2\ F$ and $SO_2F_2 \rightarrow SO_2 + 2F$. $D_0^\circ$(S–F) = 72 kcal·mol$^{-1}$ from $SF_6$ is much more consistent with $D_0^\circ$(S–F) = 74 kcal·mol$^{-1}$ from the adopted $\Delta_fH°$ than with $D_0^\circ$(S–F) = 86 kcal·mol$^{-1}$ from the electron impact value.

## Heat Capacity and Entropy

Bond lengths and bond angles are from the microwave study of Lide *et al.*[3] The resulting O–S–F angle is 108.3° and the principal moments of inertia are $I_A = 16.3467 \times 10^{-39}$, $I_B = 16.5727 \times 10^{-39}$, and $I_C = 16.5756 \times 10^{-39}$ g·cm$^2$ An early electron–diffraction study[4] is in reasonable agreement.

Vibrational frequencies are those assigned by Lide *et al.*[5] based on additional microwave and infrared data for the gaseous and matrix–isolated phases. *Assignment of the three fundamentals near 544 cm$^{-1}$* and the two near 388 cm$^{-1}$ is supported by gas phase Raman spectra,[6] by combination and overtones in the infrared[6] and by force–field calculations.[7]

Calculated values of $C_p^\circ$ agree within 0 1% with those derived by Gehri[8] from measurements of $C_p^\circ$ at temperatures of 273 to 323 K and pressures up to 1 atm. The calculated entropy, $S°$ = 63.25 cal K$^{-1}$·mol$^{-1}$ at the normal boiling point of 217.78 K, may be compared with 62 66 ± 0.15 cal K$^{-1}$ mol$^{-1}$ derived from low–temperature calorimetric data by Bockhoff *et al*[9] The discrepancy is 0.59 cal K$^{-1}$·mol$^{-1}$, it was attributed[9] to randomness in the solid at absolute zero. Bockhoff and Pace[10] *later reported an entropy discrepancy of* 1.48 cal K$^{-1}$·mol$^{-1}$, but this value resulted from an incorrect vibrational assignment.[5-7]

## References

[1] R P. Ruh, R. A. Davis and K. A Allswede, U. S. Patent 3,092,458, (June 4, 1963).
[2] R. M Reese, V. H. Dibeler and J L. Franklin, J. Chem. Phys 29, 880 (1958).
[3] D. R. Lide, D. E. Mann and R M. Fristrom, J. Chem. Phys. 26, 734 (1957).
[4] D. P. Stevenson and H. Russell, J. Amer Chem. Soc 61, 3264 (1939).
[5] D R Lide, D E. Mann and J. J. Comeford, Spectrochim. Acta 21, 497 (1965).
[6] H. V. Samuelson, Dissertation Abstr. B27, 443 (1966).
[7] H. Toyuki and K. Shimizu, Bull. Chem. Soc Japan 39, 2364 (1966).
[8] D C Gehri, Dissertation Abstr. B29, 133 (1968).
[9] F. J. Bockhoff, R. V. Petrella and E L. Pace, J. Chem. Phys. 32, 799 (1960).
[10] F. J Bockhoff and E. L. Pace, J. Chem. Phys. 36, 3502 (1962).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log K$_f$ |
| 0 | 0. | 0 | INFINITE | −13.499 | −750.138 | −750.138 | INFINITE |
| 100 | 35.872 | 230.833 | 332.132 | −10.130 | −753.270 | −740.734 | 386.920 |
| 200 | 51.609 | 260.231 | 289.215 | −5 797 | −756.419 | −726.911 | 189.850 |
| 250 | 59.368 | 272.600 | 284 672 | −3.018 | −757.620 | −719.389 | 150.308 |
| 298.15 | 65.825 | 283.623 | 283.623 | 0. | −758.559 | −711.938 | 124.729 |
| 300 | 66.054 | 284.031 | 283.625 | 0.122 | −758.592 | −711.648 | 123.909 |
| 350 | 71.723 | 294 651 | 284.450 | 3.570 | −759.375 | −703.760 | 105 030 |
| 400 | 76.513 | 304.550 | 286.351 | 7.280 | −762.221 | −695.683 | 90.847 |
| 450 | 80.558 | 313.803 | 288.893 | 11.209 | −763.401 | −687.302 | 79.780 |
| 500 | 83 975 | 322.472 | 291.822 | 15.325 | −764.529 | −678.783 | 70.912 |
| 600 | 89.324 | 338.282 | 298.274 | 24.005 | −766.067 | −661.478 | 57.587 |
| 700 | 93.205 | 352.358 | 305.014 | 33.141 | −767.083 | −643.960 | 48.053 |
| 800 | 96.066 | 365.000 | 311.736 | 42.612 | −767.770 | −626.321 | 40.895 |
| 900 | 98.215 | 376.445 | 318.300 | 52.331 | −821.368 | −607.529 | 35.260 |
| 1000 | 99.858 | 386.882 | 324.644 | 62.238 | −820.469 | −583.817 | 30.495 |
| 1100 | 101.136 | 396 462 | 330.744 | 72.290 | −819.517 | −560.198 | 26.602 |
| 1200 | 102.146 | 405.307 | 336.593 | 82.456 | −818.532 | −536.666 | 23.360 |
| 1300 | 102.956 | 413.516 | 342.198 | 92.713 | −817.531 | −513.218 | 20.621 |
| 1400 | 103 615 | 421.171 | 347.569 | 103.042 | −816.523 | −489.847 | 18.276 |
| 1500 | 104.157 | 428.339 | 352.717 | 113.432 | −815.519 | −466.549 | 16 247 |
| 1600 | 104.608 | 435.075 | 357.656 | 123.871 | −814.524 | −443.316 | 14.473 |
| 1700 | 104.986 | 441.429 | 362.399 | 134.351 | −813.544 | −420.146 | 12.910 |
| 1800 | 105.307 | 447.439 | 366.958 | 144.866 | −812.581 | −397.033 | 11.522 |
| 1900 | 105.581 | 453.140 | 371.345 | 155.411 | −811.637 | −373.973 | 10.281 |
| 2000 | 105.817 | 458.562 | 375.572 | 165.981 | −810.712 | −350.962 | 9.166 |
| 2100 | 106.021 | 463.730 | 379.648 | 176.573 | −809.804 | −327.997 | 8.158 |
| 2200 | 106.200 | 468.666 | 383.582 | 187.184 | −808.913 | −305.074 | 7.243 |
| 2300 | 106.356 | 473.391 | 387.385 | 197.812 | −808.036 | −282.192 | 6.409 |
| 2400 | 106 494 | 477.920 | 391.064 | 208.455 | −807.171 | −259.348 | 5.645 |
| 2500 | 106.616 | 482.270 | 394.626 | 219.111 | −806.313 | −236.540 | 4.942 |
| 2600 | 106.725 | 486.454 | 398.078 | 229.778 | −805.460 | −213.766 | 4.295 |
| 2700 | 106.822 | 490.483 | 401 426 | 240.455 | −804.609 | −191.024 | 3.696 |
| 2800 | 106.909 | 494.370 | 404.676 | 251.142 | −803.755 | −168.314 | 3.140 |
| 2900 | 106.988 | 498.123 | 407.834 | 261.837 | −802.897 | −145.635 | 2.623 |
| 3000 | 107.058 | 501.751 | 410.905 | 272.539 | −802.032 | −122.986 | 2.141 |
| 3100 | 107.123 | 505.262 | 413.892 | 283.248 | −801.156 | −100.365 | 1.691 |
| 3200 | 107.181 | 508 664 | 416.801 | 293.963 | −800.268 | −77.773 | 1.270 |
| 3300 | 107.235 | 511.963 | 419.635 | 304.684 | −799.366 | −55.210 | 0.874 |
| 3400 | 107.284 | 515.165 | 422.398 | 315.410 | −798.448 | −32.673 | 0.502 |
| 3500 | 107.328 | 518.276 | 425.093 | 326.141 | −797.514 | −10.164 | 0.152 |
| 3600 | 107.369 | 521.300 | 427.723 | 336.876 | −796.561 | 12.319 | −0.179 |
| 3700 | 107.407 | 524.242 | 430.292 | 347.615 | −795.590 | 34.774 | −0.491 |
| 3800 | 107.442 | 527.107 | 432.803 | 358.357 | −794.599 | 57.204 | −0.786 |
| 3900 | 107.475 | 529.898 | 435.257 | 369.103 | −793.589 | 79.607 | −1.066 |
| 4000 | 107.505 | 532.620 | 437.657 | 379.852 | −792.559 | 101.983 | −1.332 |
| 4100 | 107.532 | 535.275 | 440.006 | 390.604 | −791.511 | 124.333 | −1.584 |
| 4200 | 107.558 | 537.866 | 442.305 | 401.358 | −790.443 | 146.658 | −1.824 |
| 4300 | 107.582 | 540.398 | 444.557 | 412.115 | −789.358 | 168.958 | −2.052 |
| 4400 | 107.605 | 542.871 | 446.763 | 422.875 | −788.255 | 191.231 | −2.270 |
| 4500 | 107.626 | 545.290 | 448.926 | 433.636 | −787.135 | 213.479 | −2.478 |
| 4600 | 107.646 | 547.655 | 451.047 | 444.400 | −785.999 | 235.702 | −2.676 |
| 4700 | 107.664 | 549 971 | 453.127 | 455.165 | −784.849 | 257.901 | −2.866 |
| 4800 | 107.682 | 552.237 | 455.168 | 465.933 | −783.686 | 280.075 | −3.048 |
| 4900 | 107.698 | 554.458 | 457.172 | 476.702 | −782.511 | 302.225 | −3.222 |
| 5000 | 107 713 | 556.634 | 459 139 | 487.472 | −781.325 | 324.351 | −3.388 |
| 5100 | 107.728 | 558.767 | 461 072 | 498.244 | −780.130 | 346.452 | −3.548 |
| 5200 | 107.741 | 560.859 | 462.971 | 509.018 | −778.927 | 368.530 | −3.702 |
| 5300 | 107 754 | 562.911 | 464 837 | 519.793 | −777.718 | 390.586 | −3.849 |
| 5400 | 107.766 | 564.926 | 466.672 | 530.569 | −776.506 | 412.617 | −3.991 |
| 5500 | 107.778 | 566.903 | 468.477 | 541.346 | −775.290 | 434.626 | −4.128 |
| 5600 | 107.789 | 568.845 | 470.252 | 552.124 | −774.073 | 456.615 | −4.259 |
| 5700 | 107 799 | 570.753 | 471.998 | 562.904 | −772.857 | 478.580 | −4.386 |
| 5800 | 107.809 | 572.628 | 473.717 | 573.684 | −771.644 | 500.525 | −4.508 |
| 5900 | 107 818 | 574 471 | 475.409 | 584.465 | −770.434 | 522.447 | −4.625 |
| 6000 | 107.827 | 576.283 | 477.075 | 595 248 | −769.232 | 544.351 | −4.739 |

PREVIOUS June 1971 (1 atm) CURRENT June 1971 (1 bar)

## Phosphorus Fluoride ($PF_2$) IDEAL GAS $M_r = 68.970566$ Phosphorus Fluoride ($PF_2$) $F_2P_1(g)$

$\Delta_a H^\circ(0\ K) = [954.370 \pm 25.1]\ kJ\cdot mol^{-1}$
$S^\circ(298.15\ K) = [262.957 \pm 0.8]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H^\circ(0\ K) = [-485.280 \pm 20.9]\ kJ\cdot mol^{-1}$
$\Delta_f H^\circ(298.15\ K) = [-488.256 \pm 20.9]\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights

| $\epsilon_i$, $cm^{-1}$ | $g_i$ |
|---|---|
| 0 | 2 |
| [25000] | [2] |
| [28000] | [2] |
| [30000] | [2] |

Vibrational Frequencies and Degeneracies

| $\nu$, $cm^{-1}$ |
|---|
| 831 (1) |
| [353](1) |
| 852 (1) |

Point Group: $C_{2v}$ $\sigma = 2$
Bond Distance: P–F = [1.58] Å
Bond Angle: F–P–F = [99]°
Product of the Moments of Inertia: $I_A I_B I_C = [3\ 285613 \times 10^{-115}]\ g^3\cdot cm^6$

### Enthalpy of Formation

The adopted results are $\Delta_f H^\circ(0\ K) = 112.2 \pm 5.0\ kcal\cdot mol^{-1}$, $D_0^\circ$ (PF-F) = $122.0 \pm 10.0\ kcal\cdot mol^{-1}$, and $\Delta_a H^\circ = 228.1 \pm 6.0\ kcal\cdot mol^{-1}$. We estimate $\Delta_f H^\circ$ such that the value gives $D_0^\circ$ (PF–F)/$\Delta_a H^\circ(0\ K) = 0.535$ The value of this ratio is selected from those for $SiF_2$(0.54 ± 0.03) and $SF_2$(0.53 ± 0.05) which are calculated from the most recent JANAF tables.[1] Two previous estimates of $\Delta_f H^\circ$ are available for comparison O'Hare[2] used the relationship $D_0^\circ$ ($PF_2$–F) = 1.1 $\Delta_a H^\circ(PF_3)$ to obtain a $\Delta_f H^\circ$ of $-115.7 \pm 5\ kcal\cdot mol^{-1}$. This estimate agrees quite well with the results adopted here. An earlier JANAF table[3] gives $\Delta_f H^\circ(PF_2) = -104.7 \pm 15.0\ kcal\cdot mol^{-1}$ which was based on an estimate value for the $\Delta_a H^\circ$ of $PF_3$. We estimate that the uncertainty in the value of the ratio $D_0^\circ/\Delta_a H^\circ$ should not exceed ±0.06 which corresponds to an uncertainty in $\Delta_f H^\circ$ of $\pm 5.0\ kcal\cdot mol^{-1}$.

### Heat Capacity and Entropy

The results of electron spin resonance experiments[4,5] and molecular orbital calculations[4 6,7] are consistent with $PF_2$ having $C_{2v}$ symmetry; however, no experimental determination of the structural parameters has been reported. Numerous values for the bond length and angle have been proposed based on energy optimization[6,7] and other estimation techniques.[2 4 8 9] These estimates are widely scattered with the bond lengths ranging from (1.52 to 1.73 Å) and the bond angles ranging from 98.6 to 112°. We prefer to use molecular parameters similar to those measured[10] for the related molecule $PF_2H$. The adopted values appear quite reasonable by comparison with structural data[1] for $SiF_2$ and $SF_2$. The principal moments of inertia are: $I_A = 2.9836 \times 10^{-39}$, $I_B = 9.1077 \times 10^{-39}$, and $I_C = 12.0913 \times 10^{-39}\ g\cdot cm^2$.

The two stretching frequencies ($\nu_1$ and $\nu_3$) have been observed[11] in the infrared spectrum of $PF_2$ formed in an argon matrix by photolysis of $PF_2H$. The adopted values are rounded to the nearest $cm^{-1}$. The bending frequency ($\nu_2$) is calculated from the force constant $f_\alpha/r^2 = 0.495$ mdyn/Å. We obtain the bending force constant from the ratio $f_r/(f_\alpha/r^2)$ equal to 9.59 which is the value calculated for $SiF_2$.[1]

The ground state is expected to be $^2B_1$, as shown by Wei *et al*.[4] We assume that the upper electronic levels and their corresponding quantum weights are the same as those previously estimated for the isoelectronic $SF_2^+$ ion. The procedure used to estimate these levels is thoroughly discussed on the $SF_2^+$ table.[1]

This table essentially updates the functions previously tabulated by O'Hare.[2]

### References

[1] JANAF Thermochemical Tables. $SF_2$(g) and $SiF_2$(g), 6–30–76; $SF_2^+$(g), 12–31–76; $PF_3$(g) and $PF_5$(g), 12–31–69.
[2] P. A. G. O'Hare, Argonne National Laboratory, ANL 7459, (December 1968).
[3] JANAF Thermochemical Tables, 2nd ed., NSRDS NBS 37, (1971).
[4] M. S. Wei, J. H. Current and J. Gendell, J. Chem. Phys. 52, 1592 (1970).
[5] W. Nelson, G. Jackel, and W. Gordy, J Chem. Phys. 52, 4572 (1970).
[6] A. Hudson and J. T. Wiffen, Chem. Phys. Lett. 29, 113 (1974).
[7] D. Kilcast and C. Thomson, J. Chem. Soc., Faraday Trans. II, 68, 535 (1972).
[8] J. Kendrick, I. H. Hillier and M. F. Guest, Chem. Phys. Lett. 33, 173 (1975).
[9] J. C Cobb and A. Hinchliffe, Chem. Phys. Lett. 24, 75 (1974).
[10] R L. Kuczkowski, J. Amer. Chem. Soc. 90, 1705 (1968).
[11] J. K. Burdett, L. Hodges, V. Dunning and J. H. Current, J Phys. Chem. 74, 4053 (1970).

Enthalpy Reference Temperature = $T_r$ = 298.15 K  Standard State Pressure = $p^\circ$ = 0.1 MPa

|  | J·K⁻¹mol⁻¹ |  |  | kJ·mol⁻¹ |  |  |  |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −11.209 | −485.280 | −485.280 | INFINITE |
| 100 | 34.623 | 220.645 | 299.211 | −7.857 | −485.722 | −488.981 | 255.417 |
| 200 | 39.685 | 246.149 | 266.890 | −4.148 | −487.206 | −491.880 | 128.466 |
| 250 | 42.344 | 255.291 | 263.680 | −2.097 | −487.749 | −492.985 | 103.004 |
| 298 15 | 44.717 | 262.957 | 262.957 | 0. | −488.256 | −493.948 | 86.538 |
| 300 | 44.803 | 263.233 | 262.957 | 0.083 | −488.275 | −493.983 | 86.010 |
| 350 | 46.927 | 270.304 | 263.511 | 2.378 | −489.505 | −494.823 | 73.848 |
| 400 | 48.696 | 276.690 | 264.766 | 4.770 | −490.060 | −495.544 | 64.711 |
| 450 | 50.142 | 282.511 | 266.419 | 7.242 | −490.571 | −496.198 | 57.597 |
| 500 | 51.319 | 287.858 | 268.299 | 9.779 | −491.048 | −496.797 | 51.900 |
| 600 | 53.065 | 297.379 | 272.372 | 15.004 | −491.929 | −497.863 | 43.343 |
| 700 | 54.253 | 305.654 | 276.548 | 20.374 | −492.744 | −498.787 | 37.220 |
| 800 | 55.086 | 312.956 | 280.652 | 25.843 | −493.517 | −499.597 | 32.620 |
| 900 | 55.687 | 319.481 | 284.610 | 31.383 | −494.263 | −500.312 | 29.037 |
| 1000 | 56 134 | 325.372 | 288.397 | 36.976 | −494.994 | −500.945 | 26.167 |
| 1100 | 56.473 | 330.739 | 292.006 | 42.607 | −495.715 | −501.505 | 23.814 |
| 1200 | 56.736 | 335.664 | 295.441 | 48.268 | −560.005 | −500.921 | 21.805 |
| 1300 | 56 944 | 340.214 | 298.713 | 53.952 | −559.947 | −496.000 | 19.930 |
| 1400 | 57.111 | 344.441 | 301.830 | 59.655 | −559.898 | −491.083 | 18.323 |
| 1500 | 57.248 | 348.386 | 304.804 | 65.373 | −559.857 | −486.169 | 16.930 |
| 1600 | 57.360 | 352.084 | 307.644 | 71.104 | −559.825 | −481.258 | 15.711 |
| 1700 | 57.454 | 355.564 | 310.362 | 76.845 | −559.803 | −476.348 | 14.636 |
| 1800 | 57.533 | 358.851 | 312.965 | 82.594 | −559.790 | −471.439 | 13.681 |
| 1900 | 57.600 | 361 963 | 315.463 | 88.351 | −559.784 | −466.531 | 12.826 |
| 2000 | 57.658 | 364 919 | 317.862 | 94.114 | −559.783 | −461.623 | 12.056 |
| 2100 | 57.707 | 367 733 | 320.171 | 99.882 | −559.786 | −456.715 | 11.360 |
| 2200 | 57.751 | 370 419 | 322.394 | 105.655 | −559.787 | −451.807 | 10.727 |
| 2300 | 57.789 | 372.987 | 324.538 | 111.432 | −559.786 | −446.899 | 10.149 |
| 2400 | 57.822 | 375.447 | 326.609 | 117.213 | −559.778 | −441.991 | 9.620 |
| 2500 | 57.852 | 377.808 | 328.610 | 122.996 | −559.760 | −437.083 | 9.132 |
| 2600 | 57.879 | 380.078 | 330.546 | 128.783 | −559.728 | −432.177 | 8.683 |
| 2700 | 57.904 | 382.263 | 332.421 | 134.572 | −559.679 | −427.272 | 8.266 |
| 2800 | 57.926 | 384.369 | 334.239 | 140.364 | −559.611 | −422.369 | 7.879 |
| 2900 | 57.948 | 386.402 | 336.003 | 146.157 | −559.520 | −417.469 | 7.519 |
| 3000 | 57.968 | 388.367 | 337.716 | 151.953 | −559.405 | −412.573 | 7.184 |
| 3100 | 57.987 | 390.268 | 339.381 | 157.751 | −559.262 | −407.681 | 6.869 |
| 3200 | 58.007 | 392.109 | 341.000 | 163.551 | −559.089 | −402.794 | 6.575 |
| 3300 | 58.027 | 393.895 | 342.576 | 169.352 | −558.886 | −397.913 | 6.298 |
| 3400 | 58.047 | 395.627 | 344.111 | 175.156 | −558.651 | −393.038 | 6.038 |
| 3500 | 58.068 | 397.310 | 345.607 | 180.962 | −558.383 | −388.171 | 5.793 |
| 3600 | 58.091 | 398.946 | 347.066 | 186.770 | −558.080 | −383.312 | 5.562 |
| 3700 | 58.115 | 400.538 | 348.490 | 192.580 | −557.743 | −378.462 | 5.343 |
| 3800 | 58.142 | 402.088 | 349.880 | 198.393 | −557.370 | −373.621 | 5.136 |
| 3900 | 58.171 | 403.599 | 351.238 | 204.208 | −556.962 | −368.791 | 4.939 |
| 4000 | 58.202 | 405.072 | 352.565 | 210.027 | −556.518 | −363.972 | 4.753 |
| 4100 | 58.237 | 406.510 | 353.864 | 215.849 | −556.037 | −359.164 | 4.576 |
| 4200 | 58.275 | 407.914 | 355.134 | 221.675 | −555.521 | −354.368 | 4.407 |
| 4300 | 58.316 | 409.285 | 356.377 | 227.504 | −554.969 | −349.586 | 4.247 |
| 4400 | 58.361 | 410.626 | 357.595 | 233.338 | −554.381 | −344.816 | 4 093 |
| 4500 | 58.410 | 411.938 | 358.788 | 239.176 | −553.757 | −340.060 | 3.947 |
| 4600 | 58.462 | 413.223 | 359.958 | 245.020 | −553.098 | −335.318 | 3.808 |
| 4700 | 58.519 | 414.481 | 361.104 | 250.869 | −552.404 | −330.591 | 3.674 |
| 4800 | 58.580 | 415.713 | 362.229 | 256.724 | −551.675 | −325.879 | 3.546 |
| 4900 | 58.646 | 416.922 | 363.333 | 262.585 | −550.911 | −321.183 | 3.424 |
| 5000 | 58.716 | 418.107 | 364.417 | 268.453 | −550.114 | −316.503 | 3.306 |
| 5100 | 58.790 | 419.271 | 365.481 | 274.329 | −549.282 | −311.839 | 3.194 |
| 5200 | 58.869 | 420.413 | 366.526 | 280.211 | −548.417 | −307.191 | 3.086 |
| 5300 | 58.952 | 421.535 | 367.554 | 286.102 | −547.519 | −302.561 | 2.982 |
| 5400 | 59.039 | 422.638 | 368.564 | 292.002 | −546.588 | −297.948 | 2.882 |
| 5500 | 59.131 | 423.722 | 369.557 | 297.910 | −545.624 | −293.353 | 2.786 |
| 5600 | 59.226 | 424.789 | 370.534 | 303.828 | −544.628 | −288.774 | 2.694 |
| 5700 | 59.326 | 425.838 | 371.495 | 309.756 | −543.600 | −284.215 | 2.605 |
| 5800 | 59.430 | 426.870 | 372.440 | 315.694 | −542.540 | −279.674 | 2.519 |
| 5900 | 59.537 | 427 887 | 373.372 | 321.642 | −541.449 | −275.150 | 2.436 |
| 6000 | 59.649 | 428.889 | 374.289 | 327.601 | −540.327 | −270.647 | 2.356 |

PREVIOUS June 1977 (1 atm)  CURRENT June 1977 (1 bar)

## Phosphorus Fluoride, Ion ($PF_2^+$) IDEAL GAS $M_r$ = 68.970017 Phosphorus Fluoride, Ion ($PF_2^+$) $F_2P_1^+(g)$

$S°(298.15\ K)$ = [257.358 ± 8.4] J·K⁻¹·mol⁻¹

$\Delta_f H°(0\ K)$ = 469.054 ± 33.5 kJ·mol⁻¹

$\Delta_f H°(298.15\ K)$ = 472.273 ± 33.5 kJ·mol⁻¹

| Electronic Levels and Quantum Weights<br>$\epsilon_i$, cm⁻¹ | $g_i$ |
|---|---|
| 0 | [1] |
| [25000] | [3] |
| [40000] | [1] |

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm⁻¹ |
|---|
| [840](1) |
| [350](1) |
| [860](1) |

Point Group: $C_{2v}$ $\sigma$ = [2]

Bond Distance: P–F = [1.59] Å

Bond Angle: F–P–F = [101]°

Product of the Moments of Inertia: $I_A I_B I_C$ = [3.412079 × 10⁻¹¹⁵] g³·cm⁶

### Enthalpy of Formation

A summary of the information available on the appearance potential of $PF_2^+$ from $PF_3$ is presented below. We analyze these electron–impact results using the expression $\Delta_f H°(0\ K) = AP - E^*$ by assuming that the dissociative ionization process is $PF_3(g) + e^- = PF_2^+(g) + F(g) + 2\ e^-$. Values of $\Delta_f H°$ and the ionization potential are derived by setting $E^*$ in the above expression equal to zero. As a result, the values are listed in the table as inequalities to emphasize that they are limiting (upper) values.

| Source | AP($PF_2^+$/PF) eV | $\Delta_f H°$($PF_2^+$, g, 0 K) kcal·mol⁻¹ | IP($PF_2$) eV |
|---|---|---|---|
| 1 | 15.4 ± 0.2 | <112.78 | <9.76 |
| 2 | 15.7 ± 0.5 | <119.70 | <10.06 |
| 3 | 15.5 ± 0.2 | <115.09 | <9.86 |
| 4 | 13.5 | <68.97 | <7.86 |

The results derived from the first three studies[1-3] are in excellent accord, and we adopt the mean values of $\Delta_f H°$ = 115.861 ± 8.0 kcal·mol⁻¹ and IP = 9.89 eV. Dean *et al.*[4] were unable to offer an explanation as to why their results were significantly lower than the other literature data. This study[4] indicates that IP($PF_2$)<IP($PCl_2$) [3] which we believe is very unlikely. Harland *et al.* [1] have reported the AP for $PF_2^+$ from $PF_2CN$ as 13.4 ± 0.2 eV, suggesting the possibility that the precursor responsible for the $PF_2^+$ ion in the measurements of Dean *et al.*[4] was $PF_2CN$ rather than $PF_3$. A MO study[5] gave IP($PF_2$) = 9.88 eV based on IP(P) – 10.98 eV. Recalculation of their results using a more recent value of IP(P) = 10.486 eV[6] gives IP($PF_2$) = 9.88 eV. Our adopted value of IP (9.89 eV) is close to that for atomic phosphorus (10.49 eV). This is consistent with the results of electron spin resonance experiments[7 8] and MO calculations [5 7 9 10] which show that the ionizing orbital is slightly antibonding and located primarily on the phosphorus atom.

The mean bond energy (products $P^+(g)+2F(g)$) is 120.9 kcal mol⁻¹ which when compared with that for $PF_2$(114.1 kcal·mol⁻¹),[11] suggests that the bonding is somewhat stronger in the positive ion. This predicted increase in bond strength upon ionization is also consistent with the antibonding nature of the ionizing orbital. $\Delta_f H°$ (298 15 K) is calculated to be 117.049 kcal·mol⁻¹.

### Heat Capacity and Entropy

The molecular parameters and vibrational frequencies are assumed to lie between those for $PF_2$ and $SiF_2$.[11] The electronic levels and quantum weights are estimated by analogy with those for the isoelectronic molecule $SiF_2$.[11] The principal moments of inertia are: $I_A = 2.8983 \times 10^{-39}$, $I_B = 9.4974 \times 10^{-39}$, and $I_C = 12.3957 \times 10^{-39}$ g·cm².

### References

[1] P. W. Harland, D. W. H. Rankin and J. C. J. Thynne, Int. J. Mas Spectr. Ion Phys. 13, 395 (1974).

[2] F. E. Stafford, personal communication quoted in Harland *et al.*[1]

[3] D. F. Torgerson and J. B. Westmore, Can. J. Chem. 53, 933 (1975).

[4] C. R. S. Dean, A. Finch, P J. Gardner, and D. W. Payling, J. Chem. Soc , Faraday Trans. I, 70, 1921 (1974).

[5] A. L. Companion and Y. P. Hsia, J. Mol. Struct. 14, 117 (1972).

Continued on page 1215

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −11.207 | 469.054 | | |
| 100 | 34.659 | 215.050 | 293.584 | −7.853 | | | |
| 200 | 39.667 | 240.571 | 261.285 | −4.143 | | | |
| 250 | 42.285 | 249.705 | 258.080 | −2.094 | | | |
| 298.15 | 44.635 | 257.358 | 257.358 | 0. | 472.273 | 461.996 | −80.940 |
| 300 | 44.720 | 257.634 | 257.359 | 0.083 | 472.292 | 461.932 | −80.430 |
| 350 | 46.835 | 264.691 | 257.911 | 2.373 | 472.097 | 460.235 | −68.686 |
| 400 | 48.602 | 271.064 | 259.163 | 4.760 | 472.577 | 458.509 | −59.875 |
| 450 | 50.053 | 276.875 | 260.813 | 7.228 | 473.101 | 456.719 | −53.015 |
| 500 | 51.236 | 282.212 | 262.690 | 9.761 | 473.658 | 454.869 | −47.520 |
| 600 | 52.996 | 291.720 | 266.755 | 14.979 | 474.848 | 451.001 | −39.263 |
| 700 | 54.196 | 299.985 | 270.925 | 20.342 | 476.106 | 446.928 | −33.350 |
| 800 | 55.039 | 307.280 | 275.022 | 25.806 | 477.407 | 442.671 | −28.903 |
| 900 | 55.648 | 313.800 | 278.975 | 31.342 | 478.735 | 438.250 | −25.435 |
| 1000 | 56.101 | 319.687 | 282.757 | 36.930 | 480.079 | 433.680 | −22.653 |
| 1100 | 56.445 | 325.051 | 286.362 | 42.558 | 481.433 | 428.974 | −20.370 |
| 1200 | 56.712 | 329.974 | 289.794 | 48.217 | 419.220 | 425.224 | −18.510 |
| 1300 | 56.924 | 334.523 | 293.062 | 53.899 | 421.353 | 425.637 | −17.102 |
| 1400 | 57.093 | 338.747 | 296.176 | 59.600 | 423.480 | 425.887 | −15.890 |
| 1500 | 57.232 | 342.691 | 299.147 | 65.317 | 425.598 | 425 985 | −14.834 |
| 1600 | 57.346 | 346.389 | 301.985 | 71.046 | 427.706 | 425.942 | −13.906 |
| 1700 | 57.441 | 349.868 | 304.700 | 76.785 | 429.806 | 425.767 | −13.082 |
| 1800 | 57.522 | 353.154 | 307.302 | 82.534 | 431.896 | 425.470 | −12.347 |
| 1900 | 57.590 | 356.266 | 309.798 | 88.289 | 433.980 | 425.056 | −11.686 |
| 2000 | 57.649 | 359.221 | 312.196 | 94.051 | 436.058 | 424.532 | −11.088 |
| 2100 | 57.699 | 362.035 | 314.503 | 99.819 | 438.134 | 423.905 | −10.544 |
| 2200 | 57.743 | 364.720 | 316.725 | 105.591 | 440.209 | 423.178 | −10.048 |
| 2300 | 57.782 | 367.288 | 318.868 | 111.367 | 442.289 | 422.358 | −9.592 |
| 2400 | 57.817 | 369.748 | 320.937 | 117.147 | 444.375 | 421.447 | −9.173 |
| 2500 | 57.848 | 372.109 | 322.937 | 122.930 | 446.471 | 420.448 | −8.785 |
| 2600 | 57.876 | 374.378 | 324.872 | 128.717 | 448.581 | 419.366 | −8.425 |
| 2700 | 57.903 | 376.563 | 326.746 | 134.506 | 450.708 | 418.202 | −8.091 |
| 2800 | 57.927 | 378.669 | 328.563 | 140.297 | 452.855 | 416.959 | −7.778 |
| 2900 | 57.951 | 380.703 | 330.326 | 146.091 | 455.025 | 415.638 | −7.486 |
| 3000 | 57.975 | 382.668 | 332.038 | 151.887 | 457.220 | 414.243 | −7.213 |
| 3100 | 57.999 | 384.569 | 333.702 | 157.686 | 459.442 | 412.774 | −6.955 |
| 3200 | 58.024 | 386.411 | 335.321 | 163.487 | 461.695 | 411.232 | −6.713 |
| 3300 | 58.050 | 388.197 | 336.896 | 169.291 | 463.978 | 409.620 | −6.484 |
| 3400 | 58.079 | 389.930 | 338.431 | 175.097 | 466.295 | 407.938 | −6.267 |
| 3500 | 58.109 | 391.614 | 339.926 | 180.907 | 468.645 | 406.188 | −6.062 |
| 3600 | 58.143 | 393.251 | 341.385 | 186.719 | 471.031 | 404.370 | −5.867 |
| 3700 | 58.179 | 394.845 | 342.808 | 192.535 | 473.453 | 402.485 | −5.682 |
| 3800 | 58.219 | 396.397 | 344.198 | 198.355 | 475.911 | 400.534 | −5.506 |
| 3900 | 58.264 | 397.910 | 345.556 | 204.179 | 478.406 | 398.518 | −5.338 |
| 4000 | 58.313 | 399.386 | 346.884 | 210.008 | 480.939 | 396.437 | −5 177 |
| 4100 | 58.366 | 400.826 | 348.182 | 215.842 | 483.510 | 394.293 | −5.023 |
| 4200 | 58.424 | 402.233 | 349.452 | 221.682 | 486.119 | 392.086 | −4.876 |
| 4300 | 58.488 | 403.609 | 350.696 | 227.527 | 488.766 | 389.815 | −4.735 |
| 4400 | 58.557 | 404.954 | 351.913 | 233.379 | 491.451 | 387.483 | −4.600 |
| 4500 | 58.631 | 406.271 | 353.107 | 239.239 | 494.174 | 385.090 | −4.470 |
| 4600 | 58.711 | 407.560 | 354.277 | 245.106 | 496.935 | 382.635 | −4.345 |
| 4700 | 58.797 | 408.824 | 355.424 | 250.981 | 499.734 | 380.120 | −4.225 |
| 4800 | 58.888 | 410.063 | 356.549 | 256.865 | 502.571 | 377.546 | −4.109 |
| 4900 | 58.985 | 411.278 | 357.654 | 262.759 | 505.446 | 374.911 | −3.997 |
| 5000 | 59.087 | 412.471 | 358.738 | 268.663 | 508.357 | 372.218 | −3.889 |
| 5100 | 59.195 | 413.642 | 359.803 | 274.577 | 511.306 | 369.466 | −3.784 |
| 5200 | 59.309 | 414.792 | 360.850 | 280.502 | 514.292 | 366.656 | −3.683 |
| 5300 | 59.428 | 415.923 | 361.878 | 286.439 | 517.315 | 363.788 | −3.585 |
| 5400 | 59.551 | 417.035 | 362.889 | 292.387 | 520.374 | 360.862 | −3.491 |
| 5500 | 59.680 | 418.129 | 363.884 | 298.349 | 523.470 | 357.880 | −3.399 |
| 5600 | 59.814 | 419.206 | 364.862 | 304.324 | 526.601 | 354.841 | −3.310 |
| 5700 | 59.952 | 420.266 | 365.825 | 310.312 | 529.769 | 351.745 | −3.223 |
| 5800 | 60.094 | 421.309 | 366.773 | 316.314 | 532.971 | 348.594 | −3.139 |
| 5900 | 60.240 | 422.338 | 367.706 | 322.331 | 536.209 | 345.388 | −3.058 |
| 6000 | 60.390 | 423.352 | 368.625 | 328.362 | 539.482 | 342.126 | −2.978 |

PREVIOUS· June 1977 (1 atm) CURRENT. June 1977 (1 bar)

## Phosphorus Fluoride, Ion ($PF_2^-$) IDEAL GAS $M_r = 68.971115$ Phosphorus Fluoride, Ion ($PF_2^-$) $F_2P_1^-(g)$

$S°(298.15\ K) = [257.364 \pm 0.8]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-630.010 \pm 69.0]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-639.177 \pm 69.0]\ kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, cm$^{-1}$ |
|---|
| [820](1) |
| [355](1) |
| [845](1) |

Ground State Quantum Weight: [1]  $\sigma = [2]$

Point Group: $C_{2v}$

Bond Distance: P–F = [1.59]Å

Bond Angle: F–P–F = [98]°

Product of the Moments of Inertia: $I_A I_B I_C = [3.409086 \times 10^{-115}]\ g^3 \cdot cm^6$

### Enthalpy of Formation

The $PF_2^-$ anion has been observed in the negative ion mass spectra of $PF_3$[1] and $PF_2CN$.[2] Both studies included thermochemical calculations on plausible ion formation processes, showing that the measured appearance potentials contained large excess energy contributions. At present, definite values cannot be assigned to these contributions; thus, their studies are of little value in defining $\Delta_f H°$.

Two estimates of the electron affinity of $PF_2$ have been reported.[2, 3] Harland *et al.*[2] considered differences in bond energies for diatomic and triatomic species to obtain a value of $EA(PF_2) = 1.4$ eV. Rescaled CNDO calculations[3] have led to an EA = 1.71 eV. JANAF data[4] on the S–F system indicate that the EA values alternate between the even – and odd – electron molecules, with the odd–electron molecules having the higher EA values. Assuming the same trend is followed in the P–F system, we predict that $EA(PF_2) > EA(PF)$ which is equal to $1.1 \pm 0.5$ eV.[4] We adopt an EA of $1.5 \pm 0.5$ eV for the reaction $PF_2^-(g) = PF_2(g) + e^-$ at 0 K which leads to $\Delta_f H°(PF_2^-, g, 0\ K) = -146.822 \pm 16.5\ kcal \cdot mol^{-1}$ with $\Delta_f H°(PF_2, g, 0\ K) = -112.23 \pm 5.0\ kcal \cdot mol^{-1}$.[4] The adopted value of EA is close to that for atomic phosphorus ($0.77 \pm 0.05$ eV).[5] This is in agreement with results of MO calculations[3, 6] and electron spin resonance experiments[6, 7] which show that the electron captured by $PF_2$ goes into an antibonding orbital which is located primarily on the phosphorus atom.

$\Delta_f H°$ at 298.15 K and the fluoride–ion affinity (IA) are calculated to be $-148.594\ kcal \cdot mol^{-1}$ and $78.2\ kcal \cdot mol^{-1}$, respectively. The mean bond energy $\Delta_a H°/2$(products $P(g) + F(g) + F^-(g)$) is $92.2\ kcal \cdot mol^{-1}$ which is $21.9\ kcal \cdot mol^{-1}$ less than that for $PF_2$($114.1\ kcal\ mol^{-1}$).[4] The predicted decrease in the bond strength for the anion is also consistent with the antibonding nature of the electron orbital.

### Heat Capacity and Entropy

The molecular parameters and vibrational frequencies are assumed to lie between those for $PF_2$ and $SF_2$.[4] The ground state is assumed to be a singlet since $PF_2^-$ has no unpaired electrons. Also, we neglect excited states since these probably lie at energies which would not contribute to the partition function (refer to the table for the isoelectronic species $SF_2$). The principal moments of inertia are: $I_A = 3.0833 \times 10^{-39}$, $I_B = 9.0858 \times 10^{-39}$, and $I_C = 12.1691 \times 10^{-39}\ g \cdot cm^2$.

### References

[1] K. A. G. MacNeil and J. C. J. Thynne, J. Phys. Chem. 74, 2256 (1970).

[2] P. W. Harland, D. W H. Rankin, and J. C. J. Thynne, Int. J. Mass Spectr. Ion Phys. 13, 395 (1974).

[3] A. L. Companion and Y. P. Hsia, J. Mol. Struct. 14, 117 (1972).

[4] JANAF Thermochemical Tables: $PF^-(g)$ and $PF_2(g)$, 6–30–77; $SF_2(g)$, 6–30–76.

[5] H. S. W. Massey, "Negative Ions," 3rd ed., Cambridge University Press, Cambridge, (1976).

[6] M. S. Wei, J. H. Current, and J. Gendell, J Chem. Phys. 52, 1592 (1970).

[7] W. Nelson, G. Jackel, and W. Gordy, J. Chem. Phys. 52, 4572 (1970).

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −11.215 | −630.010 | | |
| 100 | 34.601 | 215.028 | 293.664 | −7.864 | | | |
| 200 | 39.722 | 240.527 | 261.304 | −4.155 | | | |
| 250 | 42.421 | 249.683 | 258.088 | −2.101 | | | |
| 298.15 | 44.817 | 257.364 | 257.364 | 0. | −639.177 | −636.946 | 111.590 |
| 300 | 44.903 | 257.641 | 257.365 | 0.083 | −639.235 | −636.932 | 110.900 |
| 350 | 47.035 | 264.728 | 257.919 | 2.383 | −641.499 | −636.355 | 94.971 |
| 400 | 48.802 | 271.128 | 259.177 | 4 780 | −643.087 | −635.512 | 82.989 |
| 450 | 50.242 | 276.962 | 260.834 | 7.258 | −644.632 | −634 471 | 73.648 |
| 500 | 51.412 | 282.318 | 262.718 | 9.800 | −646.144 | −633.261 | 66.156 |
| 600 | 53.142 | 291.855 | 266.799 | 15.034 | −649.096 | −630.406 | 54.882 |
| 700 | 54.315 | 300.141 | 270.983 | 20.410 | −651.982 | −627.062 | 46.792 |
| 800 | 55.137 | 307 450 | 275.094 | 25.885 | −654.828 | −623.308 | 40.698 |
| 900 | 55.729 | 313.980 | 279.058 | 31.430 | −657.648 | −619.198 | 35.937 |
| 1000 | 56.169 | 319.876 | 282.850 | 37.026 | −660.453 | −614.775 | 32.113 |
| 1100 | 56.503 | 325.246 | 286.464 | 42.660 | −663.250 | −610.072 | 28.970 |
| 1200 | 56.762 | 330.174 | 289.904 | 48.324 | −729.615 | −604.036 | 26.293 |
| 1300 | 56.966 | 334.725 | 293.179 | 54.011 | −731.634 | −593.489 | 23.847 |
| 1400 | 57.131 | 338.953 | 296.299 | 59.716 | −733.661 | −582.787 | 21.744 |
| 1500 | 57.265 | 342.900 | 299.276 | 65.436 | −735.697 | −571.939 | 19.917 |
| 1600 | 57.375 | 346.599 | 302.119 | 71.168 | −737.742 | −560.955 | 18.313 |
| 1700 | 57.467 | 350.080 | 304.839 | 76.910 | −739.798 | −549.843 | 16.895 |
| 1800 | 57.545 | 353.367 | 307.444 | 82.661 | −741.862 | −538.610 | 15.630 |
| 1900 | 57.611 | 356.480 | 309.944 | 88 419 | −743.933 | −527.262 | 14.495 |
| 2000 | 57.667 | 359.437 | 312.345 | 94.183 | −746.010 | −515.804 | 13 471 |
| 2100 | 57.716 | 362.252 | 314.655 | 99.952 | −748.090 | −504.243 | 12.542 |
| 2200 | 57.759 | 364.938 | 316.880 | 105 726 | −750.170 | −492.582 | 11.695 |
| 2300 | 57.796 | 367.506 | 319.026 | 111.504 | −752.246 | −480.827 | 10.920 |
| 2400 | 57.829 | 369.966 | 321.098 | 117.285 | −754.316 | −468.982 | 10.207 |
| 2500 | 57.857 | 372.328 | 323.100 | 123.069 | −756.376 | −457.050 | 9.550 |
| 2600 | 57.883 | 374.597 | 325.037 | 128.856 | −758.422 | −445 037 | 8.941 |
| 2700 | 57.906 | 376.782 | 326.914 | 134.646 | −760.452 | −432.945 | 8.376 |
| 2800 | 57.927 | 378.889 | 328.732 | 140.437 | −762.462 | −420.778 | 7.850 |
| 2900 | 57.945 | 380.922 | 330.497 | 146.231 | −764.450 | −408.540 | 7.359 |
| 3000 | 57.962 | 382.886 | 332.211 | 152.026 | −766.413 | −396.234 | 6.899 |
| 3100 | 57.977 | 384.787 | 333.877 | 157.823 | −768.350 | −383.863 | 6.468 |
| 3200 | 57.990 | 386.628 | 335.496 | 163.622 | −770.257 | −371.429 | 6.063 |
| 3300 | 58.003 | 388.413 | 337.073 | 169.421 | −772.135 | −358.937 | 5.681 |
| 3400 | 58.014 | 390.145 | 338.609 | 175.222 | −773.981 | −346.388 | 5.322 |
| 3500 | 58.025 | 391.826 | 340.105 | 181.024 | −775 795 | −333.785 | 4.981 |
| 3600 | 58.034 | 393.461 | 341.565 | 186.827 | −777.576 | −321.131 | 4.659 |
| 3700 | 58.043 | 395.051 | 342.989 | 192.631 | −779.324 | −308.428 | 4.354 |
| 3800 | 58.051 | 396.599 | 344.379 | 198.436 | −781.038 | −295.678 | 4.064 |
| 3900 | 58.059 | 398.107 | 345.738 | 204.241 | −782.718 | −282.883 | 3.789 |
| 4000 | 58.066 | 399.577 | 347.066 | 210.047 | −784.365 | −270.046 | 3.526 |
| 4100 | 58.072 | 401.011 | 348.364 | 215.854 | −785.978 | −257.168 | 3.276 |
| 4200 | 58.078 | 402.411 | 349.634 | 221.662 | −787.559 | −244.251 | 3.038 |
| 4300 | 58.084 | 403.777 | 350.877 | 227.470 | −789.107 | −231.297 | 2.810 |
| 4400 | 58.089 | 405.113 | 352.095 | 233.279 | −790.622 | −218.307 | 2.592 |
| 4500 | 58.094 | 406.418 | 353.288 | 239.088 | −792.106 | −205.283 | 2.383 |
| 4600 | 58.099 | 407.695 | 354.457 | 244.897 | −793.560 | −192.226 | 2.183 |
| 4700 | 58.103 | 408.945 | 355.603 | 250.708 | −794.983 | −179.138 | 1.991 |
| 4800 | 58.107 | 410.168 | 356.727 | 256.518 | −796.377 | −166.020 | 1.807 |
| 4900 | 58.111 | 411.366 | 357.830 | 262.329 | −797 743 | −152.874 | 1 630 |
| 5000 | 58.114 | 412.540 | 358.912 | 268.140 | −799.081 | −139.700 | 1.459 |
| 5100 | 58.118 | 413.691 | 359.975 | 273.952 | −800.391 | −126.499 | 1.296 |
| 5200 | 58.121 | 414.820 | 361.019 | 279.764 | −801.676 | −113.272 | 1.138 |
| 5300 | 58.124 | 415.927 | 362.044 | 285.576 | −802.935 | −100.022 | 0.986 |
| 5400 | 58.127 | 417.013 | 363.052 | 291.389 | −804.169 | −86.748 | 0.839 |
| 5500 | 58.129 | 418.080 | 364.043 | 297.201 | −805.380 | −73.451 | 0.698 |
| 5600 | 58.132 | 419.127 | 365.018 | 303.014 | −806.567 | −60.133 | 0.561 |
| 5700 | 58.134 | 420.156 | 365.976 | 308.828 | −807.732 | −46.793 | 0.429 |
| 5800 | 58.137 | 421.167 | 366.919 | 314.641 | −808.875 | −33.434 | 0.301 |
| 5900 | 58.139 | 422.161 | 367.847 | 320.455 | −809.998 | −20.054 | 0.178 |
| 6000 | 58.141 | 423.138 | 368.760 | 326.269 | −811.100 | −6.656 | 0.058 |

PREVIOUS: June 1977 (1 atm)    CURRENT: June 1977 (1 bar)

## Lead Fluoride, Alpha ($\alpha$-$PbF_2$) CRYSTAL ($\alpha$) $M_r$ = 245.196805 Lead Fluoride, Alpha ($PbF_2$) $F_2Pb_1(cr)$

$S°(298.15\ K) = [112.968 \pm 8.4]\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{trs} = 583 \pm 1\ K$

$\Delta_fH°(0\ K)$ = Unknown
$\Delta_fH°(298.15\ K) = [-676.971 \pm 4.2]\ kJ\cdot mol^{-1}$
$\Delta_{trs}H° = 1.463\ kJ\cdot mol^{-1}$

### Enthalpy of Formation

Enthalpies of formation derived from the enthalpy changes of different chemical reactions are tabulated below Due to a lack of sample characterization we can only assume from sample preparation that the following reactions involve $\alpha$-$PbF_2(cr)$.

| Source | Reaction | Method | $\Delta_rH°(298.15\ K)$ kcal·mol$^{-1}$ | $\Delta_fH°(298.15K)$ kcal·mol$^{-1}$ |
|---|---|---|---|---|
| 1 | $Pb(cr) + F_2(g) = PbF_2(\alpha)$ | emf | $-159.7 \pm 0.5$ | $-159.7 \pm 0.5$ |
| 2 | $PbO(cr) + 2\ HF(40\%\ aq) = PbF_2(\alpha) + H_2O(l)$ | calor. | $-22.9 \pm 0.3$ | $-159.4 \pm 0.5$ |
| 3 | $PbF_2(\alpha) + 2\ Na(cr) = Pb(cr) + 2\ NaF(aq)$ | emf | $-112.2 \pm 0.2$ | $-162.2 \pm 0.4$ |
| 4 | $PbF_2(\alpha) + Mg(cr) = Pb(cr) + MgF_2(cr)$ | calor. | $-109.5 \pm 1.5$ | $-159.2 \pm 2.0$ |
| 5 | $3/2\ PbF_2(cr) + Al(cr) = 3/2\ Pb(cr) + AlF_3(cr)$ | calor. | $-118.5 \pm 0.1$ | $-161.6 \pm 1.0$ |
| 6 | $3/2\ PbF_2(cr) + Al(cr) = 3/2\ Pb(cr) + AlF_3(cr)$ | calor. | $-117.7 \pm 0.6$ | $-162.2 \pm 1.0$ |

The samples used by Gross *et al.*[4, 5] could easily be $\beta$-$PbF_2$ rather than $\alpha$-$PbF_2$. Other reactions[7, 8, 9] have led to values near $\Delta_fH°(298.15\ K) = -161.8\ kcal\cdot mol^{-1}$ [10] this value is adopted and is assigned an uncertainty of $\pm 2\ kcal\cdot mol^{-1}$.

The adopted enthalpy of formation is supported by measurements[11] of the reaction $PbF_2(cr) + Be(cr) = BeF_2(cr) + Pb(cr)$ from which the enthalpy of formation of $BeF_2(cr)$ agrees with that from the direct fluorination of beryllium metal if the adopted value for $\Delta_fH°(PbF_2, \alpha, 298.15\ K)$ is used.

### Heat Capacity and Entropy

The enthalpy of $\alpha$-$PbF_2(cr)$ was measured by Linsey.[12] Twenty data points (320–728 K) were obtained using a sample encapsulated in gold while fifteen were obtained (370–595 K) using a sample encapsulated in Nichrome V. We adopt the heat capacity values calculated by Linsey[12] and extrapolate linearly to 1000 K. It should be noted, however, that Linsey[12] adjusted his experimental enthalpy for $\alpha$-$PbF_2(cr)$ so that when the orthorhombic sample was heated above $T_{trs}$, the resulting enthalpy was consistent with the cubic $PbF_2$ enthalpy.

There is no low temperature heat capacity data for $\alpha$–$PbF_2(cr)$. We estimate $S°(298.15\ K) = 27.0 \pm 2.0\ cal\ K^{-1}\cdot mol^{-1}$.

### Transition Data

The transition temperature is that obtained by Linsey[12] via enthalpy measurements on orthorhombic $PbF_2$. When heated above $T_{trs}$, orthorhombic $PbF_2$ changes quickly to the cubic form. Upon cooling the transformation is very sluggish.

The enthalpy of transition at room temperature, $240 \pm 9\ kcal\cdot mol^{-1}$, was determined by Linsey[12] by the differences in the heat of solution of the orthorhombic and cubic modifications in 1.0 M $Fe(NO_3)_3$. $\Delta_{trs}H°$ is calculated from this value using the enthalpy differences $H°(583\ K) - H°(298.15\ K)$ for the cubic and orthorhombic modifications.

### References

[1] W. Jahn-Held and K. Jellinek, Z. Elektrochem. 42, 401 (1936).
[2] H. V. Wartenberg, Z. anorg. allg. Chem. 244, 337 (1940).
[3] R. W. Ivett and T. D. Vries, J. Amer. Chem. Soc. 63, 2821 (1941).
[4] P. Gross, C. Hayman, and D. L. Levi, Trans. Faraday Soc. 50, 477 (1954).
[5] P. Gross, C. Hayman, and D L. Levi, "Physical Chemistry of Process Metallurgy," Part 2, Interscience Publishers, Inc., New York, (1961).
[6] V. P. Kolesov, A. M. Martynov, and S. M. Skuratov, Russ. J. Inorg. Chem. 6, 1326 (1961).
[7] H. H. Broene and T. DeVries, J. Amer. Chem. Soc. 69, 1644 (1947).
[8] G. G. Koerber and T. DeVries, J. Amer. Chem. Soc. 74, 5008 (1952).
[9] P. Schindler and M. Reinert, Chimia (Switz) 15, 534 (1961).
[10] E. Rudzitis, H. M. Feder, and W N. Hubbard, Inorg. Chem. 6, 1716 (1967).
[11] P. Gross, C. Hayman, and J. T. Bingham, Fulmer Research Institute, AD 721476, (1971).
[12] C. W. Linsey, Ph.D. Dissertation, North Texas State University, (1970).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 72.258 | 112.968 | 112.968 | 0. | −676.971 | −630.875 | 110.527 |
| 300 | 72.383 | 113.415 | 112.969 | 0.134 | −676.945 | −630.589 | 109.795 |
| 400 | 76.065 | 134.642 | 115.838 | 7.522 | −675.505 | −615.351 | 80.357 |
| 500 | 79.705 | 152.035 | 121.389 | 15.323 | −673.883 | −600.497 | 62.733 |
| 583.000 | 81.965 | 164.425 | 126.653 | 22.021 | ---- ALPHA <--> BETA ---- | | |
| 600 | 82.488 | 166.788 | 127.757 | 23.419 | −672.150 | −585.980 | 51.014 |
| 700 | 85.772 | 179.751 | 134.276 | 31.832 | −675.110 | −570.968 | 42.606 |
| 800 | 89.056 | 191.418 | 140.701 | 40.574 | −672.996 | −556.231 | 36.318 |
| 900 | 92.341 | 202.097 | 146.938 | 49.643 | −670.565 | −541.778 | 31.444 |
| 1000 | 95.625 | 211.996 | 152.955 | 59.042 | −667.812 | −527.613 | 27.560 |

PREVIOUS: June 1969 CURRENT: December 1973

## Lead Fluoride, Beta (β-PbF$_2$) CRYSTAL (β) $M_r = 245.196805$ Lead Fluoride, Beta (PbF$_2$) F$_2$Pb$_1$(cr)

$S°(298.15\ K) = [114.398]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{trs} = 583 \pm 1\ K$
$T_{fus} = 1103 \pm 2\ K$

$\Delta_f H°(298.15\ K) = [-675.990]\ kJ{\cdot}mol^{-1}$
$\Delta_{trs}H° = 1.463\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 14.728 \pm 1.3\ kJ{\cdot}mol^{-1}$

### Enthalpy of Formation

Linsey[1] determined the heat of transition at room temperature to be 240 ± 9 kcal·mol$^{-1}$ from heat of solution measurements of the orthorhombic and cubic modifications in 1 M Fe(NO$_3$)$_3$. We calculate and adopt $\Delta_f H°$(PbF$_2$, β, 298.15 K) by adding this heat of transition value to the $\Delta_f H°$(298.15 K) value for PbF$_2$(cr, α).

Other enthalpy of formation values derived from the enthalpy changes of different chemical reactions are tabulated below Due to a lack of sample characterization we can only assume from the sample preparation and experimental conditions that the following reactions involve β–PbF$_2$(cr).

| Source | Reaction | Method | $\Delta_r H°$(298.15 K) kcal·mol$^{-1}$ | $\Delta_f H°$(298.15K) kcal·mol$^{-1}$ |
|---|---|---|---|---|
| 2 | $PbF_2(\beta) + H_2(g) = Pb(l) + 2\ HF(g)$ | Press | 32.0 | −161.3 |
| 3 | $PbF_2(\beta) + H_2O(g) = PbO(cr) + 2\ HF(g)$ | Press | 30.06 | −154.6 |
| 4 | $1/2\ PbF_2(\beta) + 1/3\ Al(cr) = 1/2\ Pb(l) + 1/3\ AlF_3(cr)$ | emf | −116.39 | −162.0 |

The two studies by Gross *et al.*[5,6] may well involve β-PbF$_2$. Kolesov *et al.*[7] used two PbF$_2$ samples which had been fused. These samples should then be in the β-modification. The results are considerably different from those given in the α–PbF$_2$ table[8] for α–PbF$_2$.

### Heat Capacity and Entropy

Linsey[1] measured the enthalpy of cubic PbF$_2$. The enthalpy data (61 data points, 321–1164 K) revealed an anomaly in the enthalpy and heat capacity in the range 573–823 K. Linsey[1] interpreted the results in terms of a lambda–type (cooperative) transition in the heat capacity with a maximum at 716 K. We adopt the heat capacity values calculated and reported by Linsey.[1]

Banashek *et al.*[8] measured the high temperature enthalpies in the range 670–1165 K. Their data is consistent with the interpretation of Linsey.[1]

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

### Fusion Data

Refer to the liquid table for details.

### References

[1] C. W. Linsey, Ph.D. Dissertation, North Texas State University, (1970).
[2] K. Jellinek and A. Rudat, Z. Anorg. Chem. 175, 281 (1928).
[3] M. L. Domange, Compt. Rend. 200, 2180 (1935).
[4] R. J. Heus and J. J. Egan, Z. Phys. Chem. 49, S. 38 (1966).
[5] P. Gross, C. Hayman, and D. L. Levi, Trans. Faraday Soc. 50, 477 (1954).
[6] P. Gross, C. Hayman, and D. L. Levi, "Physical Chemistry of Process Metallurgy," Part 2, Interscience Publishers, Inc., New York, (1961).
[7] V. P. Kolesov, A. M. Martynov, and S. M. Skuratov, Russ. J. Inorg. Chem. 6, 1326 (1961).
[8] E. I. Banashek, N. N. Patsukova, and I. S. Rassonskaya, Izvest. Sektora Fiz.–Khim. Anal., Inst. Obshchei i Neorg. Khim., Akad. Nauk SSSR 27, 223 (1956).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ (J·K$^{-1}$mol$^{-1}$) | $S°$ (J·K$^{-1}$mol$^{-1}$) | $-[G°-H°(T_r)]/T$ (J·K$^{-1}$mol$^{-1}$) | $H°-H°(T_r)$ (kJ·mol$^{-1}$) | $\Delta_f H°$ (kJ·mol$^{-1}$) | $\Delta_f G°$ (kJ·mol$^{-1}$) | log K$_f$ |
|---|---|---|---|---|---|---|---|
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 74.266 | 114.398 | 114.398 | 0. | −675.990 | −630.320 | 110.429 |
| 300 | 74.392 | 114.857 | 114.399 | 0.138 | −675.960 | −630.037 | 109.699 |
| 400 | 76.776 | 136.571 | 117.344 | 7.691 | −674.354 | −614.971 | 80.307 |
| 500 | 80.584 | 154.051 | 122.988 | 15.531 | −672.694 | −600.315 | 62.714 |
| 583.000 | 88.868 | 166.934 | 128.336 | 22.502 | ---- ALPHA <--> BETA ---- | | |
| 600 | 91.128 | 169.518 | 129.466 | 24.031 | −670.557 | −586.025 | 51.018 |
| 700 | 147.486 | 186.826 | 136.333 | 35.345 | −670.616 | −571.426 | 42.640 |
| 800 | 105.939 | 203.976 | 143.801 | 48.140 | −664.448 | −557.729 | 36.416 |
| 900 | 94.433 | 215.393 | 151.145 | 57.823 | −661.404 | −544.583 | 31.607 |
| 1000 | 94.433 | 225.342 | 158.076 | 67.266 | −658.606 | −531 753 | 27.776 |
| 1100 | 94.433 | 234.342 | 164.607 | 76.709 | −655.807 | −519.203 | 24.655 |
| 1103 000 | 94.433 | 234.600 | 164.797 | 76.993 | ---- BETA <--> LIQUID ---- | | |
| 1200 | 94.433 | 242.559 | 170.765 | 86.153 | −653.003 | −506.908 | 22.065 |
| 1300 | 94.433 | 250.118 | 176.583 | 95.596 | −650.200 | −494.847 | 19.883 |
| 1400 | 94.433 | 257.116 | 182.088 | 105.039 | −647.410 | −483.002 | 18.021 |
| 1500 | 94.433 | 263.631 | 187.310 | 114.482 | −644.642 | −471.355 | 16.414 |

PREVIOUS: CURRENT: December 1973

# Lead Fluoride ($PbF_2$) LIQUID $M_r = 245.196806$ Lead Fluoride ($PbF_2$) $F_2Pb_1(l)$

$S°(298.15\ K) = [130.927]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [-660.320]\ kJ \cdot mol^{-1}$

$T_{fus} = 1103 \pm 4\ K$ $\Delta_{fus} H° = 14.728 \pm 2.1\ kJ \cdot mol^{-1}$

## Enthalpy of Formation

$\Delta_f H°(PbF_2,\ l,\ 298.15\ K)$ is calculated from $\Delta_f H°(PbF_2,\ cr,\ \beta,\ 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus} H°$, and the difference in enthalpy, $H°(1103\ K)–H°(298.25\ K)$, between the β-crystal and liquid.

## Heat Capacity and Entropy

The enthalpies of $PbF_2(l)$ in the temperature range 1104–1165 K were determined by Banashek *et al.*[1] Based on their reported results, the heat capacity of $PbF_2(l)$ is evaluated to be $24 \pm 2\ cal\ K^{-1} \cdot mol^{-1}$ by the least square method. Linsey[13] measured the enthalpy of $PbF_2(l)$ in the range 1105–1164 K (8 data points) and reported a constant heat capacity value of $26.10\ cal\ K^{-1} \cdot mol^{-1}$ We adopt this value and extrapolate to 700 K and 1500 K. A glass transition is assumed at 700 K below which the heat capacity values of cubic $PbF_2$ are used.

$S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

## Fusion Data

$T_{fus}$ and $\Delta_{fus} H°$ are taken from the enthalpy data of Linsey.[13] Our analysis of the enthalpy data of Banashek *et al.*[1] yields a heat of melting value of $2.98\ kcal \cdot mol^{-1}$.

Other values of $T_{fus}(K)$ reported are 1091,[2, 11] 1097,[3, 4, 5] and 1128.[6] Using the freezing point data of binary systems $PbF_2–PbBr_2$,[5] $PbF_2–PbCl_2$,[5, 7] $PbF_2–PbI_2$,[5, 8] $PbF_2–PbO$,[9] and $PbF_2–NaF$.[10] Kelley[3] evaluated the corresponding values of $\Delta_{fus} H°$ $kcal \cdot mol^{-1}$ as 1.70, 1.70, 1 96, 3.87, and 2.47. Other reported values of $\Delta_{fus} H°$ are 3.00[1] and 4.16[2] $kcal \cdot mol^{-1}$.

## Vaporization Data

From mass spectroscopic study on the vapor species in $PbF_2$, Zmbov *et al.*[4] have shown that molten $PbF_2$ vaporizes partly as molecular $PbF_2$ There is considerable disproportionation, and at 988 K the vapor composition is approximately 66% $PbF_4$, 25% $PbF_2$, 2% PbF, and 7% Pb.[4, 12] $T_{vap}$ has been reported as 1565 K[11] where the vapor is expected to be a mixture of the above species.

## References

[1] E. I. Banashek, N. N. Patsukova, and I. S. Rassonskaya, Izvest. Sektora Fiz. Khim. Anal , Inst. Obshchei i Neorg Khim., Akad. Nauk SSSR 27, 223 (1956).
[2] M Blanc, Diplome and d'Etudes Superieures, Paris, 1956, quoted by M. Blanc and G. Petit, Compt. Rend. 248, 1305 (1959).
[3] K. K. Kelley, U. S. Bur. Mines Bull. 393, (1936).
[4] K. Zmbov, J. W Hastie, and J. L. Margrave, Trans. Faraday Soc. 64, 861 (1968).
[5] C. Sandonini, Gazz. Chim. Ital. 41, II 144 (1911).
[6] Amadori, Gazz. Chim. Ital. 49, I 38 (1919).
[7] C. Sandonini, Atti Acad. Lincei, Ser. 5, 20, I 172 (1911).
[8] C. Sanconini, Atti Acad. Lincei, Ser. 5, 20, I 253 (1911).
[9] C. Sandonini, Atti Acad. Lincei, Ser. 5, 23, I 959 (1914).
[10] N. A. Puschin and A B. Baskow, J. Russ. Phys. Chem. Soc. 45, 82 (1913); Z. Anorg. Chem. 81, 347 (1913).
[11] H. V. Wartenberg and O. Bosse, Z. Elektrochem. 28, 384 (1922).
[12] R. H. Hauge, J. W Hastie, and J. L. Margrave, J. Phys. Chem. 72, 3510 (1968).
[13] C W. Linsey, Ph.D Dissertation, North Texas State University, (1970).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| $T/K$ | $C_p°$ ($J \cdot K^{-1} mol^{-1}$) | $S°$ ($J \cdot K^{-1} mol^{-1}$) | $-[G°-H°(T_r)]/T$ ($J \cdot K^{-1} mol^{-1}$) | $H°-H°(T_r)$ ($kJ \cdot mol^{-1}$) | $\Delta_f H°$ ($kJ \cdot mol^{-1}$) | $\Delta_f G°$ ($kJ \cdot mol^{-1}$) | $\log K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 74.266 | 130.927 | 130.927 | 0. | −660.320 | −619.579 | 108.548 |
| 300 | 74.392 | 131.386 | 130.928 | 0.138 | −660.290 | −619.326 | 107.834 |
| 400 | 76.776 | 153.101 | 133.873 | 7.691 | −658.685 | −605.914 | 79.124 |
| 500 | 79.705 | 170.548 | 139.517 | 15.515 | −657.040 | −592.909 | 61.941 |
| 600 | 82.634 | 185.339 | 145.951 | 23.632 | −655.286 | −580.246 | 50.515 |
| 700 | 85.563 | 198.297 | 152.522 | 32.042 | −658.249 | −567.089 | 42.317 |
| 700.000 | 85.563 | 198.297 | 152.522 | 32.042 | GLASS <––> LIQUID TRANSITION | | |
| 700 000 | 109 .202 | 198.297 | 152.522 | 32.042 | | | |
| 800 | 109.202 | 212.879 | 159.176 | 42.962 | −653.956 | −554.359 | 36.196 |
| 900 | 109.202 | 225.741 | 165.871 | 53.883 | −649.675 | −542.167 | 31.467 |
| 1000 | 109.202 | 237.247 | 172.444 | 64.803 | −645.399 | −530.451 | 27.708 |
| 1100 | 109.202 | 247 655 | 178.815 | 75.723 | −641.123 | −519.163 | 24.653 |
| 1103 000 | 109.202 | 247.952 | 179.003 | 76.051 | –––– BETA <––> LIQUID –––– | | |
| 1200 | 109.202 | 257 157 | 184.954 | 86.643 | −636.843 | −508.265 | 22.124 |
| 1300 | 109.202 | 265.897 | 190.848 | 97.564 | −632.563 | −497.723 | 19.999 |
| 1400 | 109.202 | 273.990 | 196.502 | 108.484 | −628.296 | −487.511 | 18.189 |
| 1500 | 109.202 | 281.524 | 201.922 | 119.404 | −624.050 | −477.604 | 16.632 |

PREVIOUS: June 1969 CURRENT: December 1973

# Lead Fluoride ($PbF_2$) CRYSTAL(α–β)–LIQUID $M_r = 245.196806$ Lead Fluoride ($PbF_2$) $F_2Pb_1(cr,l)$

| | | | |
|---|---|---|---|
| 0 | to | 583 | K crystal, alpha |
| 583 | to | 1103 | K crystal, beta |
| above | | 1103 | K liquid |

Refer to the individual tables for details.

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p^\circ$ = 0.1 MPa

| T/K | $C_p^\circ$ (J·K⁻¹mol⁻¹) | $S^\circ$ (J·K⁻¹mol⁻¹) | $-[G^\circ-H^\circ(T_r)]/T$ (J·K⁻¹mol⁻¹) | $H^\circ-H^\circ(T_r)$ (kJ·mol⁻¹) | $\Delta_fH^\circ$ (kJ·mol⁻¹) | $\Delta_fG^\circ$ (kJ·mol⁻¹) | log $K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 72.258 | 112.968 | 112.968 | 0. | −676.971 | −630.875 | 110.527 |
| 300 | 72.383 | 113.415 | 112.969 | 0.134 | −676.945 | −630.589 | 109.795 |
| 400 | 76.065 | 134.642 | 115.838 | 7.522 | −675.505 | −615.351 | 80.357 |
| 500 | 79.705 | 152.035 | 121.389 | 15.323 | −673.883 | −600.497 | 62.733 |
| 583.000 | 81.965 | 164.425 | 126.653 | 22.021 | ALPHA <--> BETA | | |
| 583.000 | 88.868 | 166.934 | 126.653 | 23.484 | TRANSITION | | |
| 600 | 91.128 | 169.518 | 127.831 | 25.012 | −670.557 | −586.025 | 51.018 |
| 700 | 147.486 | 186.826 | 134.931 | 36.327 | −670.616 | −571.426 | 42.640 |
| 800 | 105.939 | 203.976 | 142.574 | 49.121 | −664.448 | −557.729 | 36.416 |
| 900 | 94.433 | 215.393 | 150.055 | 58.804 | −661.404 | −544.583 | 31.607 |
| 1000 | 94.433 | 225.342 | 157.095 | 68.248 | −658.606 | −531.753 | 27.776 |
| 1100 | 94.433 | 234.343 | 163.714 | 77.691 | −655.807 | −519.203 | 24.655 |
| 1103.000 | 94.433 | 234.600 | 163.907 | 77.974 | BETA <--> LIQUID | | |
| 1103.000 | 109 .202 | 247.952 | 163.907 | 92.702 | TRANSITION | | |
| 1200 | 109.202 | 257.157 | 171.078 | 103.294 | −636.843 | −508.265 | 22.124 |
| 1300 | 109.202 | 265.897 | 178.040 | 114.215 | −632.563 | −497.723 | 19.999 |
| 1400 | 109.202 | 273.990 | 184.608 | 125.135 | −628.296 | −487.511 | 18.189 |
| 1500 | 109.202 | 281.524 | 190.821 | 136.055 | −624.050 | −477.604 | 16.632 |

PREVIOUS.    CURRENT. December 1973

**Lead Fluoride ($PbF_2$)** **IDEAL GAS** **$M_r$ = 245.196806** **Lead Fluoride ($PbF_2$)** **$F_2Pb_1(g)$**

$S°(298.15\ K) = 292.692\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -431.999 \pm 8.4\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -435.136 \pm 8.4\ kJ{\cdot}mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, cm $^{-1}$ |
|---|
| 545.7(1) |
| 170 (1) |
| 522.5(1) |

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: $C_{2v}$
Bond Distance: Pb–F = 2.13 ± 0 02 Å
Bond Angle: F–Pb–F = [90]°
Product of the Moments of Inertia: $I_A I_B I_C = [4.571688 \times 10^{-114}]\ g^3{\cdot}cm^6$

## Enthalpy of Formation

Vapor pressure data for $PbF_2$ have previously been interpreted on the assumption that $PbF_2$ was the only species present in the gas phase.[1] [2] Zmbov *et al.*[3] have studied the vapor species over $PbF_2$(cr, l) mass spectrometrically and shown that $PbF_2$vaporizes only partly as molecular $PbF_2$ and there is considerable disproportionation The vapor composition at 988 K is approximately 66% $PbF_4$, 25% $PbF_2$, 2% PbF, and 7% Pb.[3] [4] From extrapolation of the ion intensity data from 1043 to 988 K to the temperature region in which Nesmeyanov and Iofa[2] measured the saturated vapor pressures of $PbF_2$(cr), 792–988 K, by Knudsen effusion method, the partial pressure of $PbF_2$(g), at 988 K was calculated to be 0.0435 ± 0.005 torr. Based on this calculated vapor pressure, the enthalpy of sublimation $\Delta_{sub}H°$(298 15 K) of $PbF_2$(cr, β) is derived as 57.53 kcal·mol$^{-1}$ by the 3rd law method, yielding $\Delta_f H°(PbF_2, g, 298.15\ K) = -104.0 \pm 2\ kcal{\cdot}mol^{-1}$.

Due to lack of data on vapor compositions over $PbF_2$ at various temperatures, the total pressure measurements reported by Wartenberg and Bosse,[1] using boiling point method, and those of Nesmeyanov and Iofa[2] are not used for evaluation.

The adopted $\Delta_f H°$(298.15 K) leads to an atomization energy $\Delta_{at}H°(0\ K) = 8.10$ eV for the process $PbF_2(g) = Pb(g) + 2F(g)$, using auxiliary data.[5]

## Heat Capacity and Entropy

The bond distance was determined by Akishin *et al.*[6] The bond angle was estimated by Hauge *et al.*[7] from a Group IV A difluoride comparison. Hauge *et al.*[7] determined the vibrational frequencies from the infrared spectra of neon matrix isolated $PbF_2$(g).

## References

[1] H. V. Wartenberg and O. Bosse, Z. Elektrochem. 28, 384 (1922).
[2] A. N. Nesmeyanov and B. Z. Iofa, Zhur. Neorg. Khim. 4, 486 (1959).
[3] K. Zmbov, J. W Hastie, and J. L. Margrave, Trans. Faraday Soc. 64, 861 (1968).
[4] R. H Hauge, J. W. Hastie, and J. L. Margrave, J. Phys. Chem. 72, 3510 (1968).
[5] JANAF Thermochemical Tables· Pb(g), 3–31–62; F(g), 9–30–65.
[6] P. A. Akishin, V. P Spiridonov, and A. N. Khodchenkov, Zhur. Fiz. Khim. 32, 1679 (1958).
[7] R. H. Hauge, J. W. Hastie, and J. L. Margrave, J. Mol. Spectrosc. 45, 420 (1973).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −12.567 | −431.999 | −431.999 | INFINITE |
| 100 | 38.879 | 244.078 | 334.499 | −9.042 | −433.148 | −436.836 | 228.180 |
| 200 | 46.110 | 273.286 | 297.217 | −4.786 | −434.346 | −440.018 | 114.921 |
| 250 | 48.928 | 283.892 | 293.521 | −2.407 | −434.774 | −441.385 | 92.222 |
| 298.15 | 50.950 | 292.692 | 292.692 | 0. | −435.136 | −442.625 | 77.546 |
| 300 | 51.016 | 293.008 | 292.693 | 0.094 | −435.149 | −442.671 | 77.076 |
| 350 | 52.537 | 300.992 | 293.320 | 2.685 | −435.501 | −443.897 | 66.248 |
| 400 | 53.653 | 308.084 | 294.731 | 5.341 | −435.850 | −445.073 | 58.121 |
| 450 | 54.485 | 314.454 | 296.575 | 8.046 | −436.210 | −446.204 | 51.794 |
| 500 | 55.116 | 320.229 | 298.656 | 10.786 | −436.585 | −447.295 | 46.729 |
| 600 | 55.988 | 330.361 | 303.119 | 16.345 | −437.389 | −449.362 | 39.120 |
| 700 | 56.542 | 339.036 | 307.645 | 21.974 | −443.134 | −450.491 | 33.616 |
| 800 | 56.914 | 346.612 | 312.053 | 27.648 | −444.086 | −451 477 | 29.478 |
| 900 | 57.175 | 353.332 | 316.273 | 33.353 | −445.021 | −452.344 | 26.253 |
| 1000 | 57.365 | 359.366 | 320.286 | 39.080 | −445.938 | −453.109 | 23.668 |
| 1100 | 57.506 | 364.840 | 324.091 | 44.824 | −446.838 | −453 782 | 21.548 |
| 1200 | 57.615 | 369.849 | 327.699 | 50.580 | −447.722 | −454.374 | 19.778 |
| 1300 | 57.700 | 374.464 | 331.121 | 56.346 | −448.596 | −454.893 | 18.278 |
| 1400 | 57.768 | 378 743 | 334.371 | 62.120 | −449.476 | −455.345 | 16.989 |
| 1500 | 57.823 | 382.730 | 337.464 | 67.900 | −450.371 | −455.733 | 15.870 |
| 1600 | 57.869 | 386.464 | 340.411 | 73.684 | −451.287 | −456.060 | 14.889 |
| 1700 | 57.906 | 389.973 | 343.224 | 79.473 | −452.229 | −456.330 | 14.021 |
| 1800 | 57.938 | 393.284 | 345.914 | 85.265 | −453 199 | −456.543 | 13.249 |
| 1900 | 57.964 | 396.417 | 348.490 | 91.060 | −454.195 | −456.702 | 12.556 |
| 2000 | 57.987 | 399.391 | 350.962 | 96.858 | −455.219 | −456.808 | 11.931 |
| 2100 | 58.007 | 402.220 | 353.336 | 102.658 | −633.488 | −449.747 | 11.187 |
| 2200 | 58.024 | 404.919 | 355.620 | 108.459 | −634.169 | −440.981 | 10.470 |
| 2300 | 58.039 | 407.499 | 357.820 | 114.263 | −634.935 | −432 183 | 9.815 |
| 2400 | 58.052 | 409.969 | 359.941 | 120.067 | −635.785 | −423.350 | 9.214 |
| 2500 | 58.064 | 412.339 | 361.990 | 125.873 | −636.717 | −414.480 | 8.660 |
| 2600 | 58.074 | 414 617 | 363 971 | 131.680 | −637.725 | −405.570 | 8.148 |
| 2700 | 58.083 | 416.809 | 365.887 | 137.488 | −638.805 | −396.621 | 7.673 |
| 2800 | 58.092 | 418.921 | 367.744 | 143.297 | −639.950 | −387.631 | 7.231 |
| 2900 | 58.099 | 420.960 | 369.544 | 149.106 | −641 153 | −378.598 | 6.819 |
| 3000 | 58.106 | 422.930 | 371.291 | 154.916 | −642.404 | −369.523 | 6 434 |
| 3100 | 58.112 | 424.835 | 372.988 | 160.727 | −643.697 | −360.406 | 6.073 |
| 3200 | 58.117 | 426.680 | 374.637 | 166.539 | −645.023 | −351.247 | 5.734 |
| 3300 | 58.122 | 428.469 | 376.241 | 172.351 | −646.373 | −342.045 | 5 414 |
| 3400 | 58.127 | 430.204 | 377.803 | 178.163 | −647.739 | −332.803 | 5.113 |
| 3500 | 58.131 | 431.889 | 379.324 | 183.976 | −649.113 | −323.520 | 4.828 |
| 3600 | 58.135 | 433.526 | 380.807 | 189.789 | −650.488 | −314.198 | 4.559 |
| 3700 | 58.138 | 435.119 | 382.254 | 195.603 | −651.857 | −304.837 | 4.304 |
| 3800 | 58.141 | 436.670 | 383.665 | 201.417 | −653.213 | −295 441 | 4.061 |
| 3900 | 58.144 | 438.180 | 385.044 | 207.231 | −654.551 | −286.008 | 3.831 |
| 4000 | 58.147 | 439.652 | 386.391 | 213.046 | −655.865 | −276.541 | 3 611 |
| 4100 | 58.150 | 441.088 | 387.707 | 218.860 | −657 151 | −267 042 | 3.402 |
| 4200 | 58.152 | 442.489 | 388.995 | 224.676 | −658.404 | −257.512 | 3.203 |
| 4300 | 58.154 | 443.858 | 390.255 | 230.491 | −659.622 | −247.953 | 3.012 |
| 4400 | 58.157 | 445.195 | 391.489 | 236.306 | −660.800 | −238.365 | 2.830 |
| 4500 | 58.158 | 446.502 | 392.697 | 242.122 | −661.938 | −228.751 | 2.655 |
| 4600 | 58.160 | 447.780 | 393.880 | 247.938 | −663.033 | −219.113 | 2.488 |
| 4700 | 58.162 | 449.031 | 395.041 | 253.754 | −664.084 | −209.451 | 2.328 |
| 4800 | 58.164 | 450.255 | 396.178 | 259.571 | −665.089 | −199.767 | 2.174 |
| 4900 | 58.165 | 451.455 | 397.294 | 265.387 | −666.048 | −190.063 | 2.026 |
| 5000 | 58.166 | 452.630 | 398.389 | 271.204 | −666.961 | −180.340 | 1.884 |
| 5100 | 58.168 | 453.782 | 399.464 | 277.020 | −667.827 | −170.599 | 1.747 |
| 5200 | 58.169 | 454.911 | 400.519 | 282.837 | −668.648 | −160.841 | 1.616 |
| 5300 | 58.170 | 456.019 | 401.556 | 288.654 | −669.423 | −151.068 | 1.489 |
| 5400 | 58.171 | 457.106 | 402.575 | 294.471 | −670.153 | −141.281 | 1.367 |
| 5500 | 58.172 | 458.174 | 403.576 | 300.288 | −670.839 | −131 481 | 1.249 |
| 5600 | 58.173 | 459.222 | 404.560 | 306.106 | −671.483 | −121.668 | 1.135 |
| 5700 | 58.174 | 460.252 | 405.528 | 311.923 | −672.085 | −111.845 | 1.025 |
| 5800 | 58.175 | 461.263 | 406.481 | 317.741 | −672.647 | −102.011 | 0.919 |
| 5900 | 58.176 | 462.258 | 407.418 | 323.558 | −673.169 | −92.168 | 0.816 |
| 6000 | 58.177 | 463.236 | 408.340 | 329.376 | −673.654 | −82.317 | 0 717 |

PREVIOUS. December 1973 (1 atm) CURRENT: December 1973 (1 bar)

**Lead Fluoride ($PbF_2$)** **$F_2Pb_1(g)$**

$S°(298.15\ K) = [257\ 703 \pm 0.084]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -294.629 \pm 16.7\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -296\ 646 \pm 16.7\ kJ{\cdot}mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm $^{-1}$ |
|---|
| [840 ± 20] (1) |
| [357 ± 2] (1) |
| [809 ± 10] (1) |

Ground State Quantum Weight = [1] $\sigma = 2$
Point Group: $C_{2v}$
Bond Distance: S–F = 1.59208 ± 0.00008 Å
Bond Angle: F–S–F = 98.197 ± 0.011°
Product of the Moments of Inertia: $I_AI_BI_C = 3.518837 \times 10^{-115}\ g^3{\cdot}cm^6$

## Enthalpy of Formation

We calculate $\Delta_fH°$ from a 3rd law analysis of two sets of equilibrium data for the gaseous isomolecular reaction $S + SF_2 = 2\ SF$. The equilibrium data are obtained from ion currents reported in a mass spectrometric study[1] of the molecular species formed from the reaction of gaseous $SF_6$ with graphite. We do not include in the equilibrium constants a proportionality constant involving ion multiplier gain and ionization cross sections since Hildenbrand[1] has recently demonstrated that these factors tend to cancel for isomolecular reactions. Results of our analyses are presented below.

| Series | Cell Configuration | Data Points | T/K | $\Delta_rH°$(298.15 K), kcal·mol$^{-1}$ 2nd law | 3rd law | Drift cal·K$^{-1}$ mol$^{-1}$ | $\Delta_fH°$(298.15 K) kcal·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 2 | C cell/wound Pt wire | 4 | 1436–1564 | 3.1 | 10.68 ± 0 7 | 5.0 ± 2.3 | 70 77 ± 4.0 |
| 3 | C cell/Pt partition/packed with cloth and Pt wire | 7 | 1478–1588 | 7.7 | 10.87 ± 0.9 | 2.1 ± 5.0 | 70.96 ± 4.0 |

The two cell configurations used by Hildenbrand[1] yield nearly identical 3rd law $\Delta_rH°$ values; thus, we adopt the rounded average of −70.9 ± 4.0 kcal mol$^{-1}$. Our adopted $\Delta_fH°$ value corresponds to a enthalpy of atomization and average bond dissociation energy of 172.9 kcal·mol$^{-1}$ and 86.4 kcal·mol$^{-1}$, respectively In addition, the primary bond dissociation energy of $SF_2$ is calculated to be $D_0°(SF\text{–}F) = 91.7$ kcal·mol$^{-1}$, suggesting that the individual S–F bonds are somewhat stronger than that in the SF (81.2 kcal·mol$^{-1}$)[2] radical. This increase in bond strength is predicted by MO calculations[3] and has been qualitatively accounted for in terms of the valence–state model[1] of covalent bonding.

Two additional pieces of information exist which provide some support for our selected $\Delta_fH°$ value Kinetic studies[4] on the dissociation of $SF_3$ indicate that $D_0°(SF_2\text{–}F)$–72 kcal·mol$^{-1}$. We calculate $D_0°(SF_2\text{–}F) = 67$ 3 kcal·mol$^{-1}$ from JANAF data,[2] indicating that our heats of formation for $SF_3$ and $SF_2$ are consistent with these kinetic results. Di Lonardo and Trombetti[5] obtained $D_0°(SF\text{–}F) = 92.2 \pm 12$ kcal·mol$^{-1}$ from electron–impact threshold measurements on the COS/F and $SF_6$ systems. This value is to be compared with our calculated value of 91.7 kcal·mol$^{-1}$.

## Heat Capacity and Entropy

We adopt molecular data which refer to an average ground state structure for $SF_2$. These results are based on microwave measurements and force field calculations performed by Kirchhoff *et al.*[6] Earlier microwave spectroscopic observations[7] on the isotopic $^{34}SF_2$ species support the assignment of the spectrum to the difluoride and confirm its angular structure. The individual moments of inertia are: $I_A = 3.1377 \times 10^{-39}$, $I_B = 9.1367 \times 10^{-39}$, and $I_C = 12.2744 \times 10^{-39}\ g{\cdot}cm^2$.

A recent review on the chemistry of the lower sulfur fluorides includes a discussion on the vibrational spectrum of $SF_2$[8] The only observed vibrational frequency (830 cm$^{-1}$) which has so far been attributed to the difluoride appeared as a shoulder to a band at 810 cm$^{-1}$ in the infrared spectra of a mixture of S–F compounds. The band at 810 cm$^{-1}$ has been assigned[8] to the S–F equatorial stretching frequency of $F_3SSF$. We prefer not to adopt the 830 cm$^{-1}$ frequency as a fundamental since the band cannot be positively identified as due to $SF_2$. Four sets[6, 9–11] of estimated frequencies have been reported. We believe that the best estimates are those of Kirchhoff *et al*[6] which we adopt. These frequencies were obtained from force field calculations and include corrections which were made to account for the differences found between predicted and observed fundamentals for the related molecules of $OF_2$, $SO_2$, $SiF_2$, and $CF_2$. By analogy with other even electron S–F species,[2] we predict that the ground state is singlet and that there are no low–lying electronic levels which would contribute to the partition function.

Our thermal functions essentially update those reported by Wilkins.[10] Another set of functions which cover a rather short (0–2000 K) temperature interval has been reported by O'Hare.[11] We believe, however, that his estimate ($\nu_2 = 523$ cm $^{-1}$)[11] of the bending frequency is too high based on that observed for $SO_2(\nu_2 = 517\ cm^{-1})$[2] indicating that his entropies are probably too low by as much as 0.6–0.8 cal K$^{-1}$·mol$^{-1}$.

Continued on page 1215

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

|  | J·K$^{-1}$mol$^{-1}$ |  |  | kJ·mol$^{-1}$ |  |  |  |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −11.221 | −294.629 | −294.629 | INFINITE |
| 100 | 34.579 | 215.347 | 294.044 | −7.870 | −294.875 | −298.121 | 155.722 |
| 200 | 39.755 | 240.841 | 261.651 | −4.162 | −295.738 | −301.049 | 78.626 |
| 250 | 42.491 | 250.008 | 258.429 | −2.105 | −296.204 | −302.322 | 63 167 |
| 298.15 | 44.906 | 257.703 | 257.703 | 0. | −296.646 | −303.461 | 53.165 |
| 300 | 44.992 | 257.981 | 257.704 | 0.083 | −296 662 | −303.503 | 52.845 |
| 350 | 47.131 | 265.082 | 258.260 | 2.388 | −297.113 | −304.607 | 45 460 |
| 400 | 48.896 | 271.495 | 259.520 | 4.790 | −299.772 | −305.560 | 39 902 |
| 450 | 50.331 | 277.340 | 261.180 | 7.272 | −300.882 | −306.225 | 35.546 |
| 500 | 51.493 | 282.705 | 263.068 | 9.818 | −302.037 | −306.755 | 32.046 |
| 600 | 53.208 | 292.256 | 267.157 | 15.059 | −303.855 | −307.520 | 26.772 |
| 700 | 54.370 | 300.550 | 271.348 | 20 442 | −305.370 | −308.008 | 22.984 |
| 800 | 55.181 | 307.867 | 275.464 | 25.922 | −306.711 | −308.292 | 20.129 |
| 900 | 55.766 | 314.402 | 279.434 | 31 471 | −361.073 | −307.334 | 17.837 |
| 1000 | 56.200 | 320.301 | 283.231 | 37.070 | −361.020 | −301.365 | 15.742 |
| 1100 | 56.529 | 325.673 | 286.849 | 42.707 | −360.974 | −295.402 | 14.027 |
| 1200 | 56.784 | 330.603 | 290.292 | 48.373 | −360.941 | −289 443 | 12.599 |
| 1300 | 56.986 | 335.157 | 293.570 | 54.062 | −360.924 | −283.485 | 11.391 |
| 1400 | 57.148 | 339.386 | 296.694 | 59.769 | −360.925 | −277.529 | 10.355 |
| 1500 | 57.280 | 343.333 | 299.673 | 65.491 | −360.948 | −271.571 | 9.457 |
| 1600 | 57.388 | 347.034 | 302.519 | 71.224 | −360.991 | −265.611 | 8.671 |
| 1700 | 57.479 | 350.516 | 305.240 | 76.968 | −361.056 | −259.648 | 7.978 |
| 1800 | 57.555 | 353.803 | 307.848 | 82.720 | −361.140 | −253.681 | 7.362 |
| 1900 | 57.620 | 356.917 | 310.349 | 88.478 | −361.243 | −247.708 | 6.810 |
| 2000 | 57.676 | 359.874 | 312.752 | 94.243 | −361.360 | −241.729 | 6.313 |
| 2100 | 57.724 | 362.689 | 315.064 | 100.013 | −361.490 | −235.745 | 5.864 |
| 2200 | 57.766 | 365.375 | 317.290 | 105.788 | −361.627 | −229.754 | 5.455 |
| 2300 | 57.802 | 367.944 | 319.437 | 111.566 | −361.769 | −223.756 | 5.082 |
| 2400 | 57.835 | 370.405 | 321.510 | 117.348 | −361.911 | −217.753 | 4.739 |
| 2500 | 57.863 | 372.766 | 323.513 | 123.133 | −362.049 | −211.743 | 4 424 |
| 2600 | 57.888 | 375.036 | 325.451 | 128.921 | −362.180 | −205.728 | 4.133 |
| 2700 | 57.911 | 377.221 | 327.329 | 134.711 | −362.298 | −199.709 | 3.864 |
| 2800 | 57.931 | 379.328 | 329.148 | 140.503 | −362.402 | −193.685 | 3.613 |
| 2900 | 57.949 | 381.361 | 330.914 | 146.297 | −362.487 | −187.658 | 3.380 |
| 3000 | 57.966 | 383.326 | 332.628 | 152.093 | −362.551 | −181.628 | 3.162 |
| 3100 | 57.980 | 385.227 | 334.295 | 157.890 | −362.592 | −175.597 | 2.959 |
| 3200 | 57.994 | 387.068 | 335.915 | 163.689 | −362.607 | −169.564 | 2.768 |
| 3300 | 58.006 | 388.853 | 337.492 | 169.489 | −362.594 | −163.532 | 2.588 |
| 3400 | 58.017 | 390.584 | 339.029 | 175.290 | −362.554 | −157.500 | 2.420 |
| 3500 | 58.028 | 392.266 | 340.526 | 181.092 | −362.483 | −151.470 | 2.261 |
| 3600 | 58.037 | 393.901 | 341.986 | 186.895 | −362.383 | −145.442 | 2.110 |
| 3700 | 58.046 | 395.491 | 343.410 | 192.700 | −362.252 | −139.418 | 1.968 |
| 3800 | 58.054 | 397.040 | 344.802 | 198.505 | −362.091 | −133.398 | 1.834 |
| 3900 | 58.061 | 398.548 | 346.160 | 204.310 | −361.899 | −127.382 | 1.706 |
| 4000 | 58.068 | 400.018 | 347.488 | 210.117 | −361.676 | −121 371 | 1.585 |
| 4100 | 58.074 | 401.452 | 348.787 | 215.924 | −361.424 | −115.367 | 1.470 |
| 4200 | 58.080 | 402.851 | 350.058 | 221.732 | −361.142 | −109.369 | 1.360 |
| 4300 | 58.086 | 404.218 | 351.302 | 227.540 | −360.831 | −103.378 | 1.256 |
| 4400 | 58.091 | 405.553 | 352.519 | 233.349 | −360.493 | −97.394 | 1.156 |
| 4500 | 58.096 | 406.859 | 353.713 | 239.158 | −360.127 | −91.419 | 1.061 |
| 4600 | 58.100 | 408.136 | 354.882 | 244.968 | −359.735 | −85 452 | 0.970 |
| 4700 | 58.105 | 409.385 | 356.028 | 250.778 | −359.318 | −79 494 | 0.883 |
| 4800 | 58.109 | 410.609 | 357.153 | 256.589 | −358.876 | −73.544 | 0.800 |
| 4900 | 58.112 | 411.807 | 358.256 | 262.400 | −358.411 | −67.605 | 0.721 |
| 5000 | 58.116 | 412.981 | 359.339 | 268.211 | −357.923 | −61.675 | 0.644 |
| 5100 | 58.119 | 414.132 | 360.402 | 274.023 | −357.414 | −55.755 | 0.571 |
| 5200 | 58.122 | 415.260 | 361.446 | 279.835 | −356.885 | −49.845 | 0.501 |
| 5300 | 58.125 | 416.368 | 362.472 | 285.647 | −356.336 | −43.946 | 0 433 |
| 5400 | 58.128 | 417.454 | 363.480 | 291.460 | −355.768 | −38.057 | 0.368 |
| 5500 | 58.130 | 418.521 | 364.471 | 297.273 | −355 182 | −32.179 | 0.306 |
| 5600 | 58.133 | 419.568 | 365.446 | 303.086 | −354.579 | −26.311 | 0.245 |
| 5700 | 58.135 | 420.597 | 366.404 | 308.900 | −353.960 | −20.455 | 0.187 |
| 5800 | 58.138 | 421.608 | 367.347 | 314.713 | −353.326 | −14.610 | 0.132 |
| 5900 | 58.140 | 422.602 | 368.275 | 320.527 | −352.677 | −8.775 | 0 078 |
| 6000 | 58.142 | 423.579 | 369 189 | 326.341 | −352.014 | −2.952 | 0.026 |

PREVIOUS June 1976 (1 atm) CURRENT June 1976 (1 bar)

## Sulfur Fluoride, Ion (SF$_2^+$) IDEAL GAS $M_r$ = 70.056257 Sulfur Fluoride, Ion (SF$_2^+$) F$_2$S$_1^+$(g)

$S°$(298.15 K) = [263.525 ± 0.42] J·K$^{-1}$·mol$^{-1}$

$\Delta_f H°$(0 K) = 698.195 ± 46.0 kJ·mol$^{-1}$
$\Delta_f H°$(298.15 K) = 702.389 ± 46.0 kJ·mol$^{-1}$

| Electronic Levels and Quantum Weights<br>State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|
| [$^2B_1$] | [0] | [2] |
| [$^2A_1$] | [25000] | [2] |
| [$^2A_1$] | [28000] | [2] |
| [$^2A_2$] | [30000] | [2] |

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ |
|---|
| [807] (1) |
| [352] (1) |
| [844] (1) |

Point Group: [$C_{2v}$] σ = [2]
Bond Distance: S–F = [1.59] Å
Bond Angle: F–S–F = [100]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [3.4931 × 10$^{-115}$] g$^3$·cm$^6$

| Enthalpy Reference Temperature = $T_r$ = 298.15 K | | | | | Standard State Pressure = $p°$ = 0.1 MPa | | |
|---|---|---|---|---|---|---|---|
| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −11.234 | 698.195 | | |
| 100 | 34.639 | 221.100 | 299.913 | −7.881 | | | |
| 200 | 39.818 | 246.644 | 267.476 | −4.166 | | | |
| 250 | 42.536 | 255.823 | 264.251 | −2.107 | | | |
| 298.15 | 44.937 | 263.525 | 263.525 | 0 | 702.389 | 687.583 | −120 462 |
| 300 | 45.023 | 263.803 | 263.525 | 0.083 | 702.411 | 687.492 | −119.703 |
| 350 | 47.151 | 270.908 | 264.082 | 2.389 | 703.001 | 684.958 | −102.224 |
| 400 | 48.910 | 277.323 | 265.342 | 4.792 | 701.382 | 682.428 | −89.116 |
| 450 | 50.341 | 283.169 | 267.003 | 7.275 | 701.311 | 680.055 | −78.939 |
| 500 | 51.500 | 288.535 | 268.892 | 9.822 | 701.196 | 677.701 | −70.799 |
| 600 | 53.212 | 298.087 | 272.981 | 15.063 | 701.458 | 672.985 | −58.589 |
| 700 | 54.372 | 306.382 | 277.173 | 20.446 | 702.021 | 668.198 | −49.862 |
| 800 | 55.183 | 313.698 | 281.291 | 25.926 | 702.759 | 663.317 | −43.310 |
| 900 | 55.767 | 320.233 | 285.261 | 31.475 | 650.476 | 659.418 | −38.272 |
| 1000 | 56.200 | 326.133 | 289.058 | 37.074 | 652.608 | 660.297 | −34 490 |
| 1100 | 56.529 | 331.505 | 292.676 | 42.712 | 654.732 | 660.963 | −31.387 |
| 1200 | 56.785 | 336.435 | 296.120 | 48.378 | 656.844 | 661.437 | −28.792 |
| 1300 | 56.986 | 340.989 | 299.399 | 54.067 | 658.940 | 661 734 | −26.589 |
| 1400 | 57.148 | 345.218 | 302.522 | 59.774 | 661.017 | 661.871 | −24.695 |
| 1500 | 57.280 | 349.165 | 305.502 | 65.495 | 663.073 | 661.860 | −23.048 |
| 1600 | 57.388 | 352.866 | 308.348 | 71.229 | 665.108 | 661.713 | −21.603 |
| 1700 | 57.479 | 356.348 | 311.070 | 76.972 | 667.122 | 661.439 | −20.324 |
| 1800 | 57.556 | 359.635 | 313.677 | 82.724 | 669.117 | 661.047 | −19.183 |
| 1900 | 57.621 | 362.749 | 316.179 | 88.483 | 671.093 | 660.545 | −18.160 |
| 2000 | 57.676 | 365.706 | 318.582 | 94.248 | 673.054 | 659.939 | −17.236 |
| 2100 | 57.724 | 368.521 | 320.894 | 100.018 | 675.003 | 659.235 | −16.398 |
| 2200 | 57.766 | 371.208 | 323.120 | 105.793 | 676.944 | 658.439 | −15.633 |
| 2300 | 57.803 | 373.776 | 325.267 | 111.571 | 678.881 | 657.554 | −14.934 |
| 2400 | 57.835 | 376.237 | 327.340 | 117.353 | 680.818 | 656.585 | −14.290 |
| 2500 | 57.864 | 378.599 | 329.343 | 123.138 | 682.758 | 655.536 | −13.697 |
| 2600 | 57.890 | 380.869 | 331.282 | 128.926 | 684.706 | 654.409 | −13.147 |
| 2700 | 57.914 | 383.054 | 333.159 | 134.716 | 686.667 | 653.206 | −12.637 |
| 2800 | 57.936 | 385.160 | 334.979 | 140.509 | 688.642 | 651.931 | −12.162 |
| 2900 | 57.957 | 387 194 | 336.744 | 146.303 | 690.636 | 650.584 | −11 718 |
| 3000 | 57.976 | 389.159 | 338.459 | 152.100 | 692.652 | 649.169 | −11.303 |
| 3100 | 57.995 | 391.060 | 340.125 | 157.899 | 694.691 | 647.686 | −10.913 |
| 3200 | 58.014 | 392.902 | 341.746 | 163.699 | 696.756 | 646.137 | −10.547 |
| 3300 | 58.034 | 394.687 | 343.323 | 169.501 | 698.849 | 644.523 | −10.202 |
| 3400 | 58.053 | 396.420 | 344.860 | 175.306 | 700.972 | 642.845 | −9.876 |
| 3500 | 58.074 | 398.103 | 346.357 | 181.112 | 703.125 | 641.104 | −9.568 |
| 3600 | 58.097 | 399.740 | 347.817 | 186.921 | 705.309 | 639.301 | −9.276 |
| 3700 | 58.121 | 401.332 | 349.242 | 192.732 | 707.525 | 637.437 | −8.999 |
| 3800 | 58.147 | 402.882 | 350.633 | 198.545 | 709.774 | 635.512 | −8.736 |
| 3900 | 58.176 | 404.393 | 351.992 | 204.361 | 712.055 | 633.529 | −8.485 |
| 4000 | 58.207 | 405.866 | 353.321 | 210.180 | 714.369 | 631.486 | −8.246 |
| 4100 | 58.242 | 407.304 | 354.620 | 216.003 | 716.715 | 629.385 | −8.018 |
| 4200 | 58.279 | 408.708 | 355.891 | 221.829 | 719.094 | 627.226 | −7.801 |
| 4300 | 58.320 | 410.079 | 357.136 | 227.659 | 721.505 | 625.010 | −7.592 |
| 4400 | 58.365 | 411.421 | 358.354 | 233.493 | 723.947 | 622.738 | −7.393 |
| 4500 | 58.413 | 412.733 | 359.548 | 239.332 | 726.421 | 620.410 | −7.202 |
| 4600 | 58.466 | 414.017 | 360.718 | 245.176 | 728.926 | 618.027 | −7.018 |
| 4700 | 58.523 | 415.275 | 361.866 | 251.025 | 731.461 | 615.589 | −6.842 |
| 4800 | 58.584 | 416.508 | 362.991 | 256.880 | 734.026 | 613.096 | −6.672 |
| 4900 | 58.649 | 417.717 | 364.096 | 262.742 | 736.620 | 610.550 | −6.509 |
| 5000 | 58.719 | 418.902 | 365.180 | 268.610 | 739.243 | 607.951 | −6.351 |
| 5100 | 58.793 | 420.066 | 366.245 | 274.486 | 741.894 | 605.299 | −6.200 |
| 5200 | 58.872 | 421.208 | 367.291 | 280.369 | 744.574 | 602.594 | −6.053 |
| 5300 | 58.954 | 422.330 | 368.319 | 286.260 | 747.280 | 599.838 | −5.912 |
| 5400 | 59.042 | 423.433 | 369.329 | 292.160 | 750.014 | 597.031 | −5.775 |
| 5500 | 59.133 | 424.517 | 370.323 | 298.069 | 752.774 | 594.172 | −5.643 |
| 5600 | 59.229 | 425.584 | 371.300 | 303.987 | 755.560 | 591.263 | −5.515 |
| 5700 | 59.329 | 426.633 | 372.262 | 309.915 | 758.373 | 588.304 | −5.391 |
| 5800 | 59.432 | 427.666 | 373.208 | 315.853 | 761.210 | 585.296 | −5.271 |
| 5900 | 59.540 | 428.682 | 374.140 | 321.801 | 764.072 | 582.239 | −5.155 |
| 6000 | 59.651 | 429 684 | 375.057 | 327 761 | 766.959 | 579.132 | −5.042 |

PREVIOUS: December 1976 (1 atm) CURRENT. December 1976 (1 bar)

### Enthalpy of Formation

$H°$(0 K) = 166 9 ± 11.0 kcal·mol$^{-1}$ is calculated as the sum of $\Delta_f H°$(SF$_3$, g, 0 K) = −70.42 ± 4 kcal·mol$^{-1}$ [1] and IP(SF$_2$) = 10.29 ± 0.3 eV (237.29 kcal·mol$^{-1}$). IP is the electron–impact appearance potential of SF$_2^+$ which was measured by Hildenbrand[2] in a mass spectral study of the products formed from the reaction of SF$_6$ with C at about 1500 K We increase the uncertainty in IP to ±0.3 eV from the value (±0.1 eV) assigned by Hildenbrand[2] since recent photoelectron (PE) spectrometric studies on the related dihalides SCl$_2$[3] and SiF$_2^+$ show that their adiabatic ionization potentials lie 0.22 and 0.40 eV, respectively, below the corresponding vertical values. The adopted value of IP is bracketed by the accurately known adiabatic values for SCl$_2$(9.45 ± 0.05 eV),[3] and SiF$_2$(10.78 ± 0.05 eV),[4] and is close to the IP for atomic sulfur (10.36 eV).[5] MO calculations[6] predict IP(SF$_2$) = 9.6 eV.

Several fragmentation appeamce potentials for the ion–molecule systems SF$_2^+$/SF$_6$)[2,7] SF$_2^+$/SF$_4$,[2] and SF$_2^+$/NSF$_3$[8] have been reported and provide alternate paths leading to $\Delta_f H°$ once the ion formation processes are assigned. We use plausible reactions for the formation of SF$_2^+$ to calculate $\Delta_f H°$ values which cover the range 146–342 kcal·mol$^{-1}$. The scatter in these values indicate that either the dissociative ionization processes have been incorrectly assigned, or perhaps more likely, the processes involve excess kinetic and/or excitation energies.

We find that the primary bond dissociation energy $D_0°$ (SF$^+$–F) is 87.1 kcal·mol$^{-1}$ which when compared with $D_0°$ values [1] for SF$_2$(91.7 kcal·mol$^{-1}$) and SF$_2^-$(68.7 kcal·mol$^{-1}$) indicates that the trend is $D_0°$ (SF$_2^+$)–$D_0°$ (SF$_2$) >$D_0°$ (SF$_2^-$) Similar trends in bond dissociation energies have been reported[9] for the ions and neutrals of phosphorus and nitrogen difluorides.

### Heat Capacity and Entropy

According to the Walsh correlation diagram[10] for non–hydride AB$_2$ molecules, the most loosely bound pair of electrons in SF$_2$ is in a b$_1''$ orbital. The Walsh prediction is supported by the results of theoretical studies[3 11 12] and assignments of the bands in the PE spectra[3 12] for the isoelectronic molecules SCl$_2$, OF$_2$, and OCl$_2$. The b$_1''$ orbital is S–F antibonding and F–F bonding, but its binding energy[10] shows only a small positive angular dependence. We would expect then that removal of an electron from this orbital should be accompanied by a small increase in the bond angle. We adopt a bond angle of 100° which corresponds to roughly a 2° increase from that for SF$_2$.[1] The antibonding nature of the b$_1''$ orbital is also expected to produce upon ionization a decrease in the S–F bond length. However, a comparison of the S–F bond strengths in SF$_2^+$($D_0°$ = 87.1 kcal·mol$^{-1}$) and SF$_2$($D_0°$ = 91.7 kcal·mol$^{-1}$) would seem to indicate that any changes in molecular parameters are relatively small. We adopt $r_e$(SF$_2^+$) = 1.59 Å which amounts to only a 0.002 Å reduction from that for SF$_2$.[1] Our estimated molecular parameters appear reasonable in comparison with those for SiF$_2$.[1] The individual moments of inertia are: $I_A$ = 1.2375 × 10$^{-39}$, $I_B$ = 9.3597 × 10$^{-39}$, and $I_C$ = 3.0157 × 10$^{-39}$ g·cm$^2$.

We calculate the vibrational frequencies from the force constants $f_r$ = 4.7 and $f_\alpha/r^2$ = 0.49 mdyn/Å. The stretching force constant ($f_r$) is estimated from that for SiF$_2$[1] and PF$_2$.[13] We obtain the bending force constant from the ratio $f_r/(f_\alpha/r^2)$ = 9.59 which is the value calculated for SiF$_2$ [13] The changes in our frequencies on going from SF$_2$ to SF$_2^+$ are insignficant, in agreement with the view that the bonding in the two molecules is very similar.

The electronic configurations of the ground and excited states are predicted from the Walsh correlation diagram.[10] We also predict from this diagram that the two $^2A_1 \infty {}^2B_1$ spacings will strongly depend on the bond angle. This is supported at least for the first spacing by PE studies[3 12] on SCl$_2$, OCl$_2$ and OF$_2$. Based on the similarity in the bond angles for OF$_2$[3] and SF$_2$,[1] we estimate the first $^2A_1 \leftarrow {}^2B_1$ spacing to be somewhat greater than that for OF$_2^+$(23471 cm$^{-1}$).[12] The PE spectra for SCl$_2$[3] and OF$_2$[12] do not provide support for the existence of a second $^2A_1$ state. This state has been observed, however, in the PE spectrum of OCl$_2$.[12] These results show for OCl$_2^+$ that the second $^2A_1$ state lies 2258 cm$^{-1}$ above the first $^2A_1$ state. We include a second $^2A_1$–$^2A_1$ spacing of 3000 cm$^{-1}$. We estimate a somewhat larger spacing for SF$_2^+$ based on the fact that the bond angle in SF$_2^+$ is predicted to be smaller than that for OCl$_2^+$. The relative term value for the upper most state ($^2A_2$) is estimated from that for OF$_2^+$.[12]

### References

[1] JANAF Thermochemical Tables. SF$_2$(g) and SiF$_2$(g), 6–30–76; SF$_2^+$(g), 12–31–76.
[2] D. L. Hildenbrand, J. Phys. Chem. 77, 897 (1973).

Continued on page 1215

$\Delta_f H^\circ(0\ K) = [-391.116 \pm 64.9]\ kJ \cdot mol^{-1}$

$S^\circ(298.15\ K) = [267.445 \pm 0.8]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H^\circ(298.15\ K) = [-398.426 \pm 64.9]\ kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, cm$^{-1}$ |
|---|
| [479](1) |
| [286](1) |
| [594](1) |

Ground State Quantum Weight: [2] $\sigma = [2]$

Point Group: [$C_{2v}$]

Bond Distance: S–F = [1.63] Å

Bond Angle: F–S–F = [130]°

Product of the Moments of Inertia: $I_A I_B I_C = [2.856674 \times 10^{-115}]\ g^3 \cdot cm^6$

## Enthalpy of Formation

We calculate the adopted value of $\Delta_f H^\circ(0\ K) = -93.5 \pm 15.5\ kcal \cdot mol^{-1}$ as the difference between $\Delta_f H^\circ(SF_2, g, 0\ K) = -70.42 \pm 4.0\ kcal \cdot mol^{-1}$ [1] and an estimate $EA(SF_2) = 1.0 \pm 0.5$ eV ($23.06\ kcal \cdot mol^{-1}$). The value of EA is estimated from a consideration of trends in the electron affinities for other S–F species.[1] These data follow a regular pattern among the even–and odd–electron molecules, with the odd–electron molecules having, as expected, the higher electron affinities. Within each even– and odd– electron series, the EA values progressively increase as the number of fluorine atoms are increased in the ions. The only other estimate available to compare with our result is EA = 1.2 ± 0.5 eV. This estimate was made by Hildenbrand[2] who used a method similar to ours. Our $\Delta_f H^\circ$ value corresponds to a fluoride–ion affinity for SF of IA = 36.4 ± 17.0 $kcal \cdot mol^{-1}$, and $\Delta_f H^\circ$ at 298.15 K is $-95.2\ kcal \cdot mol^{-1}$ In addition, we find that the primary bond dissociation energy $D_0^\circ(SF^- – F)$ is 68.7 $kcal \cdot mol^{-1}$ which when compared with the values for $SF_2$(91.7 $kcal \cdot mol^{-1}$) and $SF_2^+$(87.1 $kcal \cdot mol^{-1}$) indicates that the trend is $D_0^\circ(SF_2^+) – D_0^\circ(SF_2) > D_0^\circ(SF_2^-)$. Similar trends in bond dissociation energies have been reported[3] for the ions and neutrals of phosphorus and nitrogen difluorides.

JANAF data[1] predict that $SF_2^-$ should be reasonably stable at moderate temperatures, with dissociative ionization ($SF + F^-$) becoming thermodynamically favorable above 1500 K. These predictions are qualitatively supported by the observations of Harland and Thynne[4,5] who have observed $SF_2^-$ in the negative ion mass spectra of $SF_6$, $SF_4$, and $SF_5Cl$. The temperature of the ion source was reported as around 325 K.

## Heat Capacity and Entropy

According to the Walsh correlation diagram[6] for non–hydride $AB_2$ molecules, the most loosely bound electron in $SF_2^-$ is in an $\bar{a}_1'$ orbital whose binding energy falls markedly with an increase in bond angle. We predict then that electron capture by $SF_2$ should be accompanied by a large increase in bond angle. Based on the bond angle reported for the isoelectronic valence (21 electrons) molecule $ClF_2$(136 ± 15°),[7] we estimate an angle for $SF_2^-$ of 130° which represents a 32° increase from that for $SF_2$.[1] The addition of an antibonding electron to $SF_2$ should also produce an increase in the S–F bond length. We estimate $r_e(SF_2^-) = r_e(Cl–F) = 1.63$ Å[1] which corresponds to $r_e(SF_2^-) – r_e(SF_2) = 0.038$ Å. The individual moments of inertia are: $I_A = 1.3702 \times 10^{-39}$, $I_B = 13.7701 \times 10^{-39}$, and $I_C = 15.1403 \times 10^{-39}\ g \cdot cm^2$.

We calculate vibrational frequencies from the force constants $f_r = 2.0$ and $f_\alpha/r^2 = 0.27$ mdyn/Å. These force constants are estimated from those for $ClF_2$($f_r = 1.94$ and $f_\alpha/r^2 = 0.26$ mdyn/Å) which are obtained from the bond angle and vibrational frequencies reported by Mamantov *et al.*[7] Our frequencies on going from $SF_2$ to $SF_2^-$ show a large decrease, in agreement with the view that the additional antibonding electron weakens the bonding in the radical anion relative to the neutral molecule.

The Walsh correlation diagram[6] predicts a ground state electronic configuration of $^2A_1$ for a 21 valence electron molecule. In addition, the existence of two doublet excited states is highly probable. We omit these excited states since no spectroscopic information is available on these states for isoelectronic molecules which would allow us to estimate the relative term values. We speculate that these levels lie above 20000 cm$^{-1}$, and thus, their contributions to the thermal functions are probably small below 3000 K.

## References

[1] JANAF Thermochemical Tables: $SF_2$(g), 6–30–76; $SF^-$(g), $SF_3^-$(g), $SF_4^-$(g), $SF_5^-$(g), and $SF_2^+$(g), 12–31–76; ClF(g), 9–30–65.

[2] D. L. Hildenbrand, J. Phys. Chem. 77, 897 (1973).

[3] P. W. Harland, D. W. H. Rankin, and J. C. J. Thynne, Int. J. Mass Spec. and Ion Phys. 13, 395 (1974).

[4] P. Harland and J. C. J. Thynne, J. Phys. Chem. 73, 4031 (1969).

[5] P. W. Harland and J. C. J. Thynne, J. Phys. Chem. 75, 3517 (1971).

[6] A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).

[7] G. Mamantov, E. J. Vasini, M. C. Moulton, D. G. Vickroy, and T. Maekawa, J. Chem. Phys. 54, 3419 (1971).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p^\circ$ = 0.1 MPa

| | $J \cdot K^{-1} mol^{-1}$ | | | $kJ \cdot mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ - H^\circ(T_r)]/T$ | $H^\circ - H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −12.125 | −391.116 | | |
| 100 | 36.153 | 220.728 | 308.077 | −8.735 | | | |
| 200 | 44.703 | 248.468 | 271.882 | −4.683 | | | |
| 250 | 47.901 | 258.804 | 268.259 | −2.364 | | | |
| 298.15 | 50.164 | 267.445 | 267.445 | 0. | −398.426 | −401.890 | 70.410 |
| 300 | 50.238 | 267.756 | 267.446 | 0.093 | −398.471 | −401.912 | 69 979 |
| 350 | 51.930 | 275.634 | 268.064 | 2.649 | −399.709 | −402.388 | 60.053 |
| 400 | 53.167 | 282.653 | 269.457 | 5.278 | −403.181 | −402.597 | 52.574 |
| 450 | 54.088 | 288.971 | 271.280 | 7.961 | −405.130 | −402.416 | 46.711 |
| 500 | 54.787 | 294.707 | 273.341 | 10.683 | −407.148 | −402.004 | 41.997 |
| 600 | 55.752 | 304.789 | 277.765 | 16.214 | −410.754 | −400.630 | 34.878 |
| 700 | 56.365 | 313.432 | 282.258 | 21.822 | −414.123 | −398.674 | 29.749 |
| 800 | 56.777 | 320.987 | 286.636 | 27.481 | −417.364 | −396.245 | 25.872 |
| 900 | 57.065 | 327.692 | 290.833 | 33.174 | −473.660 | −392.334 | 22.770 |
| 1000 | 57.275 | 333.716 | 294.825 | 38.891 | −475.568 | −383.195 | 20 016 |
| 1100 | 57.432 | 339.183 | 298.613 | 44.627 | −477.502 | −373.865 | 17.753 |
| 1200 | 57.552 | 344.185 | 302.205 | 50.376 | −479.464 | −364.357 | 15.860 |
| 1300 | 57.647 | 348.796 | 305.614 | 56.136 | −481.454 | −354.684 | 14.251 |
| 1400 | 57.722 | 353.071 | 308.853 | 61.905 | −483.473 | −344.857 | 12.867 |
| 1500 | 57.783 | 357.055 | 311.935 | 67.680 | −485.520 | −334.885 | 11.662 |
| 1600 | 57.833 | 360.786 | 314.873 | 73.461 | −487.595 | −324.775 | 10.603 |
| 1700 | 57.875 | 364.294 | 317.678 | 79.247 | −489.696 | −314.534 | 9 664 |
| 1800 | 57.909 | 367.603 | 320.360 | 85.036 | −491.821 | −304.169 | 8.827 |
| 1900 | 57.939 | 370.734 | 322.930 | 90.828 | −493.969 | −293.686 | 8.074 |
| 2000 | 57.964 | 373.707 | 325.395 | 96.624 | −496.135 | −283.088 | 7.394 |
| 2100 | 57.986 | 376.536 | 327.764 | 102.421 | −498.315 | −272.383 | 6.775 |
| 2200 | 58.005 | 379.234 | 330.042 | 108.221 | −500.506 | −261.573 | 6.211 |
| 2300 | 58.022 | 381.812 | 332.238 | 114.022 | −502.704 | −250.663 | 5 693 |
| 2400 | 58.036 | 384.282 | 334.355 | 119.825 | −504.903 | −239.657 | 5.216 |
| 2500 | 58.049 | 386.651 | 336.400 | 125.629 | −507.101 | −228.560 | 4.776 |
| 2600 | 58.061 | 388.928 | 338.377 | 131.435 | −509.292 | −217.375 | 4.367 |
| 2700 | 58.071 | 391.120 | 340.290 | 137.241 | −511.473 | −206.106 | 3.987 |
| 2800 | 58.080 | 393.232 | 342.143 | 143.049 | −513.639 | −194.757 | 3.633 |
| 2900 | 58.088 | 395.270 | 343.940 | 148.857 | −515.789 | −183.330 | 3.302 |
| 3000 | 58.095 | 397.240 | 345.684 | 154.666 | −517.918 | −171.830 | 2.992 |
| 3100 | 58.102 | 399.145 | 347.378 | 160.476 | −520.025 | −160.259 | 2.700 |
| 3200 | 58.108 | 400.989 | 349.025 | 166.287 | −522.106 | −148.620 | 2.426 |
| 3300 | 58.114 | 402.778 | 350.627 | 172.098 | −524.162 | −136.917 | 2.167 |
| 3400 | 58.119 | 404.512 | 352.186 | 177.910 | −526.189 | −125.152 | 1.923 |
| 3500 | 58.123 | 406.197 | 353.705 | 183.722 | −528.188 | −113.327 | 1.691 |
| 3600 | 58.128 | 407.835 | 355.186 | 189.534 | −530.157 | −101.446 | 1.472 |
| 3700 | 58.131 | 409.427 | 356.631 | 195.347 | −532.096 | −89.510 | 1.264 |
| 3800 | 58.135 | 410.978 | 358.041 | 201.160 | −534.004 | −77.523 | 1.066 |
| 3900 | 58.138 | 412.488 | 359.418 | 206.974 | −535.883 | −65.486 | 0.877 |
| 4000 | 58.141 | 413.960 | 360.763 | 212.788 | −537.731 | −53.401 | 0.697 |
| 4100 | 58.144 | 415.396 | 362.078 | 218.602 | −539.550 | −41.270 | 0.526 |
| 4200 | 58.147 | 416.797 | 363.364 | 224.417 | −541.340 | −29.095 | 0.362 |
| 4300 | 58.149 | 418.165 | 364.623 | 230.232 | −543.102 | −16.878 | 0.205 |
| 4400 | 58.152 | 419.502 | 365.855 | 236.047 | −544.836 | −4.620 | 0.055 |
| 4500 | 58.154 | 420.809 | 367.061 | 241.862 | −546.543 | 7.677 | −0.089 |
| 4600 | 58.156 | 422.087 | 368.244 | 247.678 | −548.224 | 20.011 | −0.227 |
| 4700 | 58.158 | 423.338 | 369.403 | 253.493 | −549.879 | 32.382 | −0.360 |
| 4800 | 58.160 | 424.562 | 370.539 | 259.309 | −551.511 | 44.788 | −0.487 |
| 4900 | 58.161 | 425.761 | 371.654 | 265.125 | −553.120 | 57.228 | −0.610 |
| 5000 | 58.163 | 426.936 | 372.748 | 270.941 | −554.706 | 69.700 | −0.728 |
| 5100 | 58.164 | 428.088 | 373.822 | 276.758 | −556.271 | 82.203 | −0.842 |
| 5200 | 58.166 | 429.217 | 374.876 | 282.574 | −557.815 | 94.738 | −0.952 |
| 5300 | 58.167 | 430.325 | 375.912 | 288.391 | −559.341 | 107.302 | −1.058 |
| 5400 | 58.168 | 431.413 | 376.930 | 294.208 | −560.847 | 119.894 | −1.160 |
| 5500 | 58.169 | 432.480 | 377.930 | 300.025 | −562.336 | 132.514 | −1.259 |
| 5600 | 58.171 | 433.528 | 378.914 | 305.842 | −563.808 | 145.161 | −1.354 |
| 5700 | 58.172 | 434.558 | 379.881 | 311.659 | −565.264 | 157.834 | −1.446 |
| 5800 | 58.173 | 435.570 | 380.832 | 317.476 | −566.705 | 170.532 | −1.536 |
| 5900 | 58.174 | 436.564 | 381.769 | 323.293 | −568.131 | 183.256 | −1.622 |
| 6000 | 58.174 | 437.542 | 382.690 | 329.111 | −569.543 | 196.003 | −1.706 |

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

## Difluorodisulfane ($FS_2F$) IDEAL GAS $M_r = 102.116806$ Difluorodisulfane (FSSF) $F_2S_2(g)$

$S°(298.15\ K) = [294.082 \pm 0.08]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-333.382 \pm 41.8]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [336.435 \pm 41.8]\ kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ | <br>$\nu$, cm$^{-1}$ |
|---|---|
| 717.0(1) | 182.5(1) |
| 614.6(1) | 680.8(1) |
| 319.8(1) | 301.0(1) |

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: $C_2$
Bond Distances: S–F = 1.635 ± 0.01 Å; S–S = 1.888 ± 0.01 Å
Bond Angles: F–S–S = 108.3 ± 0.5°; Dihedral = 87.9 ± 1.5°
Product of Moments of Inertia: $I_A I_B I_C = 7.332228 \times 10^{-114}\ g^3 \cdot cm^6$

### Enthalpy of Formation

No direct experimental measurement of $\Delta_f H°$ is available. We estimate a value from bond energy considerations. From a comparison of bond lengths and force constants for FSSF[1] and $SF_4$,[2] we expect that the S–F bond energies in FSSF would be quite similar to those for the axial S–F bonds in $SF_4$. We assume $D_0°(FSS{-}F) = D_0°(SF_3{-}F)_{axial} = 73.6\ kcal \cdot mol^{-1}$ which leads to the adopted value of $\Delta_f H°(S_2F_2, g, 0\ K) = -79.7\ kcal \cdot mol^{-1}$. We use auxiliary heat of formation data from JANAF[3] and estimate the uncertainty in $\Delta_f H°$ as ±10.0 $kcal \cdot mol^{-1}$. A previous estimate ($-83.5\ kcal \cdot mol^{-1}$) has been reported by O'Hare[4] who derived this value by a procedure identical with that used here. $\Delta_f H°(298.15\ K)$ corresponds to $-80.4\ kcal \cdot mol^{-1}$, and the atomization energy is calculated from $\Delta_f H°$ to be 247.9 $kcal \cdot mol^{-1}$.

FSSF is isomeric with $SSF_2$[3] Qualitative evidence has been presented[1] which indicates that $SSF_2$ is the more stable isomer. From our estimated free energy data, we predict a Gibbs energy change for the isomerization reaction $FSSF(g) = SSF_2(g)$ of $-15.4\ kcal \cdot mol^{-1}$ at 298.15 K, indicating that $SSF_2$ is substantially more stable than FSSF. This conflicts with relative stability predictions based on results from two independent MO studies.[5,6] These semiempirical (CNDO/2) calculations indicate that the instability of FSSF relative to $SSF_2$ amounts to only about 2.0 $kcal \cdot mol^{-1}$. If we assume that these MO calculations are correct, we calculate that $D_0°(FS{-}SF) > D_0°(S{=}SF_2)$ by roughly 7.0 $kcal \cdot mol^{-1}$. This seems very unlikely in view of what is known[1] about the S–S linkages in the two isomers Our adopted results give $D_0°(FS{-}SF) = 85.6\ kcal \cdot mol^{-1}$ which lies between that for $SSF_2$(90.4 $kcal \cdot mol^{-1}$) and $S_2O$(79.9 $kcal \cdot mol^{-1}$).[3]

### Heat Capacity and Entropy

The structural data and vibrational frequencies are taken from the recent review of Seel[1] and are based on reliable experimental measurements. We note that the molecular characteristics of FSSF are unusual in that the S–S bond length (1.888 Å) is much shorter than that in HSSH(2.05 Å),[1] and nearly equal to those in $S_2$(1.889 Å), $SSF_2$(1.860 Å), and $S_2O$(1.884 Å).[3] In contrast, the S–F bonds are longer than those in most S–F species (~1.58 Å),[3] and nearly as long as the axial S–F bonds (1.646 Å),[3] in $SF_4$ Rationale[1] has been presented to explain these unique molecular features in terms of double bond ($F^-S{=}S^+{-}F$) formation. The individual moments of inertia are: $I_A = 7.3579 \times 10^{-39}$, $I_B = 30.4921 \times 10^{-39}$, and $I_C = 32.6808 \times 10^{-39}\ g \cdot cm^2$.

We assume that there is no free internal rotation in the molecule, and the contribution from the torsional oscillation ($\nu_4 = 182.5\ cm^{-1}$) is included in the vibrational partition function. Extended Huckel calculations[7] show that the potential barrier to internal rotation is high (~40 $kcal \cdot mol^{-1}$), providing some justification for our treatment. We estimate that the uncertainty in our entropies above 2000 K should not exceed 1.0 cal $K^{-1} \cdot mol^{-1}$. The UV spectra[1] of FSSF reveal no excited states which would be significant in our calculations. Since $S_2F_2$ has no unpaired electrons, we predict that the ground state is singlet.

Our thermal functions essentially extend those reported by Brown and Pez.[8] Other published functions[4,9] are based on estimated vibrational frequencies and are considered less reliable.

### References

[1] F. Seel, in Advances in Inorganic Chemistry and Radiochemistry, Vol. 16, H. J. Emeleus and A G. Sharpe, eds., Academic Press, New York, (1974).
[2] I. W. Levin, J. Chem. Phys. 55, 5393 (1971).
[3] JANAF Thermochemical Tables· $S_2$(g), 12–31–65, F(g), 9–30–65, $SSF_2$(g) and $SF_4$(g), 6–30–76, $S_2O$(g), 9–30–65.
[4] P. A. G. O'Hare, Argonne National Laboratory, ANL–7315, (July 1968).
[5] A. L. Companion, Theoret. Chim. Acta, 25, 268 (1972).
[6] G. Wagner, H. Bock, R. Budenz, and F. Seel, Chem. Ber. 106, 1285 (1973).
[7] R. M. Minyaev, V. I. Minkin, I. I. Zakharov, and I. D. Sadekov, Teor. Eksp Khim. 9, 816 (1973).
[8] R. D. Brown and G. P. Pez, Spectrochimica Acta, 26A, 1375 (1970).
[9] B. J. McBride, S. Heimel, J. G. Ehlers, and S. Gordon, NASA Rep. SP–3001, (July 1963).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −14.595 | −333.382 | −333.382 | INFINITE |
| 100 | 42.158 | 235.778 | 345.882 | −11.010 | −334.084 | −338.120 | 176.616 |
| 200 | 56.425 | 269.610 | 299.845 | −6.047 | −335.333 | −341.670 | 89.235 |
| 250 | 61.892 | 282.811 | 295.147 | −3.084 | −335.912 | −343.186 | 71.705 |
| 298.15 | 66.041 | 294.082 | 294.082 | 0. | −336.435 | −344.539 | 60.362 |
| 300 | 66.180 | 294.491 | 294.083 | 0.122 | −336.455 | −344.590 | 59.998 |
| 350 | 69.466 | 304.951 | 294.902 | 3.517 | −336.981 | −345.904 | 51.623 |
| 400 | 71.974 | 314.398 | 296.758 | 7.056 | −341.935 | −346.967 | 45.309 |
| 450 | 73.899 | 322.991 | 299.203 | 10.705 | −343.804 | −347.501 | 40.337 |
| 500 | 75.395 | 330.858 | 301.980 | 14.439 | −345.774 | −347.801 | 36.335 |
| 600 | 77.509 | 344.805 | 307.985 | 22.092 | −348.764 | −347.912 | 30.288 |
| 700 | 78.883 | 356.864 | 314.126 | 29.916 | −351.185 | −347.573 | 25.936 |
| 800 | 79.819 | 367.462 | 320.144 | 37.854 | −353.279 | −346.912 | 22.651 |
| 900 | 80.482 | 376.904 | 325.936 | 45.871 | −461.429 | −343.838 | 19.956 |
| 1000 | 80.968 | 385.410 | 331.465 | 53.945 | −460.758 | −330.809 | 17.280 |
| 1100 | 81.333 | 393.145 | 336.726 | 62.061 | −460.105 | −317.846 | 15.093 |
| 1200 | 81.614 | 400.234 | 341.727 | 70.208 | −459.477 | −304.941 | 13.274 |
| 1300 | 81.835 | 406.776 | 346.483 | 78.381 | −458.878 | −292.088 | 11.736 |
| 1400 | 82.011 | 412.847 | 351.009 | 86.574 | −458.312 | −279.279 | 10.420 |
| 1500 | 82.154 | 418.510 | 355.322 | 94.782 | −457.781 | −266.510 | 9.281 |
| 1600 | 82.272 | 423.816 | 359.439 | 103.004 | −457.285 | −253.775 | 8.285 |
| 1700 | 82.370 | 428.807 | 363.374 | 111.236 | −456.823 | −241.070 | 7.407 |
| 1800 | 82.453 | 433.518 | 367.141 | 119.477 | −456.395 | −228.391 | 6.628 |
| 1900 | 82.523 | 437.978 | 370.753 | 127.726 | −455.996 | −215.735 | 5.931 |
| 2000 | 82.583 | 442.212 | 374.221 | 135.982 | −455.625 | −203.099 | 5.304 |
| 2100 | 82.635 | 446.243 | 377.556 | 144.243 | −455.276 | −190.482 | 4 738 |
| 2200 | 82.679 | 450.088 | 380.766 | 152.508 | −454.945 | −177 880 | 4.223 |
| 2300 | 82.719 | 453.764 | 383.860 | 160.778 | −454.627 | −165.293 | 3.754 |
| 2400 | 82.753 | 457.285 | 386.847 | 169.052 | −454.318 | −152.720 | 3.324 |
| 2500 | 82.784 | 460.664 | 389.732 | 177.329 | −454.013 | −140.160 | 2.928 |
| 2600 | 82.811 | 463.911 | 392.523 | 185.609 | −453 708 | −127.612 | 2.564 |
| 2700 | 82.835 | 467.037 | 395.226 | 193.891 | −453.396 | −115.076 | 2.226 |
| 2800 | 82.856 | 470.050 | 397.844 | 202.175 | −453.074 | −102.551 | 1.913 |
| 2900 | 82.876 | 472.958 | 400.385 | 210.462 | −452.740 | −90.038 | 1.622 |
| 3000 | 82.893 | 475.768 | 402.851 | 218.751 | −452.391 | −77.537 | 1.350 |
| 3100 | 82.909 | 478.486 | 405.247 | 227.041 | −452.022 | −65.048 | 1.096 |
| 3200 | 82.923 | 481.119 | 407.577 | 235.332 | −451.632 | −52.571 | 0.858 |
| 3300 | 82.937 | 483.670 | 409.845 | 243.625 | −451.218 | −40.107 | 0.635 |
| 3400 | 82.949 | 486.147 | 412.053 | 251.920 | −450.780 | −27.656 | 0.425 |
| 3500 | 82.960 | 488.551 | 414.204 | 260.215 | −450.318 | −15.218 | 0.227 |
| 3600 | 82.970 | 490.888 | 416.302 | 268.511 | −449.829 | −2.793 | 0.041 |
| 3700 | 82.979 | 493.162 | 418.349 | 276.809 | −449.313 | 9.618 | −0.136 |
| 3800 | 82.987 | 495.375 | 420.347 | 285.107 | −448.771 | 22.014 | −0.303 |
| 3900 | 82.995 | 497.531 | 422.298 | 293.406 | −448.202 | 34.396 | −0.461 |
| 4000 | 83.003 | 499.632 | 424.205 | 301.706 | −447.608 | 46.763 | −0.611 |
| 4100 | 83.009 | 501.682 | 426.070 | 310.007 | −446.989 | 59.114 | −0.753 |
| 4200 | 83.016 | 503.682 | 427.894 | 318.308 | −446.344 | 71.451 | −0.889 |
| 4300 | 83.022 | 505.635 | 429.680 | 326.610 | −445.677 | 83 771 | −1.018 |
| 4400 | 83.027 | 507.544 | 431.428 | 334.913 | −444.986 | 96.076 | −1.141 |
| 4500 | 83.032 | 509.410 | 433.140 | 343.215 | −444.274 | 108.365 | −1.258 |
| 4600 | 83.037 | 511.235 | 434.818 | 351.519 | −443.541 | 120.637 | −1.370 |
| 4700 | 83.042 | 513.021 | 436.463 | 359.823 | −442.789 | 132.894 | −1.477 |
| 4800 | 83.046 | 514.769 | 438.076 | 368.127 | −442.018 | 145.135 | −1.579 |
| 4900 | 83.050 | 516.482 | 439.659 | 376.432 | −441.231 | 157.359 | −1.677 |
| 5000 | 83.054 | 518.159 | 441.212 | 384.737 | −440.427 | 169.567 | −1.771 |
| 5100 | 83.057 | 519.804 | 442.737 | 393.043 | −439.609 | 181.759 | −1.862 |
| 5200 | 83.060 | 521.417 | 444.235 | 401.349 | −438.776 | 193.935 | −1.948 |
| 5300 | 83.063 | 522.999 | 445.706 | 409.655 | −437.932 | 206.094 | −2.031 |
| 5400 | 83.066 | 524.552 | 447.152 | 417.961 | −437.076 | 218.237 | −2.111 |
| 5500 | 83.069 | 526.076 | 448.573 | 426.268 | −436.209 | 230.364 | −2.188 |
| 5600 | 83.072 | 527.573 | 449.970 | 434.575 | −435.332 | 242.476 | −2.262 |
| 5700 | 83.074 | 529.043 | 451.345 | 442.882 | −434.446 | 254.572 | −2.333 |
| 5800 | 83.077 | 530.488 | 452.697 | 451.190 | −433.553 | 266.652 | −2.401 |
| 5900 | 83.079 | 531 908 | 454.027 | 459.498 | −432.652 | 278.717 | −2.468 |
| 6000 | 83.081 | 533.305 | 455.337 | 467.806 | −431.745 | 290.766 | −2.531 |

PREVIOUS June 1976 (1 atm) CURRENT June 1976 (1 bar)

# Thiothionyl Fluoride (SSF$_2$) IDEAL GAS $M_r = 102.116806$ Thiothionyl Fluoride (SSF$_2$) F$_2$S$_2$(g)

$S°(298.15\ \mathrm{K}) = 292.827 \pm 0.42\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$

$\Delta_f H°(0\ \mathrm{K}) = [-397.482 \pm 41.8]\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_f H°(298.15\ \mathrm{K}) = [-401.413 \pm 41.8]\ \mathrm{kJ\cdot mol^{-1}}$

| Electronic Levels and Quantum Weights<br>$\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|
| 0 | [1] |
| 34000 | [1] |

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|
| [760.5(1) | 330.0(1) |
| 718.5(1) | 692.3(1) |
| 411.2(1) | 274.0(1) |

Point Group C$_s$ $\sigma = 1$
Bond Distances: S–S = 1.860 ± 0.015 Å; S–F = 1.598 ± 0.012 Å
Bond Angles: S–S–F = 107.5 ± 1.0°; F–S–F = 92.5 ± 1.0°
Product of the Moments of Inertia: $I_A I_B I_C = 5.957541 \times 10^{-114}\ \mathrm{g^3\cdot cm^6}$

## Heat of Formation

No direct experimental measurement of $\Delta_f H°$ is available. We estimate two values from bond energy considerations. Seel[1] has presented a detailed discussion on the bonding *in* $S_2$, $S_2O$, and $SSF_2$ *and has shown from bond length and force constant correlations that the* S = S linkages in these molecules are very similar. We assume that $D_0°(S = SF_2) = (D_0°(S_2) + D_0°(S_2O))/2 = 90 \pm 10\ \mathrm{kcal\cdot mol^{-1}}$ which gives $\Delta_f H°(SSF_2, g, 0\ K) = -94.7 \pm 14\ \mathrm{kcal\cdot mol^{-1}}$ when the value of $D_0°$ is combined with $\Delta_f H°(SF_2, g, 0\ K) = -70.4 \pm 4\ \mathrm{kcal\cdot mol^{-1}}$ and $\Delta_f H°(S, g, 0\ K) = 65.75 \pm .01\ \mathrm{kcal\cdot mol^{-1}}$.[2] From a comparison of bond lengths and force constants[1 3] for the S–F bonds in SSF$_2$, and SF$_4$, we would expect that the mean S–F bond energies for these molecules are probably not too different. Values[2] for OSF$_2$ and SF$_4$ are 83.4 kcal·mol$^{-1}$ and 80.0 kcal·mol$^{-1}$, respectively. Using $D_0°(S_2F{-}F) = 81.5 \pm 2.5\ \mathrm{kcal\cdot mol^{-1}}$, we calculate $\Delta_r H°(0\ K) = 163.0\ \mathrm{kcal\ mol^{-1}}$ *for the dissociation* process $S_2F_2 = S_2 + 2F$ which leads to $\Delta_f H°(SSF_2, g, 0\ K) = -95.5 \pm 5.0\ \mathrm{kcal\cdot mol^{-1}}$ These two estimates are in reasonable agreement and we choose to adopt the value of $-95.0 \pm 10.0\ \mathrm{kcal\cdot mol^{-1}}$.

The heat of atomization $\Delta_a H°(0\ K)$ is calculated from our adopted $\Delta_f H°$ value to be 263.2 kcal·mol$^{-1}$ which is close to the value of 262.0 kcal·mol$^{-1}$ predicted by CNDO/2 MO calculations and energy partitioning methods.[4]

Published estimates[1,5,6] of $\Delta_f H°$ based on bond energy schemes similar to those used here include in kcal·mol$^{-1}$ −92 ± 7, −80.2, and −86.4. Wilkins[6] assumed that the mean S–F bond energy for SSF$_2$ was 80.0 kcal mol$^{-1}$ and obtained $\Delta_f H° = -86.4\ \mathrm{kcal\cdot mol^{-1}}$. We *believe that this estimate is in error.* Recalculation of his data gives $\Delta_f H° = -91.6\ \mathrm{kcal\cdot mol^{-1}}$ which is in much better agreement with our results.

## Heat Capacity and Entropy

The structural data and vibrational frequencies are taken from the recent review by Seel[1] and are based on reliable experimental measurements. *Since* SSF$_2$ *has no unpaired electrons, we predict that the* ground state is singlet. The ultra violet spectra[1] show absorption peaks at roughly 34000 cm$^{-1}$ and 42000 cm$^{-1}$, suggesting the existence of at least two excited states. We do not include the level near 42000 cm$^{-1}$ since its effect is negligible. The individual moments of inertia are: $I_A = 10.2965 \times 10^{-39}$, $I_B = 21.0146 \times 10^{-39}$, and $I_C = 27.5332 \times 10^{-39}$ g·cm$^2$.

Our thermal functions essentially extend those reported by Brown and Pez.[7] Other published functions[5 6] are based on an older set of vibrational frequencies[8] and include a bias due to incorrect analysis of the SSF$_2$ structure. O'Hare's analysis[5] *of the structural data resulted* in a value for the product of the moments of inertia which is about 7% lower than our results. In addition, he assigned SSF$_2$ to point group C$_{2v}$ and used a symmetry number of two rather than the correct value of one. The moments of inertia used by Wilkins[6] are in units of amu ucang,[2] not g cm$^2$ as assumed.

## References

[1] F. Seel, in "Advances in Inorganic Chemistry and Radio Chemistry," Vol. 16, H. J. Emeleus and A. G. Sharpe, eds., Academic Press, New York, (1974).
[2] JANAF Thermochemical Tables: S$_2$(g), 12–31–65, S$_2$O(g), 6–30–65, SF$_2$(g) and SF$_4$(g), 6–30–76, S(g), 6–30–71, OSF$_2$(g), 6–30–72.
[3] I. W. Levin, J. Chem. Phys. 55, 5393 (1971).
[4] A. L. Companion, Theoret. Chim. Acta, 25, 268 (1972).
[5] P. A. G. O'Hare, Argonne National Laboratory, ANL 7315, (July 1968).
[6] R. L. Wilkins, Aerospace Corporation, Report No. TR 0158(3240 20) 19, (July 1968).
[7] R. D. Brown and G. P. Pez, Spectrochimica Acta, 26A, 1375 (1970).
[8] R. D. Brown, G. P. Pez, and M. F. O'Dwyer, Aust. J. Chem. 18, 627 (1965).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

|  | J·K$^{-1}$mol$^{-1}$ |  |  | kJ·mol$^{-1}$ |  |  |  |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log K$_f$ |
| 0 | 0 | 0. | INFINITE | −13.718 | −397.482 | −397.482 | INFINITE |
| 100 | 38.393 | 238.662 | 341.446 | −10.278 | −398.329 | −402.654 | 210.325 |
| 200 | 52.610 | 269.714 | 298.294 | −5.716 | −399.980 | −406.337 | 106.124 |
| 250 | 58.524 | 282.110 | 293.842 | −2.933 | −400.738 | −407.837 | 85.213 |
| 298.15 | 63.127 | 292.827 | 292.827 | 0. | −401 413 | −409.143 | 71.680 |
| 300 | 63.284 | 293.218 | 292.828 | 0.117 | −401.438 | −409.191 | 71.246 |
| 350 | 67.002 | 303.264 | 293.613 | 3.378 | −402.098 | −410.430 | 61.253 |
| 400 | 69.882 | 312.408 | 295.400 | 6.803 | −407.165 | −411.401 | 53.723 |
| 450 | 72.118 | 320.773 | 297.761 | 10.356 | −409.131 | −411.830 | 47.804 |
| 500 | 73.869 | 328.466 | 300.452 | 14.007 | −411.183 | −412.015 | 43.043 |
| 600 | 76.365 | 342.171 | 306.291 | 21.528 | −414.305 | −411.873 | 35.857 |
| 700 | 78.003 | 354.074 | 312.286 | 29.252 | −416.827 | −411.263 | 30.689 |
| 800 | 79 124 | 364.568 | 318.178 | 37.111 | −418.999 | −410.316 | 26.791 |
| 900 | 79.921 | 373.936 | 323.863 | 45.066 | −527.212 | −406.950 | 23.619 |
| 1000 | 80.505 | 382.388 | 329.299 | 53.088 | −526.592 | −393.621 | 20.561 |
| 1100 | 80.946 | 390.082 | 334.481 | 61.162 | −525.981 | −380.353 | 18.061 |
| 1200 | 81.286 | 397.141 | 339.412 | 69.274 | −525.389 | −367.141 | 15 981 |
| 1300 | 81.553 | 403.658 | 344.107 | 77.417 | −524.820 | −353.977 | 14.223 |
| 1400 | 81.767 | 409.710 | 348.579 | 85.583 | −524.281 | −340.855 | 12.717 |
| 1500 | 81.941 | 415.357 | 352.845 | 93.769 | −523.772 | −327.771 | 11.414 |
| 1600 | 82.084 | 420.650 | 356.919 | 101.970 | −523.296 | −314.720 | 10.275 |
| 1700 | 82.203 | 425.630 | 360.816 | 110.185 | −522.852 | −301.698 | 9.270 |
| 1800 | 82.303 | 430.332 | 364.548 | 118.410 | −522.439 | −288.701 | 8.378 |
| 1900 | 82.388 | 434.784 | 368.129 | 126.645 | −522.055 | −275.726 | 7.580 |
| 2000 | 82.461 | 439.012 | 371.568 | 134.888 | −521.697 | −262.771 | 6.863 |
| 2100 | 82.524 | 443.037 | 374.877 | 143.137 | −521.359 | −249.833 | 6.214 |
| 2200 | 82.579 | 446.877 | 378.063 | 151.392 | −521 039 | −236.911 | 5.625 |
| 2300 | 82.626 | 450.549 | 381.135 | 159.652 | −520.731 | −224.003 | 5.087 |
| 2400 | 82.668 | 454.067 | 384.101 | 167.917 | −520.431 | −211.108 | 4.595 |
| 2500 | 82.705 | 457.442 | 386.968 | 176.186 | −520.134 | −198.226 | 4.142 |
| 2600 | 82.738 | 460.686 | 389.741 | 184.458 | −519.836 | −185.355 | 3.724 |
| 2700 | 82 767 | 463.810 | 392.427 | 192.733 | −519.531 | −172.496 | 3.337 |
| 2800 | 82 794 | 466.820 | 395.030 | 201.011 | −519.216 | −159.649 | 2.978 |
| 2900 | 82.817 | 469.726 | 397.556 | 209.292 | −518.888 | −146.813 | 2.644 |
| 3000 | 82.839 | 472.534 | 400.009 | 217.575 | −518.544 | −133.989 | 2.333 |
| 3100 | 82.858 | 475.250 | 402.392 | 225.860 | −518.180 | −121.176 | 2.042 |
| 3200 | 82.876 | 477.881 | 404.711 | 234.146 | −517.795 | −108.376 | 1.769 |
| 3300 | 82.892 | 480.432 | 406.967 | 242.435 | −517.386 | −95.588 | 1.513 |
| 3400 | 82.907 | 482.907 | 409.164 | 250.725 | −516.953 | −82.812 | 1.272 |
| 3500 | 82.921 | 485.310 | 411.305 | 259.016 | −516.494 | −70.050 | 1.045 |
| 3600 | 82.934 | 487.646 | 413.394 | 267.309 | −516.009 | −57.301 | 0.831 |
| 3700 | 82.946 | 489 919 | 415 431 | 275.603 | −515 497 | −44.566 | 0.629 |
| 3800 | 82.957 | 492.131 | 417.421 | 283.898 | −514.958 | −31.846 | 0.438 |
| 3900 | 82.968 | 494.286 | 419.364 | 292.194 | −514.392 | −19.139 | 0.256 |
| 4000 | 82.978 | 496.387 | 421.264 | 300.491 | −513.800 | −6.448 | 0.084 |
| 4100 | 82.988 | 498.436 | 423.121 | 308.790 | −513.183 | 6.228 | −0.079 |
| 4200 | 82.998 | 500.436 | 424.938 | 317.089 | −512.541 | 18.889 | −0.235 |
| 4300 | 83.007 | 502.389 | 426.717 | 325.389 | −511.875 | 31.534 | −0.383 |
| 4400 | 83.017 | 504.297 | 428.458 | 333.691 | −511.185 | 44.164 | −0.524 |
| 4500 | 83.027 | 506.163 | 430.164 | 341.993 | −510.474 | 56.777 | −0.659 |
| 4600 | 83.036 | 507.988 | 431.836 | 350.296 | −509.742 | 69.375 | −0.788 |
| 4700 | 83.046 | 509.774 | 433.476 | 358.600 | −508.989 | 81.956 | −0.911 |
| 4800 | 83.057 | 511.522 | 435.084 | 366.905 | −508.218 | 94.521 | −1.029 |
| 4900 | 83.067 | 513.235 | 436.661 | 375.211 | −507.429 | 107.070 | −1.141 |
| 5000 | 83.079 | 514.913 | 438.209 | 383.519 | −506.623 | 119.603 | −1.249 |
| 5100 | 83.090 | 516.558 | 439.730 | 391.827 | −505.802 | 132.119 | −1.353 |
| 5200 | 83.102 | 518.172 | 441.223 | 400.137 | −504.966 | 144.620 | −1.453 |
| 5300 | 83.115 | 519.755 | 442.689 | 408.448 | −504.117 | 157.104 | −1.548 |
| 5400 | 83.129 | 521.309 | 444.131 | 416.760 | −503.255 | 169.571 | −1.640 |
| 5500 | 83 143 | 522.834 | 445.548 | 425 073 | −502.381 | 182.023 | −1.729 |
| 5600 | 83.158 | 524.332 | 446.942 | 433.388 | −501.496 | 194.459 | −1.814 |
| 5700 | 83.174 | 525 804 | 448.312 | 441.705 | −500.601 | 206.878 | −1.896 |
| 5800 | 83.191 | 527.251 | 449.661 | 450.023 | −499.697 | 219.282 | −1.975 |
| 5900 | 83.208 | 528.673 | 450.988 | 458.343 | −498.784 | 231.671 | −2.051 |
| 6000 | 83.226 | 530.072 | 452.295 | 466.665 | −497.864 | 244.043 | −2.125 |

PREVIOUS: June 1976 (1 atm) CURRENT June 1976 (1 bar)

## Difluorosilylene (SiF$_2$) IDEAL GAS $M_r = 66.082306$

$S°(298.15 \text{ K}) = 256.579 \pm 0.42 \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = -587.013 \pm 12.6 \text{ kJ·mol}^{-1}$
$\Delta_f H°(298.15 \text{ K}) = -587.852 \pm 12.6 \text{ kJ·mol}^{-1}$

| Vibrational Frequencies and Degeneracies State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|
| $^1A_1$ | 0 | 1 |
| $^3B_1$ | 26310 | 3 |
| $^1B_1$ | 44109 | 1 |
| $^1B_2$ | 62280 | 1 |

| Electronic Levels and Quantum Weights $\nu$, cm$^{-1}$ |
|---|
| 855 (1) |
| 345 (1) |
| 872 (1) |

Point Group: $C_{2v}$ $\sigma = 2$
Bond Distance. Si–F = 1.591 Å
Bond Angle: F–Si–F = 100° 59'
Product of the Moments of Inertia: $I_A I_B I_C = 3.200830 \times 10^{-115} \text{ g}^3\text{·cm}^6$

### Enthalpy of Formation

Margrave *et al.*[1] have reported some approximate equilibrium constants for the reaction $Si(cr) + SiF_4(g) = 2\,SiF_2(g)$. These were calculated from yields of polymerized products and a knowledge of the total system pressure given in U.S. Patent No. 2, 840,588 (1958). The data are subjected to a 3rd law analysis using the present JANAF functions[2] and yield $\Delta_r H°(298.15 \text{ K}) = 92 \pm 11 \text{ kcal·mol}^{-1}$, which gives $\Delta_f H°(SiF_2, g, 298.15 \text{ K}) = -147 \pm 5 \text{ kcal·mol}^{-1}$.

Ehlert and Margrave[3] and Farber[13] have determined equilibrium constants mass spectrometrically. A 2nd and 3rd law analysis of the data is shown below. We adopt $\Delta_f H°(SiF_2, g, 298.15 \text{ K}) = -140.5 \pm 3 \text{ kcal·mol}^{-1}$ ($-587.852 \pm 12.6 \text{ kJ·mol}^{-1}$).

| Source | Reaction | T/K | Data Points | $\Delta_r H°$(298.15 K), kcal·mol$^{-1}$ 2nd law | 3rd law | Drift cal K$^{-1}$·mol$^{-1}$ | $\Delta_f H°$(298.15 K) kcal·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 3 | $CaF_2(cr) + Si(g) = Ca(g) + SiF_2(g)$ | 1395–1543 | 12 | 80.2 ± 14.1 | 88.0 ± 3.0 | 4.6 ± 9.7 | −140.1 |
| 3 | $CaF_2(g) + Si(g) = Ca(g) + SiF_2(g)$ | 1395–1543 | 12 | −8.3 ± 14.1 | −18.0 ± 3.0 | −6.6 ± 9.6 | −140.7 |
| 3 | $2\,CaF(g) + Si(g) = 2Ca(g) + SiF_2(g)$ | 1395–1543 | 12 | −18.6 ± 7.5 | −33.4 ± 1.8 | −10.0 ± 5.1 | −141.0 |
| 13 | $SiF_4(g) + Si(g) = 2SiF_2(g)$ | 1590–1782 | 10 | −2.0 ± 0.3 | −3.2 ± 0.3 | 0.7 ± 0.8 | −140.7 |

Using JANAF values,[2] we calculate $\Delta_a H°(0 \text{ K}) = 283.7 \pm 5 \text{ kcal·mol}^{-1}$ for the process $SiF_2(g) = Si(g) + 2\,F(g)$. Within 2 kcal·mol$^{-1}$ the average bond energies in $SiF_2(g)$, $SiF_3(g)$, and $SiF_4(g)$ are the same.

### Heat Capacity and Entropy

The electronic levels are adopted from the ultraviolet spectral work of Khanna *et al.*,[4] Rao[5] and Gole *et al.*[6] The vibrational assignments of $\nu_1 = 855 \text{ cm}^{-1}$ (symmetric stretch) and $\nu_3 = 872 \text{ cm}^{-1}$ (asymmetric stretch) of Khanna *et al.*[7] are adopted. These assignments are supported by the argon matrix studies of Milligan and Jacox,[8] the neon matrix and the argon matrix measurements of Hastie *et al.*[9] and the excited state microwave work of Shoji *et al.*[10] The bending frequency assignment, $\nu_2 = 345 \text{ cm}^{-1}$, is adopted from the ultraviolet and microwave study of Rao and Curl.[11] This assignment is also confirmed by Milligan and Jacox.[8]

The gas phase geometry was established by Rao *et al.*[12] from microwave spectra. The principal moments of inertia are: $I_A = 2.7474 \times 10^{-39}$, $I_B = 9.5072 \times 10^{-39}$, and $I_C = 12.2545 \times 10^{-39} \text{ g·cm}^2$.

### References

[1] J. L. Margrave, A. S. Kannan, and D. C. Pease, J. Phys. Chem. 66, 1200 (1962).
[2] JANAF Thermochemical Tables: Si(cr), 12–13–66; Si(g), 3–31–67, Ca(g), CaF(g), CaF$_2$(cr, g), 12–31–68, SiF$_4$(g), 6–30–76; F(g),9–30–65; SiF$_3$(g) 12–31–77.
[3] T. C. Ehlert and J. L. Margrave, J. Chem. Phys. 4, 1066 (1964).
[4] V. M. Khanna, G. Besenbruch, and J. L. Margrave, J. Chem. Phys. 46, 2310 (1967).
[5] D. R. Rao, J. Mol. Spectrosc. 34, 284 (1970).
[6] J. L. Gole, R. H. Hauge, J. L. Margrave, and J. W. Hastie, J. Mol. Spectrosc. 43, 441 (1972).
[7] V. M Khanna, R. H. Hauge, R. F. Curle, Jr., and J. L. Margrave, J. Chem. Phys. 47, 5031 (1967).
[8] D. E. Milligan and M. E. Jacox, J. Chem. Phys. 49, 4269 (1968).
[9] J. W. Hastie, R. H Hauge, and J. L. Margrave, J. Amer. Chem. Soc. 91, 2536 (1969).
[10] H. Shoji, T. Tanaka, and E. Hirota, J. Mol. Spectrosc. 47, 268 (1973).
[11] V. M. Rao and R. F. Curl, Jr., J. Chem. Phys. 45, 2032 (1966).
[12] V. M. Rao, R. F. Curl, Jr., P. L. Timms, and J. L. Margrave, J. Chem. Phys. 43, 2557 (1965).
[13] M. Farber, Space Sciences, Inc., personal communication, (October 18, 1976).

## Difluorosilylene (SiF$_2$) F$_2$Si$_1$(g)

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −11.204 | −587.013 | −587 013 | INFINITE |
| 100 | 34.719 | 214.272 | 292.766 | −7.849 | −586.832 | −590.839 | 308.622 |
| 200 | 39.648 | 239.824 | 260.498 | −4.135 | −587.225 | −594.726 | 155.327 |
| 250 | 42.199 | 248.946 | 257.299 | −2.088 | −587.531 | −596.567 | 124.646 |
| 298.15 | 44.509 | 256.579 | 256.579 | 0. | −587.852 | −598.278 | 104.816 |
| 300 | 44.593 | 256.855 | 256.580 | 0.082 | −587.865 | −598.343 | 104.181 |
| 350 | 46.691 | 263.891 | 257.131 | 2.366 | −588.205 | −600.063 | 89.554 |
| 400 | 48.456 | 270.244 | 258.379 | 4.746 | −588.542 | −601.733 | 78.578 |
| 450 | 49.912 | 276.038 | 260.024 | 7.206 | −588.873 | −603.362 | 70.036 |
| 500 | 51.105 | 281.361 | 261.896 | 9.733 | −589.199 | −604.955 | 63.199 |
| 600 | 52.886 | 290.847 | 265.950 | 14.938 | −589.843 | −608.046 | 52.935 |
| 700 | 54.106 | 299 096 | 270.109 | 20.291 | −590 489 | −611.029 | 45.596 |
| 800 | 54.964 | 306.380 | 274.196 | 25 747 | −591.151 | −613.918 | 40.085 |
| 900 | 55.586 | 312.892 | 278.140 | 31.276 | −591.839 | −616.723 | 35.794 |
| 1000 | 56.049 | 318 774 | 281.914 | 36.859 | −592.556 | −619.449 | 32.357 |
| 1100 | 56.401 | 324.133 | 285.513 | 42.483 | −593.309 | −622.103 | 29.541 |
| 1200 | 56.674 | 329.053 | 288.939 | 48.137 | −594.099 | −624.685 | 27.192 |
| 1300 | 56.891 | 333.598 | 292.201 | 53.815 | −594.930 | −627.201 | 25.201 |
| 1400 | 57.065 | 337.821 | 295.311 | 59.514 | −595.805 | −629.651 | 23.493 |
| 1500 | 57.206 | 341.763 | 298.278 | 65.227 | −596.726 | −632.036 | 22.009 |
| 1600 | 57.324 | 345.459 | 301.112 | 70.954 | −597.694 | −634.359 | 20.710 |
| 1700 | 57.421 | 348.937 | 303.824 | 76.691 | −648.887 | −636.173 | 19.547 |
| 1800 | 57.504 | 352.221 | 306.423 | 82.438 | −649.720 | −635.401 | 18.439 |
| 1900 | 57.574 | 355.332 | 308.916 | 88.192 | −650.558 | −634.583 | 17.446 |
| 2000 | 57.634 | 358.287 | 311.311 | 93.952 | −651.398 | −633.720 | 16.551 |
| 2100 | 57.686 | 361.100 | 313.615 | 99.718 | −652.239 | −632.816 | 15.740 |
| 2200 | 57.731 | 363.785 | 315.835 | 105.489 | −653.077 | −631.871 | 15.003 |
| 2300 | 57.771 | 366.352 | 317.976 | 111.264 | −653.910 | −630.888 | 14.328 |
| 2400 | 57.806 | 368.811 | 320.043 | 117.043 | −654.734 | −629.870 | 13.709 |
| 2500 | 57.837 | 371.172 | 322.042 | 122.825 | −655.546 | −628.817 | 13.138 |
| 2600 | 57.865 | 373.441 | 323.975 | 128.610 | −656.343 | −627.732 | 12.611 |
| 2700 | 57.891 | 375.625 | 325.848 | 134.398 | −657.121 | −626.617 | 12.123 |
| 2800 | 57.915 | 377.731 | 327.664 | 140.188 | −657.878 | −625.473 | 11.668 |
| 2900 | 57.938 | 379.764 | 329.425 | 145.981 | −658.610 | −624.303 | 11.245 |
| 3000 | 57.959 | 381.728 | 331.136 | 151.776 | −659.316 | −623.108 | 10.849 |
| 3100 | 57.981 | 383.629 | 332.799 | 157.573 | −659.993 | −621.890 | 10.479 |
| 3200 | 58.002 | 385 470 | 334.416 | 163.372 | −660.640 | −620.650 | 10.131 |
| 3300 | 58.024 | 387.255 | 335.991 | 169.174 | −661.254 | −619.391 | 9.804 |
| 3400 | 58.047 | 388.988 | 337.524 | 174.977 | −661.834 | −618.113 | 9.496 |
| 3500 | 58.072 | 390.671 | 339.019 | 180.783 | −662.380 | −616.819 | 9.206 |
| 3600 | 58.098 | 392.307 | 340.476 | 186.592 | −1047.041 | −605.049 | 8.779 |
| 3700 | 58.127 | 393.899 | 341.899 | 192.403 | −1047.100 | −592.771 | 8.368 |
| 3800 | 58.159 | 395.450 | 343.288 | 198.217 | −1047.124 | −580.492 | 7.979 |
| 3900 | 58.193 | 396.961 | 344.645 | 204.035 | −1047.111 | −568.212 | 7.610 |
| 4000 | 58.231 | 398.435 | 345.971 | 209.856 | −1047.062 | −555.933 | 7.260 |
| 4100 | 58.272 | 399.873 | 347.268 | 215.681 | −1046.976 | −543.656 | 6.926 |
| 4200 | 58.318 | 401.278 | 348.537 | 221.510 | −1046.852 | −531.381 | 6.609 |
| 4300 | 58.367 | 402.651 | 349.780 | 227.345 | −1046.691 | −519.110 | 6.306 |
| 4400 | 58.421 | 403.993 | 350.997 | 233.184 | −1046.491 | −506.843 | 6 017 |
| 4500 | 58.480 | 405.307 | 352.189 | 239.029 | −1046.254 | −494.580 | 5.741 |
| 4600 | 58.544 | 406.593 | 353.358 | 244.880 | −1045.979 | −482.324 | 5.477 |
| 4700 | 58.612 | 407.853 | 354.504 | 250.738 | −1045.666 | −470.074 | 5.224 |
| 4800 | 58.685 | 409.087 | 355.628 | 256.603 | −1045.315 | −457.831 | 4.982 |
| 4900 | 58.764 | 410.298 | 356.732 | 262.475 | −1044.927 | −445.596 | 4.750 |
| 5000 | 58.847 | 411.486 | 357.815 | 268.356 | −1044.502 | −433.369 | 4.527 |
| 5100 | 58.936 | 412.652 | 358.879 | 274.245 | −1044.041 | −421.151 | 4.313 |
| 5200 | 59.029 | 413.798 | 359 924 | 280.143 | −1043.542 | −408.942 | 4.108 |
| 5300 | 59.128 | 414.923 | 360.951 | 286.051 | −1043.008 | −396.743 | 3.910 |
| 5400 | 59.232 | 416.029 | 361.961 | 291.969 | −1042.438 | −384.555 | 3.720 |
| 5500 | 59.340 | 417.117 | 362.954 | 297.897 | −1041.832 | −372.377 | 3.537 |
| 5600 | 59.453 | 418.187 | 363.931 | 303.837 | −1041.192 | −360.211 | 3.360 |
| 5700 | 59.570 | 419.241 | 364.892 | 309 788 | −1040.517 | −348.057 | 3.190 |
| 5800 | 59.692 | 420.278 | 365.838 | 315.751 | −1039.809 | −335.915 | 3.025 |
| 5900 | 59.818 | 421.299 | 366 769 | 321.726 | −1039.067 | −323.784 | 2.867 |
| 6000 | 59.948 | 422.306 | 367.686 | 327.715 | −1038.292 | −311.668 | 2.713 |

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

# Strontium Fluoride ($SrF_2$) CRYSTAL $M_r = 125.616806$ Strontium Fluoride ($SrF_2$) $F_2Sr_1(cr)$

$\Delta_fH^\circ(0\ K) = -1214.807 \pm 2.9\ kJ\cdot mol^{-1}$
$\Delta_fH^\circ(298.15\ K) = -1217.126 \pm 2.9\ kJ\cdot mol^{-1}$
$S^\circ(298.15\ K) = 82.123 \pm 0.21\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{trs} = [1421]\ K$ $\Delta_{trs}H^\circ = [0.0]\ kJ\cdot mol^{-1}$
$T_{trs} = [1484]\ K$ $\Delta_{trs}H^\circ = [0.0]\ kJ\cdot mol^{-1}$
$T_{fus} = 1750 \pm 2\ K$ $\Delta_{fus}H^\circ = 29.673 \pm 0.628\ kJ\cdot mol^{-1}$

## Enthalpy of Formation

Guntz[1] measured the enthalpy of neutralization of $Sr(OH)_2$ (aq) with HF(aq) as $\Delta H = -35.8\ kcal\cdot mol^{-1}$ at 284 K. We estimate a $\Delta C_p^\circ = 105$ cal $K^{-1}\cdot mol^{-1}$ for $Sr(OH)_2\cdot 555\ H_2O + 2(HF\cdot 110\ H_2O) \rightarrow SrF_2(cr) + 2\ H_2O(l)$ which gives $\Delta H(298.15\ K) = -34.1\ kcal\cdot mol^{-1}$. This value leads to $\Delta_fH^\circ(SrF_2,\ cr,\ 298.15\ K) = -291.3\ kcal\cdot mol^{-1}$ when combined with the following enthalpies of formation: $\Delta_fH^\circ(H_2O,\ l,\ 298.15\ K) = -68.315$[2] $\Delta_fH^\circ(Sr(OH)_2\cdot 555\ H_2O,\ 298.15\ K) = -240.1$[3] and $\Delta_fH^\circ(HF\cdot 110\ H_2O,\ 298.15\ K) = -76.78\ kcal\cdot mol^{-1}$.[4]

Petersen[5] measured the enthalpy of precipitation of $SrF_2$ from an aqueous $SrCl_2$ solution with AgF(aq) as $\Delta H -34.5\ kcal\cdot mol^{-1}$ at 293 K. We estimate a $\Delta C_p^\circ = 108$ cal $K^{-1}\cdot mol^{-1}$ for $2(AgF\cdot 200\ H_2O) + SrCl_2\cdot 400\ H_2O + SrF_2(cr) + 2\ AgCl(cr)$ which gives $\Delta H(298.15\ K) = -34.0\ kcal\cdot mol^{-1}$. This value leads to $\Delta_fH^\circ(SrF_2,\ cr,\ 298.15\ K) = -290.9\ kcal\cdot mol^{-1}$ when combined with the following enthalpies of formation: $\Delta_fH^\circ(AgCl,\ cr,\ 298.15\ K) = -30.37$[6] $\Delta_fH^\circ(AgF\cdot 200\ H_2O,\ 298.15\ K) = -53.398$[6] and $\Delta_fH^\circ(SrCl_2\cdot 400\ H_2O,\ 298.15\ K) = -209.871\ kcal\cdot mol^{-1}$.[3]

Stephen and Stephen[7] have selected as a "best" value for the solubility of $SrF_2$ 0.119 g/l at 298.15 K which corresponds to $K_{sp} = 3.397 \times 10^{-9}$. Using $\Delta_fG^\circ(Sr^{+2},\ aq\ \infty,\ 298.15\ K) = -133.71$[3] and $\Delta_fG^\circ(F^-,\ aq\ \infty,\ 298.15\ K) = -66.96\ kcal\cdot mol^{-1}$,[4] we calculate $\Delta_fG^\circ(SrF_2,\ cr,\ 298.15\ K) = -279\ 18\ kcal\cdot mol^{-1}$. Based on the adopted functions for $SrF_2$, this value gives $\Delta_fH^\circ(SrF_2,\ cr,\ 298.15\ K) = -291.5\ kcal\cdot mol^{-1}$.

Very recently, Finch *et al.*[9] measured the enthalpy of precipitation of $SrF_2$ from an aqueous $SrCl_2$ solution by addition of a slight excess of NaF. X–ray diffraction patterns showed the precipitate to be crystalline $SrF_2$ Reduction of their data gives $\Delta_{sln}H^\circ = 0.42\ kcal\cdot mol^{-1}$ for $SrF_2(cr) \rightarrow Sr^{+2}(aq\ \infty) + 2\ F^-(aq\ \infty)$ from which we obtain $\Delta_fH^\circ(SrF_2,\ cr,\ 298.15\ K) = -290.5 \pm 0.5\ kcal\cdot mol^{-1}$ with $\Delta_fH^\circ(Sr^{+2},\ aq\ \infty,\ 298\ 15\ K) = -130.45$[3] and $\Delta_fH^\circ(F^-,\ aq\ \infty,\ 298.15\ K) = -79\ 82\ kcal\cdot mol^{-1}$.

The adopted enthalpy of formation, $\Delta_fH^\circ(SrF_2,\ cr,\ 298.15\ K) = -290.9 \pm 0\ 7\ kcal\cdot mol^{-1}$, is a weighted value of these four results. Barany *et al.*[8] determined the enthalpy of solution of SrO(cr) in 20.1 wt % aqueous HF, which contained some dissolved silica, as $-65.41 \pm 0.30\ kcal\cdot mol^{-1}$. We assume this value refers to the process $SrO(cr) + 2\ HF\ \infty\ 4.41\ H_2O \rightarrow SrF_2(cr) + 2\ H_2O(l)$ at 298 15 K, and we calculate $\Delta_fH^\circ(SrF_2,\ cr,\ 298.15\ K) = -291.8 \pm 2\ 0\ kcal\cdot mol^{-1}$ with $\Delta_fH^\circ(SrO,\ cr,\ 298.15\ K) = -141.5\ kcal\ mol^{-1}$).[4] These results substantiate our adopted $\Delta_fH^\circ$ value.

## Heat Capacity and Entropy

$C_p^\circ$ below 300 K is based on the low–temperature (11–300 K) heat capacities for $SrF_2$ reported by Smith *et al.*[10] The sample purity was 99 9% by petrographic examination. We have fitted a smooth polynomial curve through their data and obtained $S^\circ(298.15\ K) = 19.63 \pm 0.05$ cal $K^{-1}\cdot mol^{-1}$ based on $S(10.9) = 0.021$ cal $K^{-1}\cdot mol^{-1}$.

The only high temperature enthalpy data is that recently reported by Efremova and Matizen[11] in the temperature range 813–2126 K. Spectroscopic analysis showed the $SrF_2$ sample contained less than 0.04% of foreign metals. A second order transition was observed between the temperatures of 1421 and 1484 K. We adopt their smoothed $C_p^\circ$ data in the temperature range 900–1750 K; $C_p^\circ$'s above the melting point are obtained by graphical extrapolation. $C_p^\circ$ is assumed constant at 39.5 cal $K^{-1}\cdot mol^{-1}$ over the temperature interval (1421–1484 K) of the transition (see further discussion in Transition Data). The observed enthalpies of Efremova and Matizen[11] deviate from our adopted ones by 1.4% at the lowest temperature (813 K) of their measurements and by only a few tenths of one percent at the higher temperatures.

## Transition Data

Efremova and Matizen[11] reported that the phase transition for $SrF_2$ occurs over a short temperature interval (1421–1484 K). There are no discontinuities in their enthalpy data in this temperature range. Other alkaline earth dihalides[12] which have the calcium fluoride structure, are known to exhibit similar behavior, and this fact would seem to rule out the possibility that the observed transition resulted wholly from impurities. We speculate that the two crystalline forms, α and β, of $SrF_2$ are practically of the same energy content and can therefore, coexist over this temperature interval.

We choose to tentatively adopt two transitions with zero enthalpies, pending resolution of the phases present at these temperatures by X–ray diffraction measurements. The adopted values are placed in brackets above to emphasize that there is no confirmatory evidence for their existence.

## Fusion Data

Refer to the liquid table for details.

## Sublimation Data

Refer to the ideal gas table for details.

## References

[1] M. Guntz, Ann. Chim. Phys. 3, 5 (1884).
[2] U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).

Continued on page 1216

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p^\circ$ = 0.1 MPa

|  | $J\cdot K^{-1}mol^{-1}$ |  |  | $kJ\cdot mol^{-1}$ |  |  |  |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_fH^\circ$ | $\Delta_fG^\circ$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −13.075 | −1214.807 | −1214.807 | INFINITE |
| 100 | 36.671 | 21.017 | 137.682 | −11.666 | −1217.805 | −1200.065 | 626.850 |
| 200 | 61.636 | 55.736 | 88.303 | −6.513 | −1218.070 | −1182.045 | 308.718 |
| 298.15 | 69.985 | 82.123 | 82.123 | 0. | −1217.126 | −1164.544 | 204.023 |
| 300 | 70.103 | 82.556 | 82.125 | 0.130 | −1217.104 | −1164.218 | 202.708 |
| 400 | 74.726 | 103.406 | 84.936 | 7.388 | −1215.793 | −1146.781 | 149.754 |
| 500 | 77.320 | 120.379 | 90.380 | 14.999 | −1214.376 | −1129.691 | 118.018 |
| 600 | 78.827 | 134.616 | 96.599 | 22.810 | −1212.968 | −1112.887 | 96.885 |
| 700 | 79.914 | 146.849 | 102.924 | 30.748 | −1211.616 | −1096.315 | 81.808 |
| 800 | 80.960 | 157.585 | 109.099 | 38.789 | −1210.324 | −1079.932 | 70.512 |
| 900 | 82.341 | 167.180 | 115.028 | 46.937 | −1209.705 | −1063.636 | 61.732 |
| 1000 | 85.772 | 176.024 | 120.691 | 55.334 | −1208.031 | −1047.493 | 54.715 |
| 1100 | 90.207 | 184.388 | 126.104 | 64.113 | −1213.908 | −1031.169 | 48.966 |
| 1200 | 97.069 | 192.513 | 131.300 | 73.455 | −1212.258 | −1014.624 | 44.165 |
| 1300 | 108.784 | 200.659 | 136.321 | 83.640 | −1209.788 | −998.246 | 40.110 |
| 1400 | 143.930 | 209.735 | 141.230 | 95.907 | −1205.258 | −982.123 | 36.643 |
| 1421.000 | 165 .687 | 212.027 | 142.259 | 99.141 | ALPHA <--> BETA |  |  |
| 1421.000 | 165 .268 | 212.027 | 142.259 | 99.141 | TRANSITION |  |  |
| 1484.000 | 165.268 | 219.197 | 145.374 | 109.553 | UNDEFINED |  |  |
| 1484.000 | 165.268 | 219.197 | 145.374 | 109.553 | TRANSITION |  |  |
| 1500 | 154.808 | 220.911 | 146.171 | 112.110 | −1196.812 | −966.475 | 33.656 |
| 1600 | 125 938 | 229.799 | 151.132 | 125.867 | −1190.831 | −951.330 | 31.058 |
| 1700 | 113.805 | 237.012 | 155.978 | 137 758 | −1323.645 | −935.314 | 28.739 |
| 1750.000 | 109 .441 | 240.249 | 158.340 | 143.342 | ---- BETA <--> LIQUID ---- |  |  |
| 1800 | 107.320 | 243.303 | 160.658 | 148.762 | −1318.587 | −912.620 | 26.484 |
| 1900 | 102.717 | 248.976 | 165.159 | 159.251 | −1314.061 | −890.192 | 24.473 |
| 2000 | 99.579 | 254.159 | 169.481 | 169.356 | −1309.937 | −867.991 | 22.670 |
| 2100 | 97.696 | 258.969 | 173.629 | 179.213 | −1306.079 | −845.990 | 21.043 |
| 2200 | 96.650 | 263.487 | 177.612 | 188.925 | −1302.384 | −824.168 | 19.568 |
| 2300 | 96.232 | 267.772 | 181.440 | 198.565 | −1298.783 | −802.511 | 18.226 |
| 2400 | 96.232 | 271.868 | 185.123 | 208.189 | −1295.222 | −781.011 | 16.998 |
| 2500 | 96.232 | 275.796 | 188.672 | 217.812 | −1291.689 | −759.658 | 15.872 |

PREVIOUS:    CURRENT: December 1972

## Strontium Fluoride ($SrF_2$) LIQUID $M_r$ = 125.616806 Strontium Fluoride ($SrF_2$) $F_2Sr_1(l)$

$S°$(298.15 K) = [109.445] J·K$^{-1}$·mol$^{-1}$
$T_{fus}$ = 1750 ± 2 K

$\Delta_fH°$(298.15 K) = [−1 172 043] kJ·mol$^{-1}$
$\Delta_{fus}H°$ = 29 673 ± 0.628 kJ·mol$^{-1}$

### Enthalpy of Formation

$\Delta_fH°$($SrF_2$, l, 298.15 K) is calculated from $\Delta_fH°$($SrF_2$, cr, 298.15 K) by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°$(1750 K)–$H°$(298 15 K), between the crystal and liquid.

### Heat Capacity and Entropy

The heat capacity for liquid $SrF_2$ is obtained from the enthalpy measurements of Efremova and Matizen[1]. $C_p°$ is assumed to be constant in the temperature range 1200–3500 K. At 1200 K a glass transition is assumed below which $C_p°$ follows that of the crystal. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

### Fusion Data

Kojima *et al.*[2] determined the melting point of a $SrF_2$ sample, which had been purified by passing anhydrous HF through the melt, as 1746 ± 1 K. Porter and Brown[3] found a melting point of 1736 ± 5 K for a sample of 99.8 + % purity, while Petit and Delbove[4] reported 1735 K The adopted melting point, 1750 ± 2 K, is that determined by Efremova and Matizen[1] in their calorimetric studies of a high purity $SrF_2$ sample The enthalpy of melting, 7 092 ± 0.150 kcal mol$^{-1}$, is calculated as the difference between the adopted enthalpies of the liquid and crystal at $T_{fus}$.

### Vaporization Data

The boiling point is calculated as the temperature at which the fugacity is one atmosphere for the vaporization process. The enthalpy of vaporization is the difference in $\Delta_fH°(T_{vap})$ for the liquid and gas.

### Reference

[1] R. I. Efremova and E. V Matizen, Izv. Sib. Otd Akad. Nauk SSSR, Ser Khim. Nauk, (1), 3 (1970).
[2] H Kojima, S G. Whiteway, and C. R Masson, Can. J Chem. 46, 2968 (1968).
[3] B. Porter and E. A. Brown, J. Amer. Ceram Soc. 45, 49 (1962).
[4] G Petit and F. Delbove, Compt. rend. 254, 1388 (1962).

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 69 977 | 109 445 | 109.445 | 0 | −1172.043 | −1127.607 | 197.552 |
| 300 | 70.103 | 109.878 | 109.446 | 0.130 | −1172.021 | −1127.331 | 196.286 |
| 400 | 74 726 | 130.727 | 112.257 | 7.388 | −1170.711 | −1112.627 | 145.294 |
| 500 | 77.320 | 147 701 | 117.702 | 14.999 | −1169.293 | −1098.269 | 114.735 |
| 600 | 78.827 | 161.937 | 123.920 | 22.810 | −1167.885 | −1084.197 | 94.388 |
| 700 | 79.914 | 174.171 | 130.246 | 30.748 | −1166.533 | −1070.357 | 79.871 |
| 800 | 80.960 | 184.906 | 136.421 | 38.789 | −1165.242 | −1056.706 | 68.996 |
| 900 | 82.341 | 194.502 | 142.350 | 46.937 | −1164.622 | −1043.142 | 60.542 |
| 1000 | 85.772 | 203.346 | 148.012 | 55.334 | −1162.948 | −1029.732 | 53.788 |
| 1100 | 90.207 | 211.710 | 153.425 | 64.113 | −1168.825 | −1016.139 | 48.252 |
| 1200 | 97.069 | 219.835 | 158.622 | 73.456 | −1167.174 | −1002.327 | 43.630 |
| 1200.000 | 97 069 | 219.835 | 158.622 | 73.456 | GLASS <--> LIQUID | | |
| 1200.000 | 99.048 | 219.835 | 158.622 | 73.456 | TRANSITION | | |
| 1300 | 99.048 | 227.763 | 163.640 | 83.361 | −1164.985 | −988.678 | 39 726 |
| 1400 | 99.048 | 235.104 | 168.485 | 93.266 | −1162.817 | −975.198 | 36.385 |
| 1500 | 99.048 | 241.937 | 173 157 | 103.170 | −1160.669 | −961.872 | 33 495 |
| 1600 | 99.048 | 248.330 | 177.658 | 113.075 | −1158.539 | −948.688 | 30.971 |
| 1700 | 99.048 | 254.334 | 181.993 | 122.980 | −1293.340 | −934.457 | 28.712 |
| 1750.000 | 99.048 | 257.205 | 184.101 | 127.932 | ---- BETA <--> LIQUID ---- | | |
| 1800 | 99.048 | 259.996 | 186.171 | 132.885 | −1289.381 | −913.461 | 26.508 |
| 1900 | 99.048 | 265.351 | 190.199 | 142.790 | −1285.440 | −892.684 | 24.542 |
| 2000 | 99.048 | 270 431 | 194.084 | 152.694 | −1281.516 | −872.114 | 22.777 |
| 2100 | 99.048 | 275.264 | 197.836 | 162.599 | −1277.610 | −851.740 | 21.186 |
| 2200 | 99.048 | 279.872 | 201.461 | 172.504 | −1273.722 | −831.552 | 19.744 |
| 2300 | 99.048 | 284.275 | 204.966 | 182.409 | −1269.856 | −811.540 | 18.431 |
| 2400 | 99.048 | 288.490 | 208.359 | 192.313 | −1266.014 | −791.696 | 17.231 |
| 2500 | 99.048 | 292.533 | 211.646 | 202.218 | −1262.199 | −772.011 | 16.130 |
| 2600 | 99.048 | 296.418 | 214.832 | 212.123 | −1258.416 | −752.478 | 15.117 |
| 2700 | 99.048 | 300.156 | 217.924 | 222.028 | −1254.671 | −733.090 | 14.182 |
| 2800 | 99.048 | 303.758 | 220.925 | 231.933 | −1250.970 | −713.840 | 13.317 |
| 2900 | 99.048 | 307.234 | 223.842 | 241.837 | −1247.320 | −694.721 | 12.513 |
| 3000 | 99.048 | 310.592 | 226.678 | 251.742 | −1243 729 | −675 728 | 11.765 |
| 3100 | 99.048 | 313.840 | 229.437 | 261.647 | −1240.204 | −656.853 | 11.068 |
| 3200 | 99.048 | 316.984 | 232.124 | 271.552 | −1236.754 | −638.090 | 10.416 |
| 3300 | 99.048 | 320.032 | 234.742 | 281.457 | −1233.386 | −619.434 | 9.805 |
| 3400 | 99.048 | 322.989 | 237.294 | 291.361 | −1230.108 | −600.879 | 9.231 |
| 3500 | 99.048 | 325.860 | 239.784 | 301.266 | −1226.929 | −582.419 | 8.692 |

PREVIOUS.    CURRENT December 1972

## Strontium Fluoride ($SrF_2$) CRYSTAL(α–β–?)-LIQUID

0 to 1421 K crystal
1421 to 1484 K crystal
1484 to 1750 K crystal
above 1750 K liquid

Refer to the individual tables for details.

## $M_r$ = 125.616806 Strontium Fluoride ($SrF_2$) $F_2Sr_1(cr,l)$

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
|---|---|---|---|---|---|---|---|
| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
| 0 | 0. | 0. | INFINITE | −13.075 | −1214.807 | −1214.807 | INFINITE |
| 100 | 36.671 | 21.017 | 137.682 | −11.666 | −1217.805 | −1200.065 | 626.850 |
| 200 | 61.636 | 55.736 | 88.303 | −6.513 | −1218.070 | −1182.045 | 308.718 |
| 298.15 | 69.985 | 82.123 | 82.123 | 0. | −1217.126 | −1164.544 | 204.023 |
| 300 | 70 103 | 82.556 | 82.125 | 0.130 | −1217.104 | −1164.218 | 202.708 |
| 400 | 74.726 | 103.406 | 84.936 | 7.388 | −1215.793 | −1146.781 | 149.754 |
| 500 | 77.320 | 120.379 | 90.380 | 14 999 | −1214.376 | −1129.691 | 118.018 |
| 600 | 78.827 | 134.616 | 96.599 | 22.810 | −1212.968 | −1112.887 | 96.885 |
| 700 | 79.914 | 146.849 | 102.924 | 30.748 | −1211.616 | −1096.315 | 81.808 |
| 800 | 80.960 | 157.585 | 109.099 | 38.789 | −1210.324 | −1079.932 | 70.512 |
| 900 | 82.341 | 167.180 | 115.028 | 46.937 | −1209.705 | −1063.636 | 61.732 |
| 1000 | 85.772 | 176 024 | 120.691 | 55.334 | −1208.031 | −1047.493 | 54.715 |
| 1100 | 90.207 | 184.388 | 126.104 | 64.113 | −1213.908 | −1031.169 | 48.966 |
| 1200 | 97.069 | 192.513 | 131.300 | 73.455 | −1212.258 | −1014.624 | 44.165 |
| 1300 | 108.784 | 200.659 | 136.321 | 83.640 | −1209.788 | −998.246 | 40 110 |
| 1400 | 143.930 | 209.735 | 141.230 | 95.907 | −1205.258 | −982.123 | 36.643 |
| 1421.000 | 165.687 | 212.027 | 142.259 | 99.141 | ALPHA <––> BETA | | |
| 1421 000 | 165.268 | 212.027 | 142.259 | 99.141 | TRANSITION | | |
| 1484.000 | 165.268 | 219.197 | 145.374 | 109.553 | UNDEFINED | | |
| 1484.000 | 165.268 | 219.197 | 145.374 | 109.553 | TRANSITION | | |
| 1500 | 154.808 | 220.911 | 146.171 | 112.110 | −1196.812 | −966.475 | 33.656 |
| 1600 | 125.938 | 229.799 | 151 132 | 125.867 | −1190.831 | −951.330 | 31.058 |
| 1700 | 113.805 | 237.012 | 155.978 | 137.758 | −1323.645 | −935.314 | 28.739 |
| 1750.000 | 109.441 | 240.249 | 158.340 | 143.342 | BETA <––> LIQUID | | |
| 1750.000 | 99.048 | 257.205 | 158.340 | 173.015 | TRANSITION | | |
| 1800 | 99.048 | 259.996 | 161.125 | 177.968 | −1289.381 | −913.461 | 26.508 |
| 1900 | 99.048 | 265.351 | 166.471 | 187.872 | −1285.440 | −892.684 | 24.542 |
| 2000 | 99.048 | 270 431 | 171.543 | 197.777 | −1281.516 | −872.114 | 22.777 |
| 2100 | 99.048 | 275.264 | 176.368 | 207.682 | −1277.610 | −851.740 | 21.186 |
| 2200 | 99.048 | 279.872 | 180.969 | 217.587 | −1273.722 | −831.552 | 19 744 |
| 2300 | 99.048 | 284.275 | 185.365 | 227.492 | −1269.856 | −811.540 | 18.431 |
| 2400 | 99.048 | 288.490 | 189.575 | 237.396 | −1266.014 | −791.695 | 17.231 |
| 2500 | 99.048 | 292.533 | 193.613 | 247.301 | −1262.199 | −772.011 | 16.130 |
| 2600 | 99.048 | 296 418 | 197.493 | 257.206 | −1258.416 | −752.478 | 15.117 |
| 2700 | 99.048 | 300.156 | 201.226 | 267 111 | −1254.671 | −733.090 | 14.182 |
| 2800 | 99.048 | 303.758 | 204.824 | 277.015 | −1250 970 | −713.840 | 13.317 |
| 2900 | 99 048 | 307.234 | 208.296 | 286.920 | −1247.320 | −694.721 | 12.513 |
| 3000 | 99 048 | 310.592 | 211.650 | 296.825 | −1243.729 | −675.728 | 11.765 |
| 3100 | 99.048 | 313.840 | 214.895 | 306.730 | −1240.204 | −656.853 | 11.068 |
| 3200 | 99.048 | 316.984 | 218.036 | 316.635 | −1236.754 | −638.090 | 10.416 |
| 3300 | 99.048 | 320.032 | 221.081 | 326.539 | −1233.386 | −619.434 | 9.805 |
| 3400 | 99.048 | 322.989 | 224.035 | 336.444 | −1230.108 | −600.879 | 9.231 |
| 3500 | 99.048 | 325.860 | 226.903 | 346.349 | −1226.929 | −582.419 | 8.692 |

PREVIOUS: CURRENT: December 1972

## Strontium Fluoride ($SrF_2$) IDEAL GAS $M_r$ = 125.616806 Strontium Fluoride ($SrF_2$) $F_2Sr_1(g)$

$S°(298.15 K) = 291.715 ± 2.1 J·K^{-1}·mol^{-1}$

$\Delta_fH°(0 K) = -764.053 ± 4.2 kJ·mol^{-1}$
$\Delta_fH°(298.15 K) = -766.090 ± 4.2 kJ·mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, cm$^{-1}$ |
|---|
| 442 (1) |
| 82 (1) |
| 443 (1) |

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: $C_{2v}$
Bond Distance. Sr–F = 2.20 ± 0.03Å
Bond Angle: F–Sr–F = 108°
Product of the Moments of Inertia: $I_AI_BI_C = 4.022689 \times 10^{-114}$ g$^3$·cm$^6$

### Enthalpy of Formation

$\Delta_fH°$ is obtained from that of the crystal by addition of the adopted $\Delta_{sub}H° = 107.8 ± 0.3$ kcal·mol$^{-1}$. 2nd and 3rd law analyses of four sets of vapor pressure data for $SrF_2$(cr, l) are listed below.

| Source | Method | T/K | $\Delta_{sub}H°$(298.15 K), kcal·mol$^{-1}$ 2nd law | 3rd law | Drift cal K$^{-1}$·mol$^{-1}$ | $\Delta_fH°$(298.15 K) kcal·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| Ruff and Le Boucher[1] | Dynamic B.P. | 2095–2232 | 106.4[a] | 96.1 ± 0.8 | −4.8 ± 3.1 | −184.0 ± 1.5 |
| Bautista and Margrave[2] | Langmuir | 1235–1319 | 104.5 | 108.0 ± 0.5 | 2.8 ± 2.9 | −182.9 ± 1.2 |
| Green *et al.*[3] | Knudsen | 1207–1563[b] | 107.9 | 107.8 ± 0.3 | −0.07 ± 0.38 | −183.1 ± 1.0 |
| Hildenbrand[4] | Torsion–Effusion | 1420–1710 | 103.8 | 106.5 ± 0.4 | 1.7 | −184.4 ± 1.1 |

[a] $\Delta_{vap}H°$(298.15 K)

[b] Six of the 30 experimental points were rejected due to failure of a statistical test.

Note that the drifts are both positive and negative indicating the correctness of the functions used in the analysis. A weighted value of these four results is adopted.

### Heat Capacity and Entropy

The bond length is that measured by Akishin and Spiridonov[5] in their high–temperature electron diffraction studies of the alkaline earth dihalide vapors. Although it was inferred from these measurements that all the dihalides are linear, recent results of electric–deflection experiments[6] and matrix isolation infrared spectra[1 8] for $SrF_2$ can only be satisfactorily interpreted in terms of a molecule with a bent configuration. We adopt the vibrational frequencies and bond angle determined by Calder *et al.*[8] in their thorough investigation of the infrared spectra of isotopically enriched samples of $SrF_2$ trapped in krypton matrices. The uncertainty assigned to the entropy reflects possible errors due to matrix–shift effects in these frequencies. The adopted symmetric ($\nu_1$) and antisymmetric ($\nu_3$) stretching frequencies are in reasonable agreement with those determined by Snelson[7] for $SrF_2$ trapped in neon, argon, and krypton matrices Also, the antisymmetric frequency is quite consistent with the value 445 ± 7 cm$^{-1}$ observed by Baikov[9] in the infrared spectra of $SrF_2$ vapor at 2050 K. In an earlier paper, Baikov[10] reported observing under similar conditions a broad absorption band at 105 cm$^{-1}$ which he assigned to the symmetric bending ($\nu_2$) mode of $SrF_2$. We prefer the matrix value (82 cm$^{-1}$, since Baikov[10] recorded only the high–frequency (>90 cm$^{-1}$) portion of this band. Furthermore, Hastie *et al.*[11] have pointed out that, in general, bending frequencies are less influenced by matrix effects and in some cases may be shifted slightly upwards from the gas phase values.

The individual moments of inertia are: $I_A = 7.3594 \times 10^{-39}$, $I_B = 19.9877 \times 10^{-39}$, and $I_C = 27.3471 \times 10^{-39}$ g·cm$^2$.

### References

[1] O. Ruff and L. Le Boucher, Z. Anorg Chem 219, 376 (1934).
[2] R G. Bautista and J. L. Margrave, J. Phys. Chem. 69, 1770 (1965).
[3] J. W. Green, G. D. Blue, T. C. Ehlert and J. L. Margrave, J. Chem. Phys. 41, 2245 (1964).
[4] D L. Hildenbrand, E. Murad, N. D. Potter, L. P. Theard, and W. F. Hall, Aeronutronic Report No. U–3183, Ford Motor Company, (June 30, 1965).
[5] P. A. Akishin and V. P. Spiridonov, Kristallografiya 2, 475 (1957).
[6] L. Wharton, R. A. Berg and W. Klemperer, J Chem. Phys. 39, 2023 (1963).
[7] A. Snelson, J. Phys. Chem. 70, 3208 (1966).
[8] V. Calder, D. E. Mann, K. S Seshadri, M. Allavena, and D. White, J Chem Phys 51, 2093 (1969).
[9] V. I. Baikov, Opt. Spektrosk. 27, 923 (1969).
[10] V. I. Baikov, Opt. Spektrosk. 25, 356 (1968).
[11] J. W. Hastie, R. H. Hange and J. L. Margrave in "Spectroscopy in Inorganic Chemistry," Ed. by C N R. Rao and J R. Ferraro, Academic Press, New York, (1970).

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −13.356 | −764.053 | −764 053 | INFINITE |
| 100 | 41.833 | 240.072 | 335.836 | −9.576 | −764.680 | −768.845 | 401.604 |
| 200 | 48.936 | 271.323 | 296.453 | −5.026 | −765.547 | −772.639 | 201.793 |
| 250 | 51.366 | 282.520 | 292.579 | −2.515 | −765.841 | −774.382 | 161.798 |
| 298.15 | 52.991 | 291.715 | 291.715 | 0. | −766.090 | −775.998 | 135.952 |
| 300 | 53.042 | 292.043 | 291.716 | 0.098 | −766.100 | −776.060 | 135.124 |
| 350 | 54.207 | 300.312 | 292.366 | 2.781 | −766.358 | −777.700 | 116.065 |
| 400 | 55.034 | 307.607 | 293.825 | 5.513 | −766.633 | −779.301 | 101.766 |
| 450 | 55.637 | 314.126 | 295.725 | 8.281 | −766.934 | −780.867 | 90.641 |
| 500 | 56.087 | 320.012 | 297.864 | 11.074 | −767.266 | −782.398 | 81.737 |
| 600 | 56.698 | 330.297 | 302.437 | 16.716 | −768.027 | −785.355 | 68.371 |
| 700 | 57.081 | 339.068 | 307.059 | 22.406 | −768.922 | −788 174 | 58.814 |
| 800 | 57.335 | 346.708 | 311.548 | 28.128 | −769.950 | −790.856 | 51.638 |
| 900 | 57.513 | 353.472 | 315.837 | 33.871 | −771 735 | −793.329 | 46.044 |
| 1000 | 57.641 | 359.538 | 319.909 | 39.629 | −772.701 | −795.677 | 41.562 |
| 1100 | 57 736 | 365.037 | 323.766 | 45.398 | −781.588 | −797.561 | 37 873 |
| 1200 | 57.810 | 370.064 | 327 417 | 51.175 | −783.502 | −798.929 | 34.776 |
| 1300 | 57.867 | 374.693 | 330.878 | 56.959 | −785.434 | −800.136 | 32.150 |
| 1400 | 57.912 | 378.983 | 334.163 | 62 748 | −787.382 | −801.194 | 29.893 |
| 1500 | 57 949 | 382.980 | 337.286 | 68.542 | −789.345 | −802.112 | 27.932 |
| 1600 | 57.979 | 386.721 | 340.260 | 74.338 | −791.324 | −802.899 | 26.212 |
| 1700 | 58.005 | 390.237 | 343.097 | 80.137 | −930.231 | −802.382 | 24.654 |
| 1800 | 58.026 | 393.553 | 345.809 | 85.939 | −930.375 | −794.857 | 23.066 |
| 1900 | 58.043 | 396.691 | 348.405 | 91.742 | −930.535 | −787.324 | 21.645 |
| 2000 | 58.059 | 399.668 | 350.895 | 97.547 | −930 710 | −779.782 | 20.366 |
| 2100 | 58.072 | 402.501 | 353.285 | 103.354 | −930.902 | −772.231 | 19.208 |
| 2200 | 58.083 | 405.203 | 355.584 | 109.162 | −931.112 | −764.671 | 18.156 |
| 2300 | 58.093 | 407.785 | 357.798 | 114.971 | −931.342 | −757.100 | 17.194 |
| 2400 | 58.102 | 410.258 | 359.933 | 120.780 | −931.595 | −749.519 | 16.313 |
| 2500 | 58 110 | 412.630 | 361.993 | 126.591 | −931.874 | −741.927 | 15.502 |
| 2600 | 58.117 | 414.909 | 363.985 | 132.402 | −932.185 | −734.323 | 14.753 |
| 2700 | 58.123 | 417.102 | 365.912 | 138.214 | −932.533 | −726.706 | 14 059 |
| 2800 | 58 128 | 419.216 | 367.778 | 144.027 | −932.924 | −719.076 | 13 415 |
| 2900 | 58.133 | 421.256 | 369.587 | 149.840 | −933.365 | −711.431 | 12.814 |
| 3000 | 58.138 | 423.227 | 371.343 | 155.653 | −933.865 | −703.770 | 12.254 |
| 3100 | 58.142 | 425.134 | 373.047 | 161.467 | −934.431 | −696.091 | 11.729 |
| 3200 | 58.145 | 426.979 | 374.704 | 167.282 | −935.071 | −688.393 | 11.237 |
| 3300 | 58.148 | 428.769 | 376.315 | 173.096 | −935.794 | −680.673 | 10.774 |
| 3400 | 58.152 | 430.505 | 377.884 | 178.911 | −936.606 | −672.930 | 10.338 |
| 3500 | 58.154 | 432.190 | 379.411 | 184.727 | −937.516 | −665 162 | 9.927 |
| 3600 | 58.157 | 433.829 | 380.900 | 190.542 | −938.530 | −657.366 | 9.538 |
| 3700 | 58 159 | 435.422 | 382.352 | 196.358 | −939.654 | −649.541 | 9.170 |
| 3800 | 58.161 | 436.973 | 383.770 | 202.174 | −940.893 | −641.684 | 8.821 |
| 3900 | 58.163 | 438.484 | 385.153 | 207.990 | −942.252 | −633.792 | 8.489 |
| 4000 | 58.165 | 439.957 | 386.505 | 213.807 | −943.733 | −625.864 | 8.173 |
| 4100 | 58.167 | 441.393 | 387.826 | 219.623 | −945.338 | −617.898 | 7.872 |
| 4200 | 58.169 | 442.795 | 389.118 | 225.440 | −947.065 | −609.891 | 7.585 |
| 4300 | 58.170 | 444.163 | 390.383 | 231.257 | −948.918 | −601.842 | 7.311 |
| 4400 | 58.171 | 445.501 | 391.620 | 237.074 | −950.895 | −593.748 | 7.049 |
| 4500 | 58.173 | 446.808 | 392.832 | 242.891 | −952.992 | −585.607 | 6.798 |
| 4600 | 58.174 | 448.087 | 394.019 | 248.709 | −955.140 | −577.424 | 6.557 |
| 4700 | 58.175 | 449.338 | 395.183 | 254.526 | −957.448 | −569.188 | 6.326 |
| 4800 | 58.176 | 450.562 | 396.324 | 260.344 | −959.857 | −560.902 | 6.104 |
| 4900 | 58.177 | 451.762 | 397.443 | 266.161 | −962.365 | −552.565 | 5.890 |
| 5000 | 58.178 | 452.937 | 398.542 | 271.979 | −964.957 | −544.176 | 5.685 |
| 5100 | 58.179 | 454.089 | 399.619 | 277.797 | −967.614 | −535.736 | 5.487 |
| 5200 | 58.180 | 455.219 | 400.678 | 283.615 | −970.364 | −527.241 | 5.296 |
| 5300 | 58.181 | 456.327 | 401.717 | 289.433 | −973.181 | −518.693 | 5 112 |
| 5400 | 58 181 | 457.415 | 402.739 | 295.251 | −976.057 | −510.091 | 4.934 |
| 5500 | 58.182 | 458.482 | 403.743 | 301.069 | −978.984 | −501.435 | 4.762 |
| 5600 | 58.183 | 459.531 | 404.730 | 306.887 | −981.955 | −492.725 | 4.596 |
| 5700 | 58.183 | 460.561 | 405.700 | 312.706 | −984.962 | −483.963 | 4.435 |
| 5800 | 58.184 | 461.573 | 406.655 | 318.524 | −987.997 | −475.147 | 4.279 |
| 5900 | 58.184 | 462.567 | 407.594 | 324.342 | −990.843 | −466.302 | 4.128 |
| 6000 | 58.185 | 463.545 | 408.518 | 330.161 | −993.883 | −457.386 | 3 982 |

PREVIOUS December 1972 (1 atm)    CURRENT: December 1972 (1 bar)

IDEAL GAS

$M_r$ = 85.876806

$S°(298.15\ K) = 255.690 \pm 6.3\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -686.627 \pm 41.8\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -688.268 \pm 41.8\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

| $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|
| 0 | [3] |
| [7000] | [6] |
| [17000] | [6] |
| [22000] | [15] |

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ |
|---|
| [473](1) |
| [283](2) |
| [633](1) |

Ground State Quantum Weight: [3]  $\sigma = 2$
Point Group: [$D_{\infty h}$]
Bond Distance: Ti–F = [1.95]Å
Bond Angle: F–Ti–F = [180]°
Rotational Constant: $B_0$ = [0.116676] cm$^{-1}$

| Enthalpy Reference Temperature = $T_r$ = 298.15 K | | | | | | | Standard State Pressure = $p°$ = 0.1 MPa |
|---|---|---|---|---|---|---|---|
| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | .000 | .000 | INFINITE | −12.013 | −686.627 | −686.627 | INFINITE |
| 100 | 34.469 | 208.036 | 297.829 | −8.979 | −687.060 | −690.000 | 360.419 |
| 200 | 46.288 | 235.823 | 260.331 | −4.902 | −687.828 | −692.617 | 180.893 |
| 250 | 50.179 | 246.593 | 256.532 | −2.485 | −688.077 | −693.784 | 144.958 |
| 298.15 | 52.878 | 255.675 | 255.675 | .000 | −688.268 | −694.865 | 121.737 |
| 300 | 52.965 | 256.002 | 255.676 | .098 | −688.275 | −694.906 | 120.994 |
| 350 | 54.966 | 264.326 | 256.329 | 2.799 | −688.450 | −695.997 | 103.872 |
| 400 | 56.425 | 271.765 | 257.802 | 5.586 | −688.620 | −697.064 | 91.027 |
| 450 | 57.510 | 278.477 | 259.732 | 8.435 | −688.795 | −698.109 | 81.034 |
| 500 | 58.333 | 284.581 | 261.917 | 11.332 | −688.979 | −699.134 | 73.038 |
| 600 | 59.470 | 295.325 | 266.614 | 17.227 | −689.383 | −701.128 | 61.039 |
| 700 | 60.194 | 304.551 | 271.390 | 23.213 | −689.837 | −703.050 | 52.462 |
| 800 | 60.686 | 312.622 | 276.050 | 29.258 | −690.326 | −704.904 | 46.026 |
| 900 | 61.046 | 319.792 | 280.519 | 35.345 | −690.884 | −706.694 | 41.015 |
| 1000 | 61.336 | 326.239 | 284.774 | 41.465 | −691.576 | −708.415 | 37.004 |
| 1100 | 61.597 | 332.098 | 288.814 | 47.612 | −692.464 | −710.058 | 33.718 |
| 1200 | 61.857 | 337.468 | 292.648 | 53.784 | −697.532 | −711.491 | 30.970 |
| 1300 | 62.134 | 342.430 | 296.289 | 59.984 | −698.082 | −712.633 | 28.634 |
| 1400 | 62.437 | 347.046 | 299.752 | 66.212 | −698.703 | −713.729 | 26.630 |
| 1500 | 62.770 | 351.365 | 303.050 | 72.472 | −699.404 | −714.778 | 24.891 |
| 1600 | 63.132 | 355.427 | 306.198 | 78.767 | −700.192 | −715.778 | 23.368 |
| 1700 | 63.518 | 359.266 | 309.208 | 85.099 | −701.078 | −716.726 | 22.022 |
| 1800 | 63.924 | 362.908 | 312.091 | 91.471 | −702.069 | −717.618 | 20.825 |
| 1900 | 64.341 | 366.375 | 314.857 | 97.885 | −703.176 | −718.452 | 19.752 |
| 2000 | 64.764 | 369.686 | 317.517 | 104.340 | −719.094 | −718.771 | 18.772 |
| 2100 | 65.185 | 372.857 | 320.077 | 110.837 | −721.207 | −718.703 | 17.877 |
| 2200 | 65.599 | 375.899 | 322.546 | 117.377 | −723.281 | −718.535 | 17.060 |
| 2300 | 66.002 | 378.823 | 324.929 | 123.957 | −725.313 | −718.274 | 16.313 |
| 2400 | 66.391 | 381.641 | 327.234 | 130.577 | −727.300 | −717.925 | 15.625 |
| 2500 | 66.762 | 384.359 | 329.465 | 137.234 | −729.241 | −717.494 | 14.991 |
| 2600 | 67.113 | 386.984 | 331.627 | 143.928 | −731.133 | −716.987 | 14.404 |
| 2700 | 67.445 | 389.523 | 333.724 | 150.656 | −732.975 | −716.408 | 13.860 |
| 2800 | 67.758 | 391.982 | 335.761 | 157.417 | −734.766 | −715.761 | 13.353 |
| 2900 | 68.051 | 394.364 | 337.741 | 164.207 | −736.505 | −715.051 | 12.879 |
| 3000 | 68.325 | 396.676 | 339.667 | 171.026 | −738.191 | −714.283 | 12.437 |
| 3100 | 68.582 | 398.921 | 341.543 | 177.872 | −739.824 | −713.459 | 12.022 |
| 3200 | 68.823 | 401.102 | 343.370 | 184.742 | −741.403 | −712.583 | 11.632 |
| 3300 | 69.050 | 403.223 | 345.152 | 191.636 | −742.929 | −711.659 | 11.265 |
| 3400 | 69.263 | 405.288 | 346.890 | 198.552 | −744.401 | −710.689 | 10.918 |
| 3500 | 69.465 | 407.299 | 348.588 | 205.488 | −745.820 | −709.676 | 10.591 |
| 3600 | 69.656 | 409.258 | 350.246 | 212.444 | −747.186 | −708.624 | 10.282 |
| 3700 | 69.838 | 411.169 | 351.867 | 219.419 | −1157.598 | −699.746 | 9.879 |
| 3800 | 70.012 | 413.034 | 353.452 | 226.412 | −1157.626 | −687.372 | 9.449 |
| 3900 | 70.179 | 414.855 | 355.003 | 233.421 | −1157.657 | −674.996 | 9.041 |
| 4000 | 70.339 | 416.634 | 356.522 | 240.447 | −1157.692 | −662.620 | 8.653 |
| 4100 | 70.494 | 418.372 | 358.009 | 247.489 | −1157.730 | −650.243 | 8.284 |
| 4200 | 70.643 | 420.073 | 359.467 | 254.546 | −1157.771 | −637.864 | 7.933 |
| 4300 | 70.788 | 421.737 | 360.896 | 261.618 | −1157.812 | −625.486 | 7.598 |
| 4400 | 70.928 | 423.366 | 362.297 | 268.703 | −1157.854 | −613.105 | 7.278 |
| 4500 | 71.063 | 424.961 | 363.672 | 275.803 | −1157.896 | −600.724 | 6.973 |
| 4600 | 71.195 | 426.525 | 365.021 | 282.916 | −1157.937 | −588.342 | 6.681 |
| 4700 | 71.322 | 428.057 | 366.346 | 290.042 | −1157.975 | −575.959 | 6.401 |
| 4800 | 71.445 | 429.560 | 367.648 | 297.180 | −1158.011 | −563.575 | 6.133 |
| 4900 | 71.564 | 431.034 | 368.926 | 304.331 | −1158.043 | −551.191 | 5.876 |
| 5000 | 71.678 | 432.481 | 370.183 | 311.493 | −1158.071 | −538.806 | 5.629 |
| 5100 | 71.788 | 433.902 | 371.418 | 318.666 | −1158.093 | −526.420 | 5.392 |
| 5200 | 71.893 | 435.297 | 372.633 | 325.850 | −1158.109 | −514.034 | 5.164 |
| 5300 | 71.994 | 436.667 | 373.829 | 333.044 | −1158.118 | −501.648 | 4.944 |
| 5400 | 72.089 | 438.014 | 375.005 | 340.249 | −1158.119 | −489.262 | 4.733 |
| 5500 | 72.180 | 439.337 | 376.163 | 347.462 | −1158.112 | −476.876 | 4.529 |
| 5600 | 72.266 | 440.639 | 377.302 | 354.685 | −1158.097 | −464.490 | 4.333 |
| 5700 | 72.346 | 441.919 | 378.425 | 361.915 | −1158.072 | −452.104 | 4.143 |
| 5800 | 72.421 | 443.178 | 379.530 | 369.154 | −1158.037 | −439.719 | 3.960 |
| 5900 | 72.490 | 444.416 | 380.620 | 376.399 | −1157.992 | −427.335 | 3.783 |
| 6000 | 72.554 | 445.635 | 381.693 | 383.651 | −1157.936 | −414.951 | 3.612 |

PREVIOUS: December 1968 (1 atm)    CURRENT December 1968 (1 bar)

## Enthalpy of Formation

Zmbov and Margrave[1] have reported ion intensities and the corresponding equilibrium constants for the reaction $Ca(g) + TiF_3(g) = CaF(g) + TiF_2(g)$. 2nd and 3rd law analyses of their data give a 2nd law $\Delta_fH°(298.15\ K)$ of 7.0 kcal·mol$^{-1}$, a 3rd law $\Delta_fH°(298.15\ K)$ of 11.76 kcal·mol$^{-1}$, and a 3rd law drift of 3.1 ± 3.8 cal K$^{-1}$·mol$^{-1}$. The enthalpy of formation, $\Delta_fH°(298.15\ K)$, of $TiF_2(g)$ is calculated from the 3rd law $\Delta_fH°(298.15\ K)$, above, and the JANAF enthalpies of formation of $TiF_3(g)$, CaF(g) and Ca(g).

## Heat Capacity and Entropy

The interatomic distances are estimated from those of $TiCl_2$, $TiCl_4$, and $TiF_4$. The vibrational frequencies are estimated from a valence force field model.

The electronic levels are assumed to be the same as $TiCl_2(g)$. The levels of $TiCl_2(g)$ are estimated by assuming they correspond to the inverted states of $NiCl_2(g)$.[2] The linear configuration is assumed because experimental evidence[3] indicates that other transition metal difluorides, viz those of Mn, Co, Ni, Cu, and Zn, are linear.

## References

[1] K. F. Zmbov and J. L. Margrave, J. Phys. Chem. 71, 2893 (1967).
[2] C. W. DeKock and D. M. Gruen, J. Chem. Phys. 44, 4387 (1966).
[3] A. Buchler, J. L. Stauffer, and W. Klemperer, J. Chem. Phys. 40, 3471 (1964).

## Zirconium Fluoride ($ZrF_2$) CRYSTAL $M_r$ = 129.216806

$S°(298.15\ K) = [75.312 \pm 8.4]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = [1175 \pm 150]\ K$

$\Delta_f H°(298.15\ K) = [-962.320 \pm 63]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus} H° = [38 \pm 8]\ kJ{\cdot}mol^{-1}$
$\Delta_{sub} H°(298\ 15\ K) = [404\ 174]\ kJ{\cdot}mol^{-1}$

### Enthalpy of Formation

The adopted $\Delta_f H°(ZrF_2$, cr, 298.15 K) value is taken from NBS[1] which was estimated by Brewer.[2] More recent thermal data related to the enthalpy of formation of $ZrF_2$(cr) is unavailable.

### Heat Capacity and Entropy

The heat capacities in the temperature range 298–2000 K are estimated by comparison with those of $ZrF_4$(cr) and Zr(cr). The $S°$(298 15 K) is calculated as 17.2 and 17.0 cal $K^{-1}{\cdot}mol^{-1}$ based on the assumptions that $S(ZrF_2) = 1/2[S(ZrF_4) + S(Zr)]$ and $S(ZrF_2) = S(ZnF_2) - S(Zn) + S(Zr)$ Using the additive entropy constants $S°$(298 15 K) = 12.1 and 4.7 cal $K^{-1}{\cdot}mol^{-1}$ for Zr and F suggested by Kubaschewski and Evans[3] we obtain $S°(ZrF_2$, cr, 298.15 K) = 12.1 + 2 (4.7) = 21.5 cal $K^{-1}{\cdot}mol^{-1}$ Based on $S°$(298 15 K) = 11.5 and 3.9 cal $K^{-1}{\cdot}mol^{-1}$ for $Zr^{4}+$ and $F^{-}$ recommended by Kelley,[4] the value $S°(ZrF_2$, cr, 298.15 K) is derived as 19.3 cal $K^{-1}{\cdot}mol^{-1}$. The entropy at 298 K for $ZrF_2$(cr) is tentatively adopted as 18 ± 2 cal $K^{-1}{\cdot}mol^{-1}$.

### Sublimation Data

The difference between $\Delta_f H°$(298.15 K) for ZrF(g) and $ZrF_2$(cr) is $\Delta_{sub} H°$(298.15 K).

### References

[1] U. S. Nat. Bur. Stand. Circ 500, (1952).
[2] L. Brewer, University of California, Berkeley, California, unpublished data.
[3] O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, (1958).
[4] K. K. Kelley, U.S. Bur. Mines, personal communication, June, (1960).
[5] R A McDonald, G. C. Sinke, and D. R. Stull, J. Chem. Eng. Data 7, 83 (1962).

## Zirconium Fluoride ($ZrF_2$) $F_2Zr_1$(cr)

Enthalpy Reference Temperature = $T_r$ = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298 15 | 65.940 | 75.312 | 75.312 | 0 | −962.320 | −912 724 | 159.905 |
| 300 | 66.024 | 75.720 | 75.313 | 0.122 | −962.303 | −912.416 | 158.866 |
| 400 | 69.873 | 95.253 | 77.950 | 6.921 | −961.282 | −895.937 | 116.997 |
| 500 | 73.220 | 111.212 | 83.054 | 14.079 | −960.115 | −879.733 | 91.905 |
| 600 | 76.149 | 124.827 | 88.908 | 21.551 | −958.807 | −863.777 | 75.198 |
| 700 | 78.659 | 136.761 | 94.909 | 29.296 | −957.380 | −848.050 | 63.282 |
| 800 | 80.626 | 147.395 | 100.817 | 37.262 | −955.874 | −832.533 | 54.359 |
| 900 | 82.425 | 156.997 | 106.535 | 45.416 | −954.322 | −817.209 | 47.430 |
| 1000 | 84.015 | 165.766 | 112.026 | 53 741 | −952.743 | −802.058 | 41.895 |
| 1100 | 85.270 | 173.834 | 117.283 | 62.206 | −951.168 | −787.066 | 37.375 |
| 1175.000 | 86.107 | 179 486 | 121.074 | 68.633 | --- CRYSTAL <--> LIQUID --- | | |
| 1200 | 86.400 | 181.302 | 122.310 | 70.790 | −953.333 | −771.995 | 33.604 |
| 1300 | 87 404 | 188.258 | 127.119 | 79.481 | −951.279 | −756.966 | 30 415 |
| 1400 | 88.282 | 194.770 | 131.721 | 88.268 | −949.193 | −742.097 | 27.688 |
| 1500 | 88.826 | 200.879 | 136.130 | 97.124 | −947.112 | −727.377 | 25.330 |
| 1600 | 89.328 | 206.629 | 140.358 | 106.033 | −945.058 | −712.796 | 23.270 |
| 1700 | 89.621 | 212 053 | 144.418 | 114.981 | −943.056 | −698.341 | 21.457 |
| 1800 | 89.914 | 217 185 | 148.319 | 123.960 | −941.123 | −684.002 | 19.849 |
| 1900 | 89.956 | 222.048 | 152.073 | 132.954 | −939.282 | −669.768 | 18.413 |
| 2000 | 89.956 | 226.663 | 155.688 | 141.950 | −937.554 | −655.628 | 17.123 |

PREVIOUS· June 1961 CURRENT: June 1969

# Zirconium Fluoride ($ZrF_2$) LIQUID $M_r$ = 129.216806 Zirconium Fluoride ($ZrF_2$) $F_2Zr_1(l)$

$S°$(298.15 K) = [100.846] J·K$^{-1}$·mol$^{-1}$
$T_{fus}$ = [1175 ± 150] K

$\Delta_f H°$(298.15 K) = [−936.951] kJ·mol$^{-1}$
$\Delta_{fus}H°$ = [38 ± 8] kJ·mol$^{-1}$

## Enthalpy of Formation

$\Delta_f H°(ZrF_2$, l, 298.15 K) is calculated from $\Delta_f H°(ZrF_2$, cr, 298 15 K) by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°$(1175 K)–$H°$(298 15 K), between the crystal and liquid.

## Heat Capacity and Entropy

The heat capacity is estimated from those of $ZrF_4$(l), $CaF_2$(l), Zr(l) and Ca(l) and is assumed to be constant in the temperature range 800–3000 KA glass transition temperature is assumed at 800 K. The $C_p°$ values below 800 K are adopted from the $ZrF_2$(cr) table. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

## Fusion Data

Both $T_{fus}$ and $\Delta_{fus}H°$ are estimated. The derived entorpy of melting, 2.55 cal K$^{-1}$·mol$^{-1}$/atom, is the same as that of $ZrF_4$(cr) which was obtained from experimental measurements.[1] Therefore these estimated values are tentatively adopted.

## Vaporization Data

The boiling point, $T_{vap}$, is calculated as the temperature at which the fugacity is one atmosphere for the process $ZrF_2(l) = ZrF_2(g)$.

## Reference

[1] R. A. McDonald, G. C. Sinke and D. R. Stull, J. Chem. Eng. Data 7, 83 (1962).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

|  | J·K$^{-1}$mol$^{-1}$ |  |  | kJ·mol$^{-1}$ |  |  |  |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 |  |  |  |  |  |  |  |
| 100 |  |  |  |  |  |  |  |
| 200 |  |  |  |  |  |  |  |
| 298.15 | 65.940 | 100.846 | 100.846 | 0. | −936.951 | −894.968 | 156.795 |
| 300 | 66.024 | 101.254 | 100.847 | 0.122 | −936.934 | −894.708 | 155.782 |
| 400 | 69.873 | 120.787 | 103.484 | 6.921 | −935.914 | −880.782 | 115.018 |
| 500 | 73.220 | 136.746 | 108.588 | 14.079 | −934.746 | −867 131 | 90.589 |
| 600 | 76.149 | 150.361 | 114.442 | 21.551 | −933.439 | −853.729 | 74.324 |
| 700 | 78.659 | 162.295 | 120.443 | 29.296 | −932.012 | −840.555 | 62.723 |
| 800 | 80.626 | 172.933 | 126.351 | 37.265 | −930.502 | −827.592 | 54.036 |
| 800.000 | 80.626 | 172.933 | 126.351 | 37.265 | GLASS <−−> LIQUID |  |  |
| 800 000 | 100.416 | 172.933 | 126.351 | 37.265 | TRANSITION |  |  |
| 900 | 100.416 | 184.760 | 132.197 | 47.306 | −927.063 | −814.936 | 47.298 |
| 1000 | 100.416 | 195.340 | 137.992 | 57.348 | −923.767 | −802.656 | 41.926 |
| 1100 | 100.416 | 204.910 | 143.647 | 67.390 | −920 616 | −790.698 | 37.547 |
| 1175.000 | 100.416 | 211.534 | 147.771 | 74.921 | −−− CRYSTAL <−−> LIQUID −−− |  |  |
| 1200 | 100.416 | 213.648 | 149.122 | 77.431 | −921.322 | −778.800 | 33.900 |
| 1300 | 100.416 | 221.685 | 154.398 | 87.473 | −917 919 | −767.061 | 30.821 |
| 1400 | 100.416 | 229.127 | 159.474 | 97.514 | −914.578 | −755.583 | 28.191 |
| 1500 | 100.416 | 236.055 | 164.351 | 107.556 | −911.311 | −744.340 | 25.920 |
| 1600 | 100.416 | 242.536 | 169.037 | 117.598 | −908.125 | −733.313 | 23.940 |
| 1700 | 100.416 | 248.623 | 173.541 | 127.639 | −905.029 | −722.483 | 22.199 |
| 1800 | 100.416 | 254.363 | 177.874 | 137.681 | −902.033 | −711.832 | 20.657 |
| 1900 | 100.416 | 259.792 | 182.043 | 147.722 | −899.144 | −701.344 | 19.281 |
| 2000 | 100 416 | 264.943 | 186.061 | 157 764 | −896.371 | −691.006 | 18.047 |
| 2100 | 100.416 | 269.842 | 189.935 | 167.806 | −893 719 | −680.804 | 16.934 |
| 2200 | 100.416 | 274.513 | 193.674 | 177.847 | −912.521 | −669 979 | 15.907 |
| 2300 | 100.416 | 278.977 | 197.286 | 187.889 | −910.551 | −658.998 | 14.966 |
| 2400 | 100.416 | 283.251 | 200.780 | 197 930 | −908.577 | −648.103 | 14.106 |
| 2500 | 100.416 | 287.350 | 204.161 | 207.972 | −906.594 | −637.291 | 13.315 |
| 2600 | 100.416 | 291.288 | 207 437 | 218.014 | −904.599 | −626.558 | 12.588 |
| 2700 | 100 416 | 295.078 | 210.613 | 228.055 | −902.587 | −615.902 | 11.915 |
| 2800 | 100.416 | 298.730 | 213.695 | 238.097 | −900.557 | −605.321 | 11.292 |
| 2900 | 100.416 | 302.254 | 216.689 | 248.138 | −898.505 | −594.813 | 10 714 |
| 3000 | 100.416 | 305.658 | 219.598 | 258.180 | −896.429 | −584.377 | 10.175 |

PREVIOUS June 1961 CURRENT· June 1969

## Zirconium Fluoride ($ZrF_2$) CRYSTAL-LIQUID

0 to 1175 K crystal
above 1175 K liquid

Refer to the individual tables for details.

## $M_r = 129.216806$ Zirconium Fluoride ($ZrF_2$) $F_2Zr_1(cr,l)$

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p^\circ$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 65.940 | 75.312 | 75.312 | 0. | −962.320 | −912.724 | 159.905 |
| 300 | 66.024 | 75.720 | 75.313 | 0.122 | −962.303 | −912.416 | 158.866 |
| 400 | 69.873 | 95.253 | 77.950 | 6.921 | −961.282 | −895.937 | 116.997 |
| 500 | 73.220 | 111.212 | 83.054 | 14.079 | −960.115 | −879.733 | 91.905 |
| 600 | 76.149 | 124.827 | 88.908 | 21.551 | −958.807 | −863.777 | 75.198 |
| 700 | 78.659 | 136.761 | 94.909 | 29.296 | −957.380 | −848.050 | 63.282 |
| 800 | 80.626 | 147.395 | 100.817 | 37.262 | −955.874 | −832.533 | 54.359 |
| 900 | 82.425 | 156.997 | 106.535 | 45.416 | −954.322 | −817.209 | 47.430 |
| 1000 | 84.015 | 165 766 | 112.026 | 53.741 | −952.743 | −802.058 | 41.895 |
| 1100 | 85.270 | 173.834 | 117.283 | 62.206 | −951.168 | −787.066 | 37.375 |
| 1175.000 | 86.107 | 179.486 | 121.074 | 68.633 | CRYSTAL <−−> LIQUID | | |
| 1175 000 | 100.416 | 211.534 | 121.074 | 106.289 | TRANSITION | | |
| 1200 | 100.416 | 213.648 | 122.981 | 108.800 | −915.322 | −772.800 | 33.639 |
| 1300 | 100.416 | 221.685 | 130.269 | 118.841 | −911.919 | −761.061 | 30.580 |
| 1400 | 100.416 | 229.127 | 137.068 | 128.883 | −908.578 | −749.583 | 27.967 |
| 1500 | 100 416 | 236.055 | 143.438 | 138.925 | −905.311 | −738.340 | 25 711 |
| 1600 | 100.416 | 242.536 | 149.432 | 148.966 | −902.125 | −727.313 | 23 744 |
| 1700 | 100 416 | 248.623 | 155.089 | 159.008 | −899.029 | −716.483 | 22.015 |
| 1800 | 100.416 | 254.363 | 160.447 | 169.049 | −896.033 | −705.832 | 20.483 |
| 1900 | 100 416 | 259.792 | 165.534 | 179.091 | −893.144 | −695.344 | 19.116 |
| 2000 | 100.416 | 264.943 | 170.376 | 189.133 | −890.371 | −685.006 | 17.891 |
| 2100 | 100.416 | 269.842 | 174.997 | 199.174 | −887.719 | −674.803 | 16.785 |
| 2200 | 100.416 | 274.513 | 179.415 | 209.216 | −906.521 | −663.979 | 15.765 |
| 2300 | 100.416 | 278.977 | 183.648 | 219.257 | −904.551 | −652.998 | 14.830 |
| 2400 | 100.416 | 283.251 | 187.709 | 229.299 | −902.577 | −642.103 | 13.975 |
| 2500 | 100 416 | 287.350 | 191.614 | 239.341 | −900.594 | −631.291 | 13.190 |
| 2600 | 100.416 | 291.288 | 195.372 | 249.382 | −898.599 | −620.558 | 12.467 |
| 2700 | 100.416 | 295.078 | 198.995 | 259.424 | −896.587 | −609.902 | 11 799 |
| 2800 | 100.416 | 298.730 | 202.492 | 269.465 | −894.557 | −599.321 | 11.180 |
| 2900 | 100.416 | 302.254 | 205.872 | 279.507 | −892.505 | −588.813 | 10.606 |
| 3000 | 100 416 | 305.658 | 209.142 | 289.549 | −890.429 | −578.377 | 10.070 |

PREVIOUS· CURRENT: June 1969

## Zirconium Fluoride ($ZrF_2$) IDEAL GAS $M_r = 129.216806$ Zirconium Fluroide ($ZrF_2$) $F_2Zr_1(g)$

$S^\circ$(298 15 K) = [283.434 ± 8.4] J·K$^{-1}$·mol$^{-1}$

$\Delta_f H^\circ$(0 K) = −555.653 ± 20.9 kJ·mol$^{-1}$
$\Delta_f H^\circ$(298.15 K) = −558.146 ± 20.9 kJ·mol$^{-1}$

| Electronic Levels and Quantum Weights<br>$\epsilon_i$, cm | $g_i$ |
|---|---|
| 0 | [3] |
| [7000] | [6] |
| [17000] | [6] |
| [22000] | [15] |

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ |
|---|
| [560](1) |
| [300](1) |
| [670](1) |

Ground State Quantum Weight: [3] $\sigma = 2$
Point Group: $C_{2v}$
Bond Distance: Zr–F = [1.92] Å
Bond Angle: F–Zr–F = [125]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.396810 \times 10^{-114}]$ g$^3$·cm$^6$

### Enthalpy of Formation

Murad and Hildenbrand[1] studied the gaseous equlibria involving $ZrF_4$, $ZrF_3$, $ZrF_2$, Ca, and CaF, mass–spectrometrically. Ion intensities were measured 3 cal K$^{-1}$·mol$^{-1}$ above threshold over the temperature range *1665–1747* K, and *the equilibrium constants for the reaction* 2 Ca(g) + $ZrF_4$(g) = 2 CaF(g) + $ZrF_2$(g) were calculated. Using the reported equilibrium constants, the enthalpy changes $\Delta_r H^\circ$(298.15 K) of this reaction are evaluated by the 2nd and 3rd law methods to be 15.4 and 50.9 kcal·mol$^{-1}$, respectively. The drift in 3rd law values is 20.4 ± 17.6 cal K$^{-1}$·mol$^{-1}$. Based on the 3rd law *$\Delta_r H^\circ$(298 15 K)* value and $\Delta_f H^\circ$(298.15 K) = 42.85 ± 0.3, −65.0 ± 2, and −400.0 ± 0.5 kcal·mol$^{-1}$ for Ca(g), CaF(g), and $ZrF_4$, respectively, we obtain $\Delta_f H^\circ$($ZrF_2$, g, 298.15 K) = −133.4 ± 5 kcal·mol$^{-1}$(−558.146 ± 20.9 kJ·mol$^{-1}$) which is adopted.

*Using Gibbs energy functions* derived from different molecular constants for the reactants and products, Murad and Hildenbrand[1] derived a 3rd law $\Delta_r H^\circ$(298.15 K) = 42.6 ± 5 and $\Delta_f H^\circ$($ZrF_2$, g, 298.15 K) = −141 ± 5 kcal·mol$^{-1}$, which are in fair agreement with the adopted values.

### Heat Capacity and Entropy

According to the correlations of Charkin and Dyatkina,[2] the $ZrF_2$(g) molecule has an angular configuration. The F–Zr–F angle is estimated at 125°, which is similar to the value reported by Hastie *et al.*[4] for $TiF_2$(g). The F–Zr bond distance is estimated from that of $ZrF_4$(g). The vibrational frequencies are calculated based on the method suggested by Herzberg.[3] The value $\nu_1$ is calculated from the vibrational frequency ($\nu$) of ZrF(g) by use of the relation $\nu_1 = \nu[Zr/(Zr+F)]^{12}$ where Zr and F are gram atomic weights of zirconium and fluorine. $\nu_3$ is derived from $\nu_1$ using the formula $\nu_3 = \nu_1[(Zr_1+2F)/Zr]^{1/2}$ and $\nu_2$ is calculated as 0.44 $\nu_3$ where the value 0.44 is estimated by comparison with the ratios of $\nu_2/\nu_3$ or other related compounds. Ground state quantum weight is taken to be the same as that of $TiF_2$(g). The three principal moments of inertia are: $I_A = 3.5010 \times 10^{-39}$, $I_B = 18.3005 \times 10^{-39}$, and $I_C = 21.8015 \times 10^{-39}$ g·cm$^2$. The electronic levels and quantum weights are estimated to be the same as those of $TiF_2$(g).

### References

[1] E. Murad and D. L. Hildenbrand, J. Chem. Phys. 45, 4751 (1966).
[2] O. P. Charkin and M. E. Dyatkina, Russ. *J. Struct. Chem. 6*, 550 (1965).
[3] G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, (1945).
[4] J. W. Hastie, R. H. Hauge and J. L. Margrave, J. Chem. Phys. 51, 2648 (1969).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p^\circ$ = 0.1 MPa

| T/K | $C_p^\circ$ (J·K$^{-1}$mol$^{-1}$) | $S^\circ$ (J·K$^{-1}$mol$^{-1}$) | $-[G^\circ - H^\circ(T_r)]/T$ (J·K$^{-1}$mol$^{-1}$) | $H^\circ - H^\circ(T_r)$ (kJ·mol$^{-1}$) | $\Delta_f H^\circ$ (kJ·mol$^{-1}$) | $\Delta_f G^\circ$ (kJ·mol$^{-1}$) | log $K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0. | 0. | INFINITE | −11.829 | −555.653 | −555.653 | INFINITE |
| 100 | 35.603 | 238.172 | 322.695 | −8.452 | −556.069 | −561.444 | 293.268 |
| 200 | 43.051 | 265.112 | 287.723 | −4.522 | −557.261 | −566.343 | 147.914 |
| 250 | 46.243 | 275.074 | 284.222 | −2.287 | −557.744 | −568.556 | 118.793 |
| 298.15 | 48.652 | 283.434 | 283.434 | 0. | −558.146 | −570.601 | 99.967 |
| 300 | 48.732 | 283.735 | 283.435 | 0.090 | −558.160 | −570.678 | 99.364 |
| 350 | 50.617 | 291.396 | 284.036 | 2.576 | −558.534 | −572.735 | 85.476 |
| 400 | 52.039 | 298.252 | 285.392 | 5.144 | −558.885 | −574.739 | 75.053 |
| 450 | 53.121 | 304.447 | 287.170 | 7.774 | −559.226 | −576.700 | 66.942 |
| 500 | 53.956 | 310.089 | 289.184 | 10.452 | −559.567 | −578.624 | 60.448 |
| 600 | 55.128 | 320.038 | 293.520 | 15.911 | −560.273 | −582.369 | 50.700 |
| 700 | 55.886 | 328.597 | 297.934 | 21.464 | −561.038 | −585.992 | 43.727 |
| 800 | 56.405 | 336.095 | 302.245 | 27.080 | −561.881 | −589.501 | 38.490 |
| 900 | 56.787 | 342 762 | 306.383 | 32.741 | −562.823 | −592.898 | 34.411 |
| 1000 | 57.094 | 348.761 | 310.326 | 38.435 | −563.874 | −596.184 | 31.141 |
| 1100 | 57.368 | 354.216 | 314.072 | 44.158 | −565.042 | −599.360 | 28.461 |
| 1200 | 57.638 | 359.219 | 317.628 | 49.908 | −570.039 | −602.202 | 26.213 |
| 1300 | 57.923 | 363.844 | 321.008 | 55.686 | −570.899 | −604.848 | 24.303 |
| 1400 | 58.233 | 368.147 | 324.223 | 61.494 | −571.793 | −607.426 | 22.663 |
| 1500 | 58.572 | 372.176 | 327.287 | 67.334 | −572.727 | −609.939 | 21.240 |
| 1600 | 58.938 | 375.968 | 330.212 | 73.209 | −573.707 | −612.388 | 19.992 |
| 1700 | 59.329 | 379.553 | 333.010 | 79.123 | −574.740 | −614.774 | 18.890 |
| 1800 | 59.738 | 382.955 | 335.691 | 85.076 | −575.833 | −617.097 | 17.908 |
| 1900 | 60.158 | 386.197 | 338.265 | 91.070 | −576.991 | −619.359 | 17.027 |
| 2000 | 60.583 | 389.293 | 340.739 | 97.107 | −578.221 | −621.557 | 16.233 |
| 2100 | 61.006 | 392.259 | 343.122 | 103.187 | −579.532 | −623.692 | 15.513 |
| 2200 | 61.423 | 395.107 | 345.421 | 109.308 | −602.253 | −625.017 | 14.840 |
| 2300 | 61.827 | 397.846 | 347.641 | 115.471 | −604.163 | −626.009 | 14.217 |
| 2400 | 62.217 | 400.486 | 349.788 | 121.673 | −606.028 | −626.918 | 13.645 |
| 2500 | 62.589 | 403.033 | 351.868 | 127.914 | −607.846 | −627.751 | 13.116 |
| 2600 | 62.942 | 405.495 | 353.883 | 134.191 | −609.616 | −628.512 | 12.627 |
| 2700 | 63.275 | 407.877 | 355.839 | 140.502 | −611.335 | −629.206 | 12.173 |
| 2800 | 63.588 | 410.184 | 357.739 | 146.845 | −613.003 | −629.838 | 11.750 |
| 2900 | 63.882 | 412.420 | 359.586 | 153.219 | −614.619 | −630.410 | 11.355 |
| 3000 | 64.157 | 414.591 | 361.384 | 159.621 | −616.183 | −630.928 | 10.985 |
| 3100 | 64.415 | 416.698 | 363.134 | 166.050 | −617.692 | −631.394 | 10.639 |
| 3200 | 64.657 | 418.747 | 364.840 | 172.503 | −619.149 | −631.813 | 10.313 |
| 3300 | 64.884 | 420.741 | 366.504 | 178.980 | −620.551 | −632.187 | 10.007 |
| 3400 | 65.098 | 422.681 | 368.128 | 185.480 | −621.900 | −632.519 | 9.717 |
| 3500 | 65.300 | 424.571 | 369.714 | 192.000 | −623.196 | −632.812 | 9.444 |
| 3600 | 65.492 | 426.413 | 371.263 | 198.539 | −624.439 | −633.069 | 9.186 |
| 3700 | 65.674 | 428.210 | 372.778 | 205.098 | −625.629 | −633.293 | 8.940 |
| 3800 | 65.848 | 429.964 | 374.260 | 211.674 | −626.768 | −633.485 | 8.708 |
| 3900 | 66.016 | 431.676 | 375.710 | 218.267 | −627.855 | −633.647 | 8.487 |
| 4000 | 66.176 | 433.350 | 377.130 | 224.877 | −628.891 | −633.782 | 8.276 |
| 4100 | 66.331 | 434.986 | 378.522 | 231.502 | −629.878 | −633.892 | 8.076 |
| 4200 | 66.481 | 436.586 | 379.885 | 238.143 | −630.816 | −633.978 | 7.885 |
| 4300 | 66.625 | 438.152 | 381.222 | 244.798 | −631.707 | −634.043 | 7.702 |
| 4400 | 66.765 | 439.685 | 382.533 | 251.468 | −632.550 | −634 088 | 7.528 |
| 4500 | 66.901 | 441.187 | 383.820 | 258.151 | −633.347 | −634.113 | 7.361 |
| 4600 | 67.033 | 442.659 | 385.083 | 264.848 | −634.099 | −634.122 | 7.201 |
| 4700 | 67.160 | 444.102 | 386.324 | 271.557 | −634.808 | −634.115 | 7.047 |
| 4800 | 67.283 | 445.517 | 387.542 | 278.280 | −1196.410 | −622.476 | 6.774 |
| 4900 | 67.402 | 446.906 | 388.740 | 285.014 | −1196.686 | −610.516 | 6.508 |
| 5000 | 67.517 | 448.269 | 389.917 | 291.760 | −1196.939 | −598.551 | 6.253 |
| 5100 | 67.627 | 449.607 | 391.074 | 298.517 | −1197.169 | −586.581 | 6.008 |
| 5200 | 67.732 | 450.921 | 392.212 | 305.285 | −1197.375 | −574.606 | 5.772 |
| 5300 | 67.833 | 452.212 | 393.332 | 312.064 | −1197.557 | −562.628 | 5.545 |
| 5400 | 67.929 | 453.481 | 394.434 | 318.852 | −1197.715 | −550.647 | 5.326 |
| 5500 | 68.020 | 454.728 | 395.519 | 325.649 | −1197.850 | −538.663 | 5.116 |
| 5600 | 68.105 | 455.955 | 396.588 | 332.455 | −1197.960 | −526.677 | 4.913 |
| 5700 | 68.186 | 457.161 | 397.640 | 339.270 | −1198.047 | −514.689 | 4.717 |
| 5800 | 68.261 | 458.347 | 398.676 | 346.092 | −1198.110 | −502.700 | 4.527 |
| 5900 | 68.330 | 459.515 | 399.698 | 352.922 | −1198.150 | −490.709 | 4.344 |
| 6000 | 68.394 | 460.664 | 400.704 | 359.758 | −1198.165 | −478.719 | 4.168 |

PREVIOUS December 1969 (1 atm) CURRENT: December 1969 (1 bar)

Iron Fluoride (FeF$_3$) CRYSTAL $M_r$ = 112.842209

$\Delta_f H°$(0 K) = Unknown

$S°$(298.15 K) = [98.324 ± 8.4] J·K$^{-1}$·mol$^{-1}$ $\Delta_f H°$(298 15 K) = −1041.816 ± 12.6 kJ·mol$^{-1}$

## Enthalpy of Formation

The equilibrium pressures for the reaction 2 FeF$_3$(cr) + H$_2$(g) = 2 FeF$_2$(cr) + 2 HF(g) have been measured at temperatures 623, 723, and 823 K by Jellinek and Rudat.[1] Using the reported data, the enthalpy change of the reaction was evaluated as 37.9 and 31.3 kcal·mol$^{-1}$ by the 3rd and 2nd law, respectively. The corresponding $\Delta_f H°$(FeF$_3$, cr, 298 15 K) values are calculated to be −252.4 and −249 2 kcal·mol$^{-1}$. The equilibrium constants for the reaction 2 FeF$_3$(cr) + 3 H$_2$O(g) = Fe$_2$O$_3$(cr) + 6 HF(g) were determined by Domange [2] Based on the 3rd law value of $\Delta_r H°$(298 15 K), 62.0 kcal·mol$^{-1}$, the $\Delta_f H°$(FeF$_3$, cr, 298.15 K) was calculated as −237.4 kcal·mol$^{-1}$ The value of $\Delta_f H°$(298.15 K) for FeF$_3$(cr) is selected to be −249 ± 3 kcal mol$^{-1}$.

## Heat Capacity and Entropy

The heat capacities of FeF$_3$(cr) at temperatures 100–450 K were determined by Bizette *et al.*[3] The results were presented graphically by plotting $C_p°$ vs T. The $C_p°$ curve shows a peak at 367 K An antiferromagnetic transition at about 394 K was reported by Wollan *et al.*[4] The heat capacities above 450 K and $S°$(298.15 K) were estimated by comparison with those for FeCl$_3$(cr), AlCl$_3$(cr) and AlF$_3$(cr).

## Sublimation Data

The phenomenon that FeF$_3$(cr) sublimes without fusion at temperatures near 1000°C has been observed and reported by Poulenc.[5] Based on this data, the value of $T_{sub}$ was estimated. The value of heat of sublimation, $\Delta_{sub}H°$(298 15 K), is calculated using an estimated entropy of sublimation, $\Delta_{sub}S°$ = 40 cal K$^{-1}$·mol$^{-1}$ in order to have $\Delta_r G°$(1200 K) = 0 for the reaction FeF$_3$(cr) = FeF$_3$(g).

## References

[1] Jellinek and A. Rudat, Z. anorg. allg. Chem. **175**, 281 (1928).
[2] Domange, Ann. Chim. 7, 225 (1937).
[3] Bizette, R. Mainard and J Picard, Comp Rend. 5508 (1965).
[4] O Wollan, H R Child, W C. Koehler and M. K. Wilkinson, Phys. Rev. **112**, 1132 (1958).
[5] Poulenc, Ann. Chim. Phys. (7), **2**, 1 (1894).

Iron Fluoride (FeF$_3$) F$_3$Fe1(cr)

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| $T$/K | $C_p°$ (J·K$^{-1}$mol$^{-1}$) | $S°$ (J·K$^{-1}$mol$^{-1}$) | $-[G°-H°(T_r)]/T$ (J·K$^{-1}$mol$^{-1}$) | $H°-H°(T_r)$ (kJ·mol$^{-1}$) | $\Delta_f H°$ (kJ·mol$^{-1}$) | $\Delta_f G°$ (kJ·mol$^{-1}$) | log $K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 91.002 | 98 324 | 98.324 | 0. | −1041.816 | −972.293 | 170.342 |
| 300 | 91.630 | 98.889 | 98.326 | 0.169 | −1041.780 | −971.862 | 169.216 |
| 367.000 | 113 047 | 119.010 | 100.268 | 6.878 | $C_p$ LAMBDA MAXIMUM TRANSITION | | |
| 367.000 | 113 408 | 119.021 | 100.268 | 6.882 | | | |
| 400 | 96.371 | 127.516 | 102.176 | 10.136 | −1039.270 | −948.929 | 123.917 |
| 500 | 95.667 | 148.882 | 109.462 | 19 710 | −1037.598 | −926.547 | 96.796 |
| 600 | 96 818 | 166.429 | 117.536 | 29.336 | −1036.268 | −904.466 | 78.741 |
| 700 | 98.073 | 181 448 | 125.619 | 39.080 | −1035.177 | −882.588 | 65.860 |
| 800 | 99.328 | 194.626 | 133.438 | 48.950 | −1034.335 | −860.851 | 56.208 |
| 900 | 100.583 | 206.397 | 140.902 | 58.946 | −1033.850 | −839.199 | 48.706 |
| 1000 | 101.839 | 217.060 | 147.993 | 69.067 | −1034 011 | −817.571 | 42.706 |
| 1100 | 103.094 | 226.825 | 154.722 | 79.314 | −1034.986 | −795.865 | 37.792 |
| 1200 | 104.349 | 235.849 | 161.111 | 89.686 | −1035.323 | −774.130 | 33.697 |
| 1300 | 105.604 | 244.251 | 167.187 | 100.183 | −1033.923 | −752.421 | 30.233 |
| 1400 | 106.859 | 252.123 | 172.976 | 110.807 | −1032.513 | −730.820 | 27.267 |
| 1500 | 108.115 | 259.539 | 178.502 | 121.555 | −1031.091 | −709.320 | 24 701 |
| 1600 | 109.370 | 266.556 | 183.788 | 132.429 | −1029.654 | −687.915 | 22.458 |
| 1700 | 110.625 | 273.224 | 188.854 | 143.429 | −1029.151 | −666.582 | 20.482 |
| 1800 | 111.880 | 279.583 | 193 719 | 154.554 | −1028.012 | −645.288 | 18.726 |
| 1900 | 113 135 | 285.666 | 198.400 | 165.805 | −1040.947 | −623.355 | 17 137 |
| 2000 | 114.391 | 291.501 | 202.910 | 177.182 | −1039 994 | −601.400 | 15.707 |

PREVIOUS: CURRENT: September 1965

Iron Fluoride (FeF$_3$) F$_3$Fe$_1$(cr)

## Iron Fluoride ($FeF_3$) IDEAL GAS $M_r = 112.842209$ Iron Fluoride ($FeF_3$) $F_3Fe_1(g)$

$S°(298.15\ K) = [304.236]\ J·K^{-1}·mol^{-1}$

$\Delta_fH°(0\ K) = [-817.965 \pm 20.9]\ kJ·mol^{-1}$
$\Delta_fH°(298.15\ K) = [-820.901 \pm 20.9]\ kJ·mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ | <br>$\nu$, cm$^{-1}$ |
|---|---|
| [600](1) | [800](2) |
| [250](1) | [220](2) |

Ground State Quantum Weight: [1] $\sigma = [6]$
Point Group: $[D_{3h}]$
Bond Distance: Fe–F = [1.9] Å
Bond Angle: F–Fe–F = [120]°
Product of the Moments of Inertia: $I_AI_BI_C = [9.971132 \times 10^{-114}]\ g^3·cm^6$

### Enthalpy of Formation

The value of $\Delta_fH°(FeF_3, g, 298.15\ K)$ is calculated from $\Delta_{sub}H°(298.15\ K)$ and $\Delta_fH°(298.15\ K)$ for $FeF_3(cr)$. The value $\Delta_{sub}H°(298.15\ K) = 65.5\ kcal·mol^{-1}$ is derived from $\Delta_{sub}H°(1200\ K)$. Refer to the crystal table for details.

### Heat Capacity and Entropy

The molecular structure, bond distance and angle are estimated by comparison with those for $AlF_3(g)$. The vibrational frequencies are estimated by comparison with those for $AlF_3(g)$, $TiF_3(g)$ and $ZrF_3(g)$. The three principal moments of inertia are: $I_A = I_B = 17.0833 \times 10^{-39}$ and $I_C = 34.1666 \times 10^{-39}\ g·cm^2$.

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −14.808 | −817.965 | −817.965 | INFINITE |
| 100 | 44.171 | 244.781 | 356.426 | −11.164 | −819.104 | −817.420 | 426.977 |
| 200 | 57.084 | 279.760 | 309.982 | −6.044 | −820.147 | −815.313 | 212.938 |
| 250 | 61.796 | 293.020 | 305.295 | −3.069 | −820.563 | −814.055 | 170.088 |
| 298.15 | 65.546 | 304.236 | 304.236 | 0. | −820.901 | −812.771 | 142.394 |
| 300 | 65.676 | 304.642 | 304.238 | 0.121 | −820.913 | −812.720 | 141.507 |
| 350 | 68.783 | 315.009 | 305.049 | 3.486 | −821.218 | −811.330 | 121.084 |
| 400 | 71.241 | 324.360 | 306.888 | 6.989 | −821.502 | −809.898 | 105.762 |
| 450 | 73.180 | 332.868 | 309.309 | 10.601 | −821.788 | −808.431 | 93.840 |
| 500 | 74.717 | 340.661 | 312.060 | 14.300 | −822.092 | −806.930 | 84.299 |
| 600 | 76.939 | 354.494 | 318.009 | 21.891 | −822.797 | −803.834 | 69.980 |
| 700 | 78.415 | 366.472 | 324.096 | 29.663 | −823.678 | −800.607 | 59.742 |
| 800 | 79.434 | 377.014 | 330.065 | 37.559 | −824.812 | −797.237 | 52.054 |
| 900 | 80.162 | 386.414 | 335.813 | 45.541 | −826.340 | −793.704 | 46.065 |
| 1000 | 80.699 | 394.889 | 341.304 | 53.585 | −828.578 | −789.968 | 41.264 |
| 1100 | 81.105 | 402.600 | 346.531 | 61.676 | −831.709 | −785.941 | 37.321 |
| 1200 | 81.418 | 409.672 | 351.503 | 69.803 | −834.291 | −781.685 | 34.026 |
| 1300 | 81.665 | 416.199 | 356.231 | 77.957 | −835.234 | −777.264 | 31.231 |
| 1400 | 81.863 | 422.258 | 360.734 | 86.134 | −836.270 | −772.766 | 28.832 |
| 1500 | 82.025 | 427.912 | 365.026 | 94.329 | −837.402 | −768.191 | 26.751 |
| 1600 | 82.157 | 433.210 | 369.124 | 102.538 | −838.630 | −763.538 | 24.927 |
| 1700 | 82.268 | 438.194 | 373.041 | 110.760 | −840.905 | −758.785 | 23.315 |
| 1800 | 82.361 | 442.899 | 376.793 | 118.991 | −842.660 | −753.905 | 21.878 |
| 1900 | 82.440 | 447.354 | 380.390 | 127.231 | −858.605 | −748.222 | 20.570 |
| 2000 | 82.508 | 451.585 | 383.845 | 135.479 | −860.782 | −742.356 | 19.388 |
| 2100 | 82.566 | 455.612 | 387.168 | 143.733 | −862.961 | −736.381 | 18.316 |
| 2200 | 82.617 | 459.454 | 390.367 | 151.992 | −865.139 | −730.303 | 17.340 |
| 2300 | 82.661 | 463.127 | 393.451 | 160.256 | −867.309 | −724.125 | 16.445 |
| 2400 | 82.700 | 466.646 | 396.428 | 168.524 | −869.469 | −717.853 | 15.624 |
| 2500 | 82.735 | 470.023 | 399.305 | 176.796 | −871.611 | −711.492 | 14.866 |
| 2600 | 82.765 | 473.268 | 402.087 | 185.071 | −873.732 | −705.045 | 14.165 |
| 2700 | 82.793 | 476.393 | 404.782 | 193.349 | −875.826 | −698.517 | 13.514 |
| 2800 | 82.817 | 479.404 | 407.394 | 201.629 | −877.889 | −691.912 | 12.908 |
| 2900 | 82.839 | 482.311 | 409.927 | 209.912 | −879.917 | −685.234 | 12.342 |
| 3000 | 82.859 | 485.119 | 412.387 | 218.197 | −881.907 | −678.487 | 11.814 |
| 3100 | 82.877 | 487.837 | 414.777 | 226.484 | −883.854 | −671.675 | 11.318 |
| 3200 | 82.893 | 490.468 | 417.102 | 234.772 | −1234.057 | −657.376 | 10.731 |
| 3300 | 82.908 | 493.019 | 419.364 | 243.062 | −1234.012 | −639.355 | 10.120 |
| 3400 | 82.922 | 495.494 | 421.567 | 251.354 | −1233.952 | −621.336 | 9.546 |
| 3500 | 82.934 | 497.898 | 423.713 | 259.647 | −1233.874 | −603.319 | 9.004 |
| 3600 | 82.946 | 500.235 | 425.807 | 267.941 | −1233.780 | −585.304 | 8.493 |
| 3700 | 82.956 | 502.507 | 427.849 | 276.236 | −1233.669 | −567.292 | 8.009 |
| 3800 | 82.966 | 504.720 | 429.843 | 284.532 | −1233.541 | −549.284 | 7.550 |
| 3900 | 82.975 | 506.875 | 431.791 | 292.829 | −1233.397 | −531.279 | 7.116 |
| 4000 | 82.983 | 508.976 | 433.694 | 301.127 | −1233.239 | −513.278 | 6.703 |
| 4100 | 82.991 | 511.025 | 435.555 | 309.426 | −1233.068 | −495.281 | 6.310 |
| 4200 | 82.998 | 513.025 | 437.376 | 317.725 | −1232.884 | −477.288 | 5.936 |
| 4300 | 83.005 | 514.978 | 439.158 | 326.025 | −1232.691 | −459.301 | 5.579 |
| 4400 | 83.011 | 516.886 | 440.903 | 334.326 | −1232.489 | −441.317 | 5.239 |
| 4500 | 83.017 | 518.752 | 442.613 | 342.627 | −1232.281 | −423.338 | 4.914 |
| 4600 | 83.022 | 520.577 | 444.288 | 350.929 | −1232.069 | −405.364 | 4.603 |
| 4700 | 83.028 | 522.362 | 445.930 | 359.232 | −1231.854 | −387.394 | 4.305 |
| 4800 | 83.032 | 524.110 | 447.541 | 367.535 | −1231.640 | −369.429 | 4.020 |
| 4900 | 83.037 | 525.822 | 449.121 | 375.838 | −1231.428 | −351.469 | 3.747 |
| 5000 | 83.041 | 527.500 | 450.672 | 384.142 | −1231.221 | −333.512 | 3.484 |
| 5100 | 83.045 | 529.145 | 452.194 | 392.447 | −1231.021 | −315.560 | 3.232 |
| 5200 | 83.049 | 530.757 | 453.690 | 400.751 | −1230.831 | −297.612 | 2.990 |
| 5300 | 83.052 | 532.339 | 455.159 | 409.056 | −1230.654 | −279.667 | 2.756 |
| 5400 | 83.056 | 533.892 | 456.602 | 417.362 | −1230.492 | −261.725 | 2.532 |
| 5500 | 83.059 | 535.416 | 458.021 | 425.668 | −1230.348 | −243.787 | 2.315 |
| 5600 | 83.062 | 536.912 | 459.417 | 433.974 | −1230.225 | −225.850 | 2.107 |
| 5700 | 83.065 | 538.382 | 460.789 | 442.280 | −1230.127 | −207.916 | 1.905 |
| 5800 | 83.068 | 539.827 | 462.140 | 450.587 | −1230.057 | −189.984 | 1.711 |
| 5900 | 83.070 | 541.247 | 463.469 | 458.893 | −1230.018 | −172.051 | 1.523 |
| 6000 | 83.073 | 542.643 | 464.776 | 467.201 | −1230.014 | −154.120 | 1.342 |

PREVIOUS: September 1965 (1 atm)    CURRENT: September 1965 (1 bar)

## Trifluorosilane ($SiHF_3$) IDEAL GAS $M_r = 86.088649$ Trifluorosilane ($SiHF_3$) $F_3H_1Si_1(g)$

$S°(298.15\ K) = 277.268 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-1193\ 663 \pm 20.9]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-1200.808 \pm 20.9]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|
| 2316(1) | 998(2) |
| 858(1) | 844(2) |
| 425(1) | 306(2) |

Ground State Quantum Weight: [1]  $\sigma = 3$
Point Group: $C_{3v}$
Bond Distances. Si–H = 1.4468 Å; Si–F = 1.5624 Å
Bond Angles: H–Si–F = 110.64°; F–Si–F = 108.28°
Product of the Moments of Inertia: $I_A I_B I_C = 2\ 726959 \times 10^{-114}\ g^3 \cdot cm^6$

### Enthalpy of Formation

There are no reported experimental studies leading to the enthalpy of formation of $SiHF_3(g)$. We estimate this value via a linear interpolation between the established $\Delta_f H°(298.15\ K)$ values of $SiH_4(g)$ and $SiF_4(g)$.[1] The reasonableness of this approach has been demonstrated by Lapidus *et al.*,[2] Hunt and Sirtl,[3] and Seiter and Sirtl.[4] Lapidus *et al.*[2] comparatively examined the thermodynamic properties of halogenated silanes and methanes. Hunt and Sirtl[3] and Seiter and Sirtl[4] studied the chlorinated silanes and proposed a linear $\Delta_f H°$ relationship within the sequence $SiH_4(g)$ to $SiCl_4(g)$.

### Heat Capacity and Entropy

The adopted vibrational frequencies are from the infrared gas phase studies of Buerger *et al.*[5,6] These values are all within ±1 cm$^{-1}$ of the suggested values in the compilation by Shimanouchi,[7] as derived from Newman *et al.*[8]

The adopted bond angles and bond distances are obtained from the microwave spectrum study of six isotopic species of $HSiF_3$.[9] Earlier work by Sheridan and Gordy[10] and Heath *et al.*[11] is in good agreement with these values The moments of inertia are calculated to be $I_A = I_B = 11.6094 \times 10^{-39}\ g\ cm^2$ and $I_C = 20.2329 \times 10^{-39}\ g \cdot cm^2$.

### References

[1] JANAF Thermochemical Tables: $SiH_4(g)$ and $SiF_4(g)$, 6–30–76.
[2] I. I. Lapidus, L. A. Nisel'son, and A. L. Seifer in "Thermophysical Properties of Gases and Liquids," No. 1, V. A. Rabinovich, Ed., Israel Program for Scientific Translations, Jerusalem, pp. 102–135, (1970).
[3] L. P. Hunt and E. Sirtl, J. Electrochem. Soc. **119**, 1741 (1972).
[4] H. Seiter and E. Sirtl, Z. Naturforsch. **21a**, 1956 (1966).
[5] H. Buerger, S. Biedermann, and A. Ruoff, Specrochim. Acta, Part A **27**, 1687 (1971).
[6] H Buerger, S. Biedermann, and A. Ruoff, Spectrochim. Acta, Part A **30**, 1655 (1974).
[7] T. Shimanouchi, J. Phys. Chem. Ref. Data **1**, 189 (1972).
[8] C. Newman, S. R. Polo, and M. K. Wilson, Spectrochim. Acta **15**, 793 (1959).
[9] A. R. Hoy, M. Bertram, and I. M. Mills, J. Mol. Spectrosc. **46**, 429 (1973).
[10] J. Sheridan and W. Gordy, J. Chem. Phys. **19**, 965 (1951).
[11] G. A. Heath, L. F. Thomas, and J. Sheridan, Trans. Faraday Soc. **50**, 779 (1954).

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −13.544 | −1193.663 | −1193.663 | INFINITE |
| 100 | 38.013 | 224.001 | 325.165 | −10.116 | −1196.362 | −1187.787 | 620.436 |
| 200 | 51.293 | 254.467 | 282.691 | −5.645 | −1198.809 | −1178.233 | 307.723 |
| 250 | 57.690 | 266.604 | 278.281 | −2.919 | −1199.886 | −1172.962 | 245.077 |
| 298.15 | 63.485 | 277.268 | 277.268 | 0. | −1200.808 | −1167.691 | 204.575 |
| 300 | 63.696 | 277.662 | 277.269 | 0.118 | −1200.841 | −1167.485 | 203.277 |
| 350 | 69.048 | 287.892 | 278.065 | 3.439 | −1201.662 | −1161.859 | 173.398 |
| 400 | 73.663 | 297.421 | 279.896 | 7.010 | −1202.352 | −1156.125 | 150.974 |
| 450 | 77.588 | 306.330 | 282.343 | 10.794 | −1202.923 | −1150.311 | 133.525 |
| 500 | 80.918 | 314.682 | 285.164 | 14.759 | −1203.391 | −1144.439 | 119.559 |
| 600 | 86.189 | 329.926 | 291.379 | 23.128 | −1204.073 | −1132.579 | 98.600 |
| 700 | 90.118 | 343.521 | 297.875 | 31.952 | −1204.492 | −1120.628 | 83.622 |
| 800 | 93.123 | 355.759 | 304.358 | 41.121 | −1204.724 | −1108.629 | 72.386 |
| 900 | 95.469 | 366.868 | 310.696 | 50.555 | −1204.820 | −1096.610 | 63.646 |
| 1000 | 97.332 | 377.027 | 316.829 | 60.198 | −1204.824 | −1084.586 | 56.653 |
| 1100 | 98.831 | 386.377 | 322.732 | 70.009 | −1204.769 | −1072.565 | 50.932 |
| 1200 | 100.052 | 395.030 | 328.401 | 79 955 | −1204.679 | −1060.550 | 46.165 |
| 1300 | 101.057 | 403.080 | 333.839 | 90.012 | −1204.577 | −1048.543 | 42.131 |
| 1400 | 101.891 | 410.600 | 339.056 | 100.161 | −1204.478 | −1036.545 | 38.674 |
| 1500 | 102.591 | 417.655 | 344.064 | 110.386 | −1204.397 | −1024.552 | 35.678 |
| 1600 | 103.183 | 424.295 | 348.873 | 120.676 | −1204.343 | −1012.565 | 33.057 |
| 1700 | 103.687 | 430.566 | 353.495 | 131.020 | −1254.498 | −1000.133 | 30.730 |
| 1800 | 104.119 | 436.505 | 357.944 | 141.411 | −1254.284 | −985.176 | 28.589 |
| 1900 | 104.492 | 442.145 | 362.228 | 151.842 | −1254.066 | −970.232 | 26.674 |
| 2000 | 104.816 | 447.513 | 366.359 | 162.307 | −1253.847 | −955.298 | 24.950 |
| 2100 | 105.099 | 452.634 | 370.346 | 172.804 | −1253.624 | −940.377 | 23.391 |
| 2200 | 105.347 | 457.529 | 374.199 | 183.326 | −1253.394 | −925.466 | 21.973 |
| 2300 | 105.567 | 462.217 | 377.925 | 193.872 | −1253.156 | −910.565 | 20.680 |
| 2400 | 105.761 | 466.714 | 381.531 | 204.439 | −1252.905 | −895.675 | 19 494 |
| 2500 | 105.934 | 471.035 | 385.025 | 215.024 | −1252.636 | −880.796 | 18.403 |
| 2600 | 106.089 | 475.193 | 388.414 | 225.625 | −1252.347 | −865.928 | 17.397 |
| 2700 | 106.228 | 479.199 | 391.702 | 236.241 | −1252.032 | −851.072 | 16.465 |
| 2800 | 106.353 | 483.065 | 394.897 | 246.870 | −1251.688 | −836.227 | 15.600 |
| 2900 | 106.466 | 486.799 | 398.002 | 257.511 | −1251.312 | −821.396 | 14.795 |
| 3000 | 106.569 | 490.410 | 401.022 | 268.163 | −1250.901 | −806.578 | 14.044 |
| 3100 | 106.662 | 493.906 | 403.962 | 278.825 | −1250.450 | −791.775 | 13.341 |
| 3200 | 106.747 | 497.294 | 406.826 | 289.495 | −1249.960 | −776.987 | 12.683 |
| 3300 | 106.825 | 500.580 | 409.618 | 300.174 | −1249.426 | −762.214 | 12.065 |
| 3400 | 106.896 | 503.770 | 412.340 | 310.860 | −1248.848 | −747.459 | 11.483 |
| 3500 | 106.961 | 506.869 | 414.997 | 321.553 | −1248.225 | −732.721 | 10.935 |
| 3600 | 107.021 | 509.883 | 417.591 | 332.252 | −1631.707 | −707.541 | 10.266 |
| 3700 | 107.077 | 512.816 | 420.125 | 342.957 | −1630.577 | −681.885 | 9.626 |
| 3800 | 107.128 | 515.673 | 422.602 | 353.667 | −1629.402 | −656.261 | 9.021 |
| 3900 | 107.175 | 518.456 | 425.025 | 364.382 | −1628.182 | −630.667 | 8.447 |
| 4000 | 107.220 | 521.170 | 427.394 | 375.102 | −1626.917 | −605.106 | 7.902 |
| 4100 | 107.261 | 523.818 | 429.714 | 385.826 | −1625.606 | −579.577 | 7.384 |
| 4200 | 107.299 | 526.403 | 431.986 | 396.554 | −1624.251 | −554.080 | 6.891 |
| 4300 | 107.334 | 528.928 | 434.211 | 407.286 | −1622.851 | −528.617 | 6.421 |
| 4400 | 107.368 | 531.396 | 436.392 | 418.021 | −1621.408 | −503.186 | 5.974 |
| 4500 | 107.399 | 533.810 | 438.530 | 428.759 | −1619.922 | −477.788 | 5.546 |
| 4600 | 107.428 | 536.170 | 440.627 | 439.501 | −1618.395 | −452.424 | 5.137 |
| 4700 | 107.455 | 538.481 | 442.684 | 450.245 | −1616.826 | −427.094 | 4.747 |
| 4800 | 107.481 | 540.744 | 444.704 | 460.992 | −1615.217 | −401.797 | 4.372 |
| 4900 | 107.505 | 542.960 | 446.686 | 471.741 | −1613.570 | −376.535 | 4.014 |
| 5000 | 107.528 | 545.132 | 448.634 | 482.492 | −1611.885 | −351.306 | 3.670 |
| 5100 | 107.549 | 547.262 | 450.547 | 493.246 | −1610.162 | −326.112 | 3.340 |
| 5200 | 107.569 | 549.350 | 452.427 | 504.002 | −1608 404 | −300.951 | 3.023 |
| 5300 | 107.589 | 551.399 | 454.275 | 514.760 | −1606.611 | −275.824 | 2.718 |
| 5400 | 107.607 | 553.411 | 456.092 | 525.520 | −1604.785 | −250.732 | 2.425 |
| 5500 | 107.624 | 555.385 | 457.880 | 536.282 | −1602.925 | −225.675 | 2.143 |
| 5600 | 107.640 | 557.325 | 459.638 | 547.045 | −1601.034 | −200.651 | 1.872 |
| 5700 | 107.655 | 559.230 | 461.369 | 557.809 | −1599.113 | −175.661 | 1.610 |
| 5800 | 107.670 | 561.102 | 463.072 | 568.576 | −1597.161 | −150.705 | 1.357 |
| 5900 | 107.684 | 562 943 | 464.749 | 579.343 | −1595.181 | −125.783 | 1.114 |
| 6000 | 107.697 | 564.753 | 466.401 | 590.113 | −1593.173 | −100.896 | 0.878 |

PREVIOUS. June 1976 (1 atm)    CURRENT: June 1976 (1 bar)

Trifluorosilane ($SiHF_3$)    $F_3H_1Si_1(g)$

# Hydrogen Fluoride ($H_3F_3$) IDEAL GAS $M_r$ = 60.019029 Hydrogen Fluoride ($H_3F_3$) $F_3H_3(g)$

$S°(298.15\ K) = [288.458 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -869.289 \pm 12.6\ kJ\ mol^{-1}$
$\Delta_f H°(298.15\ K) = -879\ 100 \pm 12.6\ kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm $^{-1}$ |
|---|
| [202](3) |
| [962](3) |
| [552](3) |
| [3060](3) |

Ground State Quantum Weight: 1 $\sigma = [3]$
Point Group: $C_3$
Interatomic Distance: F–F = [2.5] Å
Product of the Moments of Inertia: $I_A I_B I_C = [2.237956 \times 10^{-114}]\ g^3 \cdot cm^6$

## Enthalpy of Formation

The enthalpy of 3 HF(g) → $H_3F_3(g)$ was taken as the mean of 3rd law values which were determined from the equilibrium data of two investigations. Briegleb and Strohmeier[1] measured the vapor density of HF between 20 and 60°C and between 50 and 650 torr. Franck and Meyer[2] measured $C_p°$ between −20 and 100°C and between 100 and 700 torr. Each investigation evaluted $K_p$ at n = 2, 3, 4, ... for the reactions n(HF) → $(HF)_n$ and reported 2nd law values of $\Delta_r H°$ and $\Delta_r S°$. At $n = 3$, their 2nd law values differed by 2.7 $kcal \cdot mol^{-1}$ which was taken as an estimate of error, while the 3rd law values differed by 0.20 $kcal \cdot mol^{-1}$. Using $\Delta_r H°(298.15\ K) = -14.69\ kcal \cdot mol^{-1}$ and auxiliary JANAF data[3] gives the enthalpy of formation of $H_3F_3(g)$.

## Heat Capacity and Entropy

The molecular structure of $H_3F_3$ was assumed as planar with the F atoms forming the vertices of a regular triangle and with the H atoms also lying on the circumscribed circle. That rings are more stable than open chains was confirmed by *Del Bene and Pople's*[4] *theoretical* molecular-orbital studies on HF polymers. The length of side (F-F axis) was taken from Atoji and Lipscomb's[5] X-studies of solid HF (F–F = 2.49 Å) and agrees with 2.52 Å which Janzen and Bartell[6] determined for HF gaseous polymers by electron diffraction. Vibrational frequencies were taken from Kittelberger and Hornig's[7] work on crystalline HF. Huong and Couzi[8] and Smith[9] have made spectral studies of the gas phase in the range from 350 to 4000 $cm^{-1}$.

The National Bureau of Standards prepared this table[10] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[10] we recalculate the table in terms of 1973 fundamental constants,[11] 1975 atomic weights,[12] and current JANAF reference states for the elements.

## References

[1] G. Briegleb and W. Strohmeier, Z. Elektrochem. 57, 668 (1953).
[2] E. U. Franck and F. Meyer, Z. Elektrochem. 63, 571 (1959).
[3] JANAF Thermochemical Tables: HF(g), 6-30-77.
[4] J. E. Del Bene and J. A. Pople, J. Chem. Phys. 55, 2296 (1971).
[5] M. Atoji and W. N. Lipscomb, Acta Cryst. 7, 173 (1954).
[6] J. Janzen and L. S. Bartell, J. Chem. Phys. 50, 3611 (1969).
[7] J. S. Kittelberger and D. F. Hornig, J. Chem. Phys. 46, 3099 (1967).
[8] P. V. Huong and M. Couzi, J. Chim. Phys. 66, 1309 (1969).
[9] D. F. Smith, J. Chem. Phys. *28*, 1040 (1958); 48, 1429 (1968).
[10] S. Abramowitz et al., U.S. Nat. Bur. Stand. Report 10904, 239, (1972).
[11] CODATA Task Group on Fundamental Constants, CODATA Bulletin 11, (December 1973).
[12] IUPAC Commission on Atomic Weights, Pure Appl. Chem. 47, 75 (1976).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0 | INFINITE | −16.127 | −869.289 | −869.289 | INFINITE |
| 100 | 46.713 | 223.110 | 346.863 | −12.375 | −874.397 | −856.043 | 447.151 |
| 200 | 63.124 | 260.767 | 295.010 | −6.849 | −877.304 | −836.438 | 218.455 |
| 250 | 70.045 | 275.612 | 289.675 | −3.516 | −878.320 | −826.100 | 172.604 |
| 298.15 | 75.849 | 288.458 | 288.458 | 0. | −879.100 | −815.968 | 142.954 |
| 300 | 76.055 | 288.928 | 288.460 | 0.141 | −879.127 | −815.577 | 142.005 |
| 350 | 81.120 | 301.044 | 289.405 | 4.074 | −879.750 | −804.933 | 120.130 |
| 400 | 85.327 | 312.160 | 291.564 | 8.238 | −880.217 | −794.212 | 103.713 |
| 450 | 88.821 | 322.418 | 294.430 | 12.595 | −880.552 | −783.440 | 90.939 |
| 500 | 91.760 | 331.932 | 297.710 | 17.111 | −880.776 | −772.636 | 80.717 |
| 600 | 96.495 | 349.099 | 304.876 | 26.534 | −880.957 | −750.986 | 65.379 |
| 700 | 100.303 | 364.269 | 312.298 | 36.380 | −880.846 | −729.329 | 54.423 |
| 800 | 103.575 | 377.881 | 319.659 | 46.577 | −880.492 | −707.705 | 46.208 |
| 900 | 106.478 | 390.251 | 326.826 | 57.082 | −879.930 | −686.139 | 39.822 |
| 1000 | 109.082 | 401.607 | 333.744 | 67.863 | −879.190 | −664 645 | 34.717 |
| 1100 | 111.416 | 412.115 | 340.397 | 78.890 | −878.301 | −643.232 | 30.545 |
| 1200 | 113.502 | 421.900 | 346.786 | 90.138 | −877.290 | −621.906 | 27.071 |
| 1300 | 115.359 | 431.060 | 352.920 | 101.582 | −876.180 | −600.668 | 24.135 |
| 1400 | 117.008 | 439.671 | 358.812 | 113.202 | −874.992 | −579.519 | 21.622 |
| 1500 | 118.470 | 447 794 | 364.476 | 124.978 | −873.744 | −558.457 | 19.447 |
| 1600 | 119.767 | 455.482 | 369.925 | 136.891 | −872.451 | −537.480 | 17.547 |
| 1700 | 120.917 | 462.778 | 375.175 | 148.926 | −871.124 | −516.585 | 15.873 |
| 1800 | 121.938 | 469.719 | 380.236 | 161 070 | −869.771 | −495.769 | 14.387 |
| 1900 | 122.847 | 476.337 | 385.121 | 173.310 | −868.398 | −475.028 | 13.059 |
| 2000 | 123.657 | 482.659 | 389.841 | 185.636 | −867.008 | −454.360 | 11.867 |
| 2100 | 124.380 | 488.710 | 394.406 | 198.039 | −865 604 | −433.763 | 10.789 |
| 2200 | 125.029 | 494.512 | 398.825 | 210.510 | −864.186 | −413.232 | 9.811 |
| 2300 | 125.611 | 500.082 | 403.108 | 223.042 | −862.752 | −392.766 | 8.920 |
| 2400 | 126.135 | 505.440 | 407.260 | 235.630 | −861.301 | −372.363 | 8.104 |
| 2500 | 126.608 | 510.598 | 411.291 | 248.267 | −859.831 | −352.020 | 7.355 |
| 2600 | 127.037 | 515.573 | 415.207 | 260.950 | −858.338 | −331.737 | 6.665 |
| 2700 | 127.425 | 520.374 | 419 014 | 273.673 | −856.821 | −311.512 | 6.027 |
| 2800 | 127.779 | 525.015 | 422.717 | 286.434 | −855.276 | −291.344 | 5.435 |
| 2900 | 128.101 | 529.505 | 426.323 | 299.228 | −853.701 | −271.231 | 4.885 |
| 3000 | 128.395 | 533.853 | 429.835 | 312.053 | −852.093 | −251.173 | 4.373 |
| 3100 | 128.665 | 538.067 | 433.259 | 324.906 | −850.452 | −231.170 | 3.895 |
| 3200 | 128.912 | 542.156 | 436.598 | 337.785 | −848.775 | −211.220 | 3.448 |
| 3300 | 129.139 | 546.126 | 439.857 | 350.688 | −847.061 | −191.322 | 3.028 |
| 3400 | 129.349 | 549.985 | 443.040 | 363.613 | −845.309 | −171.478 | 2.634 |
| 3500 | 129.543 | 553.737 | 446.149 | 376.557 | −843.520 | −151.685 | 2.264 |
| 3600 | 129.722 | 557.389 | 449.189 | 389.521 | −841.691 | −131.944 | 1.914 |
| 3700 | 129.887 | 560.945 | 452.161 | 402.501 | −839.825 | −112.254 | 1.585 |
| 3800 | 130.041 | 564.411 | 455.070 | 415.498 | −837.920 | −92.616 | 1.273 |
| 3900 | 130.184 | 567.791 | 457.917 | 428.509 | −835.979 | −73.027 | 0.978 |
| 4000 | 130.318 | 571.089 | 460.705 | 441.534 | −834.000 | −53.490 | 0.699 |
| 4100 | 130.442 | 574.308 | 463.437 | 454.572 | −831.986 | −34.002 | 0.433 |
| 4200 | 130.558 | 577.453 | 466.114 | 467.622 | −829.937 | −14.563 | 0.181 |
| 4300 | 130.667 | 580.526 | 468.739 | 480.684 | −827.854 | 4.825 | −0.059 |
| 4400 | 130.768 | 583.531 | 471.314 | 493.756 | −825.738 | 24.166 | −0.287 |
| 4500 | 130.864 | 586.471 | 473.841 | 506.837 | −823.591 | 43.458 | −0.504 |
| 4600 | 130.953 | 589.349 | 476.321 | 519.928 | −821.413 | 62.701 | −0.712 |
| 4700 | 131.037 | 592.166 | 478.756 | 533.028 | −819.206 | 81.897 | −0.910 |
| 4800 | 131.116 | 594.925 | 481.147 | 546.135 | −816.970 | 101.047 | −1.100 |
| 4900 | 131.191 | 597.630 | 483.497 | 559.251 | −814.706 | 120.148 | −1.281 |
| 5000 | 131.261 | 600.281 | 485.806 | 572.373 | −812.415 | 139.204 | −1.454 |
| 5100 | 131.328 | 602.881 | 488.076 | 585.503 | −810.099 | 158.213 | −1.620 |
| 5200 | 131.391 | 605.432 | 490.309 | 598.639 | −807.757 | 177.177 | −1.780 |
| 5300 | 131.450 | 607.935 | 492.504 | 611.781 | −805.390 | 196.096 | −1.933 |
| 5400 | 131.507 | 610.392 | 494.665 | 624.929 | −802.998 | 214.969 | −2.079 |
| 5500 | 131.560 | 612.806 | 496.791 | 638.082 | −800.582 | 233.797 | −2.220 |
| 5600 | 131.611 | 615.177 | 498.884 | 651.241 | −798.143 | 252.583 | −2.356 |
| 5700 | 131.659 | 617.507 | 500.945 | 664.404 | −795.679 | 271.324 | −2.486 |
| 5800 | 131.704 | 619.797 | 502.974 | 677.572 | −793.192 | 290.022 | −2.612 |
| 5900 | 131.748 | 622.049 | 504.973 | 690.745 | −790.681 | 308.676 | −2.733 |
| 6000 | 131.789 | 624.263 | 506.943 | 703.922 | −788.145 | 327.287 | −2.849 |

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

## Lithium Fluoride ((LiF)$_3$) IDEAL GAS $M_r = 77.818209$

$S°(298\ 15\ \mathrm{K}) = [318.087 \pm 8.4]\ \mathrm{J\ K^{-1}{\cdot}mol^{-1}}$

$\Delta_f H°(0\ \mathrm{K}) = -1510.529 \pm 25.1\ \mathrm{kJ{\cdot}mol^{-1}}$
$\Delta_f H°(298.15\ \mathrm{K}) = -1517\ 202 \pm 25\ 1\ \mathrm{kJ\ mol^{-1}}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm $^{-1}$ | $\nu$, cm $^{-1}$ |
|---|---|
| 280 (1) | 530 (2) |
| [430](1) | 755 (2) |
| [640](1) | 245 (2) |
| [480](1) | [140](2) |

Ground State Quantum Weight: [1] $\sigma = 6$
Point Group: [$D_{3h}$]
Bond Distance: Li–F = [1.68] Å
Bond Angles: F–Li–F = [120]°; Li–F–Li = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.212852 \times 10^{-113}]\ \mathrm{g^3{\cdot}cm^6}$

### Enthalpy of Formation

$\Delta_f H°(\mathrm{Li_3F_3}$, g, 298.15 K) is derived based on the adopted value $\Delta_r H°(298.15\ \mathrm{K}) = 79.73\ \mathrm{kcal{\cdot}mol^{-1}}$ for the reaction $3\mathrm{LiF(cr)} = \mathrm{Li_3F_3(g)}$, using $\Delta_f H$(LiF, cr, 298.15 K) = $-147\ 45\ \mathrm{kcal{\cdot}mol^{-1}}$. The $\Delta_r H°(298.15\ \mathrm{K})$ value is calculated to be 73.9 kcal·mol$^{-1}$ at 1000 K, which is consistent with the values $\Delta_r H°(1000\ \mathrm{K}) = 73.9 \pm 3$ and $74.9 \pm 1$ kcal·mol$^{-1}$ reported by Buchler and Stauffer[1] and Akishin *et al.*,[2] respectively. Using the adopted $\Delta_f H°(298\ 15\ \mathrm{K})$ values for monomer, dimer, and trimer, we also evaluate the value $\Delta_r H°(1073\ \mathrm{K}) = 53.8$ kcal mol$^{-1}$ for the reaction $\mathrm{Li_3F_3(g)} = \mathrm{Li_2F_2(g)} + \mathrm{LiF(g)}$ which is in agreement with the value $50 < \Delta_r H°(1073\ \mathrm{K}) < 65$ kcal·mol$^{-1}$ reported by Porter and Schoonmaker.[3] Rothberg *et al.*[4] have determined the partial pressures of LiF monomer, dimer, and trimer in the temperature range 980–1070 K, using the molecular-beam velocity-selector method.[5] However, the total pressures derived from these data are too low in comparison with the other reported vapor pressures. Thus their data are not adopted for evaluation.

### Heat Capacity and Entropy

The molecular structure is assumed to be the same as that of the BeO trimer. The Li–F bond distance is taken from that of the $\mathrm{Li_2F_2}$ molecule determined by Akishin and Rambidi.[6] Four vibrational frequencies, $A_2''$ and three E', are reported by Snelson[7] from analysis of the infrared spectra of LiF Using the matrix isolation technique. The reported frequencies are corrected to the average isotopic species The other four frequencies, $E_2''$ and three A', are estimated by comparison with those for the isoelectronic molecule $\mathrm{Be_3O_3}$ The three principal moments of inertia are: $I_A = I_B = 18.2358 \times 10^{-39}$ and $I_C = 36\ 4717 \times 10^{-39}\ \mathrm{g{\cdot}cm^2}$.

### References

[1] A Buchler and J. C. Stauffer, Thermodynamics, Vol. I, International Atomic Agency, Vienna, 271, (1966).
[2] P A. Akishin, L. N. Gorokhov, and L. N. Sidorov, Russ. J. Phys. Chem. 33, 648 (1959).
[3] R F. Porter and R. C. Schoonmaker, J. Chem. Phys. 29, 1070 (1958).
[4] G M. Rothberg, M. Eisenstadt, and P. Kusch, J. Chem. Phys. 30, 517 (1959).
[5] R C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956); 27, 981 (1957).
[6] P A. Akinshin and N. G. Rambid, Z. Physik. Chem. 213, 111 (1960).
[7] A Snelson, IITRI-U6001-13, (14 May 1963)-(12 August 1966), Illinois Institute of Technology Research Institute, Chicago, Illinois.

## Lithium Fluoride ((LiF)$_3$) $\mathrm{F_3Li_3(g)}$

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0 | 0 | INFINITE | -20.431 | -1510.529 | -1510.529 | INFINITE |
| 100 | 55.829 | 232.778 | 396.049 | -16.327 | -1512.271 | -1507 790 | 787.589 |
| 200 | 84.315 | 280.714 | 326.946 | -9.247 | -1515.108 | -1502.160 | 392.324 |
| 250 | 94.780 | 300.702 | 319.734 | -4.758 | -1516.258 | -1498.785 | 313.154 |
| 298 15 | 102.501 | 318.087 | 318.087 | 0. | -1517.202 | -1495.332 | 261.976 |
| 300 | 102 757 | 318 722 | 318.089 | 0.190 | -1517.236 | -1495.197 | 260.337 |
| 350 | 108.755 | 335.035 | 319.364 | 5.485 | -1518 113 | -1491.453 | 222.587 |
| 400 | 113.278 | 349.866 | 322.264 | 11.041 | -1519.015 | -1487.584 | 194.259 |
| 450 | 116 724 | 363 416 | 326.095 | 16.795 | -1520.032 | -1483.596 | 172.211 |
| 500 | 119.386 | 375.858 | 330.457 | 22.700 | -1530.203 | -1478.565 | 154.465 |
| 600 | 123 131 | 397.982 | 339.914 | 34.840 | -1532.223 | -1468.041 | 127.804 |
| 700 | 125.556 | 417.157 | 349.610 | 47.283 | -1533.883 | -1457.208 | 108.738 |
| 800 | 127.203 | 434.037 | 359.130 | 59.926 | -1535.343 | -1446.154 | 94.424 |
| 900 | 128.368 | 449.091 | 368.304 | 72.708 | -1536.716 | -1434.922 | 83.281 |
| 1000 | 129.220 | 462.662 | 377.073 | 85.589 | -1538.028 | -1423.541 | 74.358 |
| 1100 | 129.860 | 475.009 | 385.423 | 98.545 | -1539.296 | -1412.030 | 67.052 |
| 1200 | 130.352 | 486.330 | 393.367 | 111.556 | -1540.531 | -1400.406 | 60.958 |
| 1300 | 130.739 | 496.780 | 400.925 | 124.612 | -1541.746 | -1388.680 | 55.798 |
| 1400 | 131.048 | 506.481 | 408.122 | 137.702 | -1542.940 | -1376.860 | 51.371 |
| 1500 | 131.299 | 515.531 | 414.985 | 150.819 | -1544.111 | -1364.957 | 47.532 |
| 1600 | 131.506 | 524.012 | 421.537 | 163.960 | -1545.262 | -1352.975 | 44.170 |
| 1700 | 131.677 | 531.989 | 427.801 | 177.119 | -1982.103 | -1319.394 | 40.540 |
| 1800 | 131.822 | 539.520 | 433.801 | 190.294 | -1980.958 | -1280.444 | 37.158 |
| 1900 | 131.944 | 546.651 | 439.554 | 203.483 | -1979.823 | -1241.558 | 34.133 |
| 2000 | 132.049 | 553.421 | 445.080 | 216.683 | -1978.696 | -1202.731 | 31 412 |
| 2100 | 132.140 | 559.866 | 450.394 | 229.892 | -1977.576 | -1163.961 | 28.952 |
| 2200 | 132.218 | 566.015 | 455.510 | 243.110 | -1976.463 | -1125.243 | 26.717 |
| 2300 | 132.287 | 571.894 | 460 444 | 256.336 | -1975.356 | -1086.576 | 24.677 |
| 2400 | 132.347 | 577.525 | 465.206 | 269.567 | -1974.253 | -1047.957 | 22.808 |
| 2500 | 132 400 | 582.929 | 469.807 | 282.805 | -1973.154 | -1009.384 | 21.090 |
| 2600 | 132.447 | 588.123 | 474.259 | 296.047 | -1972.059 | -970.855 | 19.505 |
| 2700 | 132.490 | 593.122 | 478.569 | 309.294 | -1970.968 | -932.368 | 18.038 |
| 2800 | 132.527 | 597.941 | 482.747 | 322.545 | -1969.882 | -893.921 | 16.676 |
| 2900 | 132.561 | 602.593 | 486.800 | 335.799 | -1968.801 | -855.513 | 15.409 |
| 3000 | 132.592 | 607.087 | 490.735 | 349.057 | -1967.728 | -817.142 | 14.228 |
| 3100 | 132.620 | 611.435 | 494.559 | 362.318 | -1966.665 | -778.807 | 13.123 |
| 3200 | 132.645 | 615.646 | 498.277 | 375.581 | -1965.613 | -740.506 | 12.088 |
| 3300 | 132.668 | 619.728 | 501.896 | 388.847 | -1964.575 | -702.237 | 11.115 |
| 3400 | 132.689 | 623.689 | 505.420 | 402.114 | -1963.555 | -664.000 | 10.201 |
| 3500 | 132.708 | 627.536 | 508.854 | 415.384 | -1962.556 | -625.792 | 9.339 |
| 3600 | 132.726 | 631.274 | 512.203 | 428.656 | -1961.582 | -587.612 | 8.526 |
| 3700 | 132.742 | 634.911 | 515.471 | 441.929 | -1960.635 | -549.460 | 7.757 |
| 3800 | 132.757 | 638.451 | 518.661 | 455.204 | -1959.721 | -511.333 | 7.029 |
| 3900 | 132.771 | 641.900 | 521.777 | 468.481 | -1958.844 | -473.228 | 6.338 |
| 4000 | 132.783 | 645.262 | 524.822 | 481.758 | -1958.008 | -435.146 | 5.682 |
| 4100 | 132.795 | 648.540 | 527.800 | 495.037 | -1957.218 | -397.085 | 5.059 |
| 4200 | 132.806 | 651.741 | 530.713 | 508.317 | -1956.480 | -359.042 | 4.465 |
| 4300 | 132.817 | 654.866 | 533.564 | 521.599 | -1955.798 | -321.016 | 3.900 |
| 4400 | 132.826 | 657 919 | 536.355 | 534.881 | -1955.115 | -283.010 | 3.360 |
| 4500 | 132.835 | 660.904 | 539.090 | 548.164 | -1954.533 | -245.015 | 2.844 |
| 4600 | 132.844 | 663.824 | 541.770 | 561.448 | -1954.026 | -207.031 | 2.351 |
| 4700 | 132.851 | 666.681 | 544.398 | 574.733 | -1953.593 | -169.058 | 1.879 |
| 4800 | 132.859 | 669.478 | 546.974 | 588.018 | -1953.238 | -131.093 | 1.427 |
| 4900 | 132.866 | 672.218 | 549.503 | 601.304 | -1952.969 | -93.134 | 0.993 |
| 5000 | 132.872 | 674.902 | 551.984 | 614.591 | -1952.790 | -55.181 | 0.576 |
| 5100 | 132.878 | 677.533 | 554.420 | 627.879 | -1952.690 | -17.231 | 0.176 |
| 5200 | 132.884 | 680.114 | 556.812 | 641.167 | -1952.706 | 20.720 | -0.208 |
| 5300 | 132.890 | 682.645 | 559.163 | 654.455 | -1952.830 | 58.671 | -0.578 |
| 5400 | 132.895 | 685.129 | 561.472 | 667.745 | -1953.067 | 96.626 | -0.935 |
| 5500 | 132.900 | 687.567 | 563.743 | 681.034 | -1953.424 | 134.586 | -1.278 |
| 5600 | 132.904 | 689.962 | 565.976 | 694.325 | -1953.907 | 172.554 | -1.610 |
| 5700 | 132.909 | 692.314 | 568.171 | 707.615 | -1954.521 | 210.531 | -1.929 |
| 5800 | 132.913 | 694.626 | 570.332 | 720.906 | -1955.273 | 248.521 | -2.238 |
| 5900 | 132.917 | 696.898 | 572.458 | 734.198 | -1956.167 | 286.526 | -2.537 |
| 6000 | 132.921 | 699.132 | 574.550 | 747.490 | -1957.210 | 324.546 | -2.825 |

PREVIOUS: December 1968 (1 atm)    CURRENT: December 1968 (1 bar)

## Molybdenum Fluoride (MoF$_3$) IDEAL GAS $M_r$ = 152.935209 Molybdenum Fluoride (MoF$_3$) F$_3$Mo$_1$(g)

$S°(298.15\ K) = [295.968 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-603.975 \pm 16.7]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -607.098 \pm 16.7\ kJ \cdot mol^{-1}$

| Electronic Levels and Quantum Weights | |
|---|---|
| $\epsilon_i$, cm$^{-1}$ | $g_i$ |
| 0 | [2] |
| [3505] | [2] |
| [10861] | [4] |
| [11062] | [4] |

| Vibrational Frequencies and Degeneracies | |
|---|---|
| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
| [600](1) | [650](2) |
| [300](1) | [250](2) |

Ground State Quantum Weight: [2] $\sigma = [6]$
Point Group: $D_{3h}$
Bond Distance: Mo–F = [1.82] Å
Bond Angle: F–Mo–F = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [7.702846 \times 10^{-114}]\ g^3 \cdot cm^6$

### Enthalpy of Formation

The adopted enthalpy of formation at 298.15 K is that derived by Brewer[1] from the high temperature mass spectrometric measurements of equilibria among gaseous molybdenum fluorides by Hildenbrand [1664 and 2146 K][2] and among gaseous and hetrogeneous phases by Alikhanyan *et al.* [911 and 964 K].[3] The value of $\Delta_f H°(0\ K)$ combined with JANAF data[4] for Mo(g) and F(g) gives $\Delta_{at} H°(0\ K) = 356.5 \pm 6\ kcal \cdot mol^{-1}$ and an average Mo–F bond energy of $\Delta_{at} H°(0\ K)/3 = 118.8 \pm 2\ kcal \cdot mol^{-1}$.

### Heat Capacity and Entropy

We use the vibrational frequencies and degeneracies estimated by Hildenbrand[2] and adopted by Brewer.[1] The correlation of Drake and Rosenblatt[5] leads to a planar configuration for MoF$_3$(g). The Mo–F distances of 1.82 Å from MoF$_6$(g) is used. The observed electronic levels[4] of the isoelectronic TaO(g) are assumed, as suggested by Brewer,[1] up through 11062 cm$^{-1}$. The principal moments of inertia are: $I_A = I_B = 15.6750 \times 10^{-39}$ and $I_C = 31.3500 \times 10^{-39}\ g \cdot cm^2$.

This table is based on the critical analysis of data existing in 1978 by Brewer.[1]

### References

[1] L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication, (Sept. 1978), of preliminary draft of review to be submitted for publication in Atomic Energy Review International Atomic Energy Agency, Vienna, Austria.
[2] D. L. Hildenbrand, J. Chem. Phys. 65, 614 (1976).
[3] A. S. Ailikhanyan, V. S. Pervov, I. P. Malkerova, V. D. Butskii, and V. I. Gorgoraki, Russ. J. Inorg. Chem. 23, 817 (1978).
[4] JANAF Thermochemical Tables: Mo(g), 3–31–78; F(g), 9–30–65; TaO(g), 9–31–73.
[5] M. C. Drake and G M. Rosenblatt in Proc. Symp. on High Temperature Metal Halide Chemistry, D. L. Hildenbrand and D. D. Cubicciotti, Eds., The Electrochem. Soc., Vol. 78–1, pp. 199–209, (1978).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −14.699 | −603.975 | −603.975 | INFINITE |
| 100 | 41.852 | 237.013 | 348.551 | −11.154 | −605.282 | −602.725 | 314.831 |
| 200 | 57.340 | 271.083 | 301.828 | −6.149 | −606.513 | −599.638 | 156.609 |
| 250 | 62.957 | 284.508 | 297.050 | −3.135 | −606.871 | −597.875 | 124.919 |
| 298.15 | 67.093 | 295.968 | 295.968 | 0. | −607.098 | −596.120 | 104.438 |
| 300 | 67.230 | 296.383 | 295.969 | 0.124 | −607.105 | −596.052 | 103.782 |
| 350 | 70.430 | 306.999 | 296.800 | 3.570 | −607.257 | −594.197 | 88.679 |
| 400 | 72.834 | 316.568 | 298.683 | 7.154 | −607.360 | −592.324 | 77.350 |
| 450 | 74.665 | 325.257 | 301.160 | 10.844 | −607.436 | −590.439 | 68.536 |
| 500 | 76.087 | 333.200 | 303.973 | 14.614 | −607.498 | −588.547 | 61.485 |
| 600 | 78.145 | 347.267 | 310.047 | 22.332 | −607.606 | −584.747 | 50.907 |
| 700 | 79.599 | 359.428 | 316.252 | 30.223 | −607.715 | −580.929 | 43.349 |
| 800 | 80.737 | 370.134 | 322.332 | 38.242 | −607.832 | −577.094 | 37.680 |
| 900 | 81.694 | 379.700 | 328.184 | 46.364 | −607.957 | −573.244 | 33.270 |
| 1000 | 82.528 | 388.351 | 333.775 | 54.576 | −608.092 | −569.380 | 29.741 |
| 1100 | 83.262 | 396.252 | 339.101 | 62.867 | −608.245 | −565.502 | 26.853 |
| 1200 | 83.908 | 403.525 | 344.170 | 71.226 | −608.423 | −561.609 | 24.446 |
| 1300 | 84.472 | 410.264 | 348.998 | 79.645 | −608.638 | −557.699 | 22.409 |
| 1400 | 84.963 | 416.543 | 353.601 | 88.118 | −608.902 | −553.771 | 20.661 |
| 1500 | 85.391 | 422.419 | 357.995 | 96.636 | −609.224 | −549.822 | 19.147 |
| 1600 | 85.766 | 427.943 | 362.196 | 105.194 | −609.616 | −545.850 | 17.820 |
| 1700 | 86.101 | 433.152 | 366.218 | 113.788 | −610.086 | −541.850 | 16.649 |
| 1800 | 86.405 | 438.082 | 370.075 | 122.413 | −610.642 | −537.821 | 15.607 |
| 1900 | 86.689 | 442.762 | 373.779 | 131.068 | −611.289 | −533.758 | 14.674 |
| 2000 | 86.958 | 447.215 | 377.340 | 139.751 | −612.035 | −529.659 | 13.833 |
| 2100 | 87.220 | 451.464 | 380.769 | 148.460 | −612.883 | −525.520 | 13.072 |
| 2200 | 87.479 | 455.528 | 384.076 | 157.195 | −613.838 | −521.338 | 12.378 |
| 2300 | 87.736 | 459.422 | 387.268 | 165.955 | −614.904 | −517.109 | 11.744 |
| 2400 | 87.993 | 463.161 | 390.352 | 174.742 | −616.086 | −512.833 | 11.162 |
| 2500 | 88.250 | 466.759 | 393.337 | 183.554 | −617.389 | −508.504 | 10.625 |
| 2600 | 88.506 | 470.225 | 396.228 | 192.392 | −618.830 | −504.121 | 10.128 |
| 2700 | 88.760 | 473.570 | 399.031 | 201.255 | −620.444 | −499.679 | 9.667 |
| 2800 | 89.011 | 476.803 | 401.751 | 210.144 | −622.287 | −495.173 | 9.238 |
| 2900 | 89.256 | 479.930 | 404.393 | 219.057 | −660.323 | −490.547 | 8.836 |
| 3000 | 89.493 | 482.960 | 406 962 | 227.995 | −660.823 | −484.684 | 8.439 |
| 3100 | 89.721 | 485.898 | 409.461 | 236.955 | −661.260 | −478.806 | 8.068 |
| 3200 | 89.938 | 488.750 | 411.895 | 245.938 | −661.631 | −472.914 | 7.720 |
| 3300 | 90.144 | 491.521 | 414.266 | 254.943 | −661.936 | −467.011 | 7.392 |
| 3400 | 90.335 | 494.215 | 416.578 | 263.967 | −662.174 | −461.101 | 7.084 |
| 3500 | 90.512 | 496.836 | 418.834 | 273.009 | −662.345 | −455.184 | 6.793 |
| 3600 | 90.674 | 499.388 | 421.036 | 282.069 | −662.449 | −449.263 | 6.519 |
| 3700 | 90.820 | 501.875 | 423.187 | 291.144 | −662.487 | −443.341 | 6.259 |
| 3800 | 90.950 | 504.299 | 425.290 | 300.232 | −662.460 | −437.419 | 6.013 |
| 3900 | 91.064 | 506.663 | 427.346 | 309.333 | −662.369 | −431.497 | 5.779 |
| 4000 | 91.162 | 508.969 | 429.358 | 318.445 | −662.216 | −425.579 | 5.557 |
| 4100 | 91.245 | 511.221 | 431.328 | 327.565 | −662.004 | −419.666 | 5.347 |
| 4200 | 91.312 | 513.421 | 433.256 | 336.693 | −661.734 | −413.758 | 5.146 |
| 4300 | 91.364 | 515.570 | 435.145 | 345.827 | −661.408 | −407.858 | 4.954 |
| 4400 | 91.402 | 517.671 | 436.997 | 354.965 | −661.028 | −401.966 | 4.772 |
| 4500 | 91.426 | 519.726 | 438.813 | 364.107 | −660.597 | −396.083 | 4.598 |
| 4600 | 91.438 | 521.735 | 440.594 | 373.250 | −660.117 | −390.210 | 4.431 |
| 4700 | 91.437 | 523.702 | 442.341 | 382.394 | −659.590 | −384.348 | 4.272 |
| 4800 | 91.425 | 525.627 | 444.056 | 391.537 | −659.018 | −378.498 | 4.119 |
| 4900 | 91.403 | 527.512 | 445.740 | 400.679 | −658.405 | −372.660 | 3.973 |
| 5000 | 91.371 | 529.358 | 447.394 | 409.817 | −1249.136 | −361.104 | 3.772 |
| 5100 | 91.329 | 531.167 | 449.019 | 418.953 | −1250.123 | −343.333 | 3.516 |
| 5200 | 91.280 | 532.940 | 450.616 | 428.083 | −1251.221 | −325.542 | 3.270 |
| 5300 | 91.223 | 534.678 | 452.186 | 437.208 | −1252.428 | −307.730 | 3.033 |
| 5400 | 91.159 | 536.383 | 453.729 | 446.327 | −1253.745 | −289.893 | 2.804 |
| 5500 | 91.089 | 538.055 | 455.247 | 455.440 | −1255.172 | −272.031 | 2.584 |
| 5600 | 91.013 | 539.695 | 456.741 | 464.545 | −1256.709 | −254.142 | 2.371 |
| 5700 | 90.933 | 541.305 | 458.210 | 473.642 | −1258.352 | −236.225 | 2.165 |
| 5800 | 90.848 | 542.886 | 459.657 | 482.731 | −1260.102 | −218.278 | 1.966 |
| 5900 | 90.759 | 544 438 | 461.080 | 491.812 | −1261.955 | −200.300 | 1.773 |
| 6000 | 90.667 | 545.963 | 462.483 | 500.883 | −1263.914 | −182.290 | 1.587 |

PREVIOUS: December 1978 (1 atm) CURRENT: December 1978 (1 bar)

## Nitrogen Fluoride ($NF_3$) IDEAL GAS $M_r$ = 71.001909 Nitrogen Fluoride ($NF_3$) $F_3N_1(g)$

$S°(298.15 K) = 260.773 \pm 0.21 J·K^{-1}·mol^{-1}$

$\Delta_fH°(0 K) = -126.366 \pm 1.13 kJ·mol^{-1}$

$\Delta_fH°(298.15 K) = -132.089 \pm 1.13 kJ·mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, $cm^{-1}$ |
|---|
| 1032(1) |
| 642(1) |
| 906(2) |
| 492(2) |

Ground State Quantum Weight: 1 $\sigma = 3$
Point Group: $C_{3v}$
Bond Distance: N–F = 1.371 Å
Bond Angle: F–N–F = 102°9'
Product of the Moments of Inertia: $I_AI_BI_C = 8.858632 \times 10^{-115} g^3·cm^6$

### Enthalpy of Formation

The adopted enthalpy of formation is the mean of values calculated from the reaction processes listed below and weighted inversely as the squares of the standard deviations. Auxiliary enthalpies of formation were taken from NBS [1] or from simultaneous adjustment of several interconnecting pieces of data.[2] Also given below are the references, individual and averaged measured values of enthalpies of reaction and their uncertainties, the value of enthalpy of formation calculated from each process and its uncertainty, and the weighted mean.

| Source | Reaction | $\Delta_rH°$(298.15 K), kcal·mol$^{-1}$ | $\Delta_fH°$(298.15 K), kcal·mol$^{-1}$ |
|---|---|---|---|
| | $NF_3(g)+3/2 H_2(g)=3 HF(aq, 50 H_2O)+1/2 N_2(g)$ | −199.42 ± 0.22 | −30.92 ± 1.72 |
| 3 | 196.3 ± 64 | | |
| 4 | −199.49 ± 0.22 | | |
| 5 | We derive −196.23 ± 0.77 | | |
| 6 | $S(cr, rh)+2 NF_3(g)=SF_6(g)+N_2(g)$ | −228.26 ± 0.2 | −31.77 ± 0.33 |
| 7 | $NF_3(g)\rightarrow 1/2 N_2(g)+3/2 F_2(g)$ | 31.44 ± 0.3 | −31.44 ± 0.3 |
| 8 | $NF_3(g)+3 C_2N_2(g)=6 CF_4(g)+7 N_2(g)$ | −1308.8 ± 1.3 | −31.4 ± 4.4 |
| 9 | $B(cr)+NF_3(g)=BF_3(g)+1/2 N_2(g)$ | −239.7 ± 1.2 | −31.7 ± 1.6 |
| 3 | $NF_3(g)+4 NH_3(g)=3 NH_4F(cr)+N_2(g)$ | −259.5 ± 1.0 | −29.0 ± 3.0 |
| | | Weighted Mean | −31.57 ± 0.27 |

### Heat Capacity and Entropy

The vibrational frequencies are from the infrared studies of Schatz and Levin [10] and are in good agreement with those of Pace and Pierce,[11] and Wilson and Polo.[12] The adopted values are also in agreement with the Raman studies of Kotov and Tatevskii.[13] The bond length and angle are from the microwave studies of Sheridan and Gordy,[14] whose values are in substantial agreement with the electron diffraction results of Schomaker and Lu.[15]

The principal moments of inertia are $I_A = I_B = 7.8554 \times 10^{-39}$ g cm$^2$ and $I_C = 14.3560 \times 10^{-39}$ g·cm$^2$.

Pierce and Pace [16] have obtained the entropy of the gas at 144.15 K from solid heat capacity measurements and the heats of melting and vaporization. Their reported value of 54.50 cal $K^{-1}·mol^{-1}$ is in good agreement with our calculated value of 54.56 cal $K^{-1}·mol^{-1}$.

The National Bureau of Standards prepared this table [17] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_fH°$ selected by NBS,[17] we recalculate the table in terms of 1973 fundamental constants,[18] 1975 atomic weights,[19] and current JANAF reference states for the elements.

### References

[1] U S. Nat. Bur. Stand. Tech. Note 270-3, (1968).
[2] A. N. Syverud, The Dow Chemical Company, AD867952, 76 pp. (1970).
[3] G T Armstrong, S. Marantz, and C. F. Coyle, J. Amer. Chem. Soc 81, 3798 (1959).
[4] G. C. Sinke, J. Chem. Eng. Data 10, 295 (1965).
[5] A. N Zercheninov, V. I Chesnokov, and A. V. Pankratov, Zh. Fiz. Khim, 43, 390 (1969).
[6] L. C. Walker, J. Phys. Chem. 71, 361 (1967).
[7] G. C. Sinke, J. Phys. Chem. 71, 359 (1967).
[8] L. C. Walker, Paper presented at 22nd Annual Calorimetry Conference, Thousand Oaks, California, (June 1967).
[9] J. R. Ludwig and W. J. Cooper, J. Chem. Eng. Data 8, 76 (1963).

Continued on page 1216

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
|---|---|---|---|---|---|---|---|
| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
| 0 | 0. | 0. | INFINITE | −11.850 | −126.366 | −126.366 | INFINITE |
| 100 | 34.037 | 215.800 | 300.931 | −8.513 | −128.841 | −116.875 | 61.049 |
| 200 | 42.777 | 241.672 | 265.323 | −4.730 | −130.907 | −104.047 | 27.174 |
| 250 | 48.357 | 251.819 | 261.624 | −2.451 | −131.609 | −97.246 | 20.319 |
| 298.15 | 53.370 | 260.773 | 260.773 | 0. | −132.089 | −90.582 | 15.870 |
| 300 | 53.551 | 261.104 | 260.774 | 0.099 | −132.104 | −90.324 | 15.727 |
| 350 | 58.068 | 269.707 | 261 443 | 2.892 | −132.422 | −83.334 | 12.437 |
| 400 | 61.860 | 277.717 | 262.983 | 5.894 | −132.597 | −76.307 | 9.965 |
| 450 | 64.994 | 285.190 | 265.040 | 9.067 | −132.656 | −69.267 | 8.040 |
| 500 | 67.568 | 292.175 | 267.408 | 12.384 | −132.625 | −62.224 | 6.501 |
| 600 | 71.430 | 304.858 | 272.615 | 19.346 | −132.365 | −48.165 | 4.193 |
| 700 | 74.090 | 316.081 | 278.039 | 26.630 | −131.929 | −34.164 | 2.549 |
| 800 | 75.971 | 326.104 | 283.432 | 34.138 | −131.390 | −20.234 | 1.321 |
| 900 | 77.340 | 335.135 | 288.683 | 41.807 | −130 791 | −6.375 | 0.370 |
| 1000 | 78.360 | 343.339 | 293.745 | 49.594 | −130.158 | 7.416 | −0.387 |
| 1100 | 79.138 | 350.846 | 298.599 | 57.471 | −129.510 | 21.142 | −1.004 |
| 1200 | 79.744 | 357.759 | 303.245 | 65.416 | −128.858 | 34.809 | −1.515 |
| 1300 | 80.224 | 364.161 | 307.688 | 73.416 | −128.210 | 48.421 | −1.946 |
| 1400 | 80.611 | 370.121 | 311.937 | 81.458 | −127.570 | 61.984 | −2.313 |
| 1500 | 80.926 | 375.694 | 316.004 | 89.535 | −126.942 | 75.501 | −2.629 |
| 1600 | 81.186 | 380.925 | 319.899 | 97.641 | −126.329 | 88.978 | −2.905 |
| 1700 | 81.404 | 385.854 | 323.636 | 105.771 | −125.730 | 102.416 | −3.147 |
| 1800 | 81.587 | 390.512 | 327.223 | 113.921 | −125.144 | 115.819 | −3.361 |
| 1900 | 81.744 | 394.928 | 330.671 | 122.088 | −124.570 | 129.190 | −3.552 |
| 2000 | 81.877 | 399.124 | 333.990 | 130.269 | −124.005 | 142.532 | −3.723 |
| 2100 | 81.993 | 403.122 | 337.187 | 138.463 | −123.444 | 155.845 | −3.876 |
| 2200 | 82.094 | 406.939 | 340.272 | 146.667 | −122.884 | 169.131 | −4.016 |
| 2300 | 82.182 | 410.590 | 343.250 | 154.881 | −122.319 | 182.392 | −4.142 |
| 2400 | 82.259 | 414.089 | 346.129 | 163.103 | −121.745 | 195.628 | −4.258 |
| 2500 | 82.328 | 417.448 | 348.915 | 171.333 | −121.156 | 208.840 | −4.363 |
| 2600 | 82.389 | 420.679 | 351.614 | 179.568 | −120.546 | 222.028 | −4.461 |
| 2700 | 82.443 | 423.789 | 354.230 | 187.810 | −119.912 | 235.192 | −4.550 |
| 2800 | 82.492 | 426.788 | 356.768 | 196.057 | −119.249 | 248.332 | −4.633 |
| 2900 | 82.535 | 429.684 | 359.233 | 204.308 | −118.552 | 261.447 | −4.709 |
| 3000 | 82.575 | 432.482 | 361.628 | 212.564 | −117.818 | 274.538 | −4.780 |
| 3100 | 82.611 | 435.191 | 363.957 | 220.823 | −117.044 | 287.604 | −4.846 |
| 3200 | 82.643 | 437.814 | 366.225 | 229.086 | −116.226 | 300.644 | −4.908 |
| 3300 | 82.673 | 440.357 | 368.433 | 237.352 | −115.364 | 313.658 | −4.965 |
| 3400 | 82.700 | 442.826 | 370.585 | 245.620 | −114.454 | 326.645 | −5.018 |
| 3500 | 82.725 | 445.224 | 372.683 | 253.892 | −113.495 | 339.605 | −5.068 |
| 3600 | 82.748 | 447.554 | 374.731 | 262.165 | −112.486 | 352.537 | −5.115 |
| 3700 | 82.769 | 449.822 | 376.730 | 270.441 | −111.427 | 365.440 | −5.159 |
| 3800 | 82.788 | 452.029 | 378.682 | 278.719 | −110.318 | 378.313 | −5.200 |
| 3900 | 82.806 | 454.180 | 380.591 | 286.999 | −109.157 | 391.157 | −5.239 |
| 4000 | 82.823 | 456.277 | 382.457 | 295.280 | −107.945 | 403.970 | −5.275 |
| 4100 | 82.838 | 458.322 | 384.282 | 303.563 | −106 683 | 416.752 | −5.309 |
| 4200 | 82.852 | 460.318 | 386.069 | 311.848 | −105.371 | 429.504 | −5.342 |
| 4300 | 82.866 | 462.268 | 387.818 | 320.134 | −104.010 | 442.222 | −5.372 |
| 4400 | 82.878 | 464 173 | 389.532 | 328.421 | −102.600 | 454.909 | −5.400 |
| 4500 | 82.890 | 466.036 | 391.212 | 336.709 | −101.142 | 467.564 | −5.427 |
| 4600 | 82.901 | 467.858 | 392.858 | 344.999 | −99.638 | 480.185 | −5.453 |
| 4700 | 82.911 | 469.641 | 394.473 | 353.289 | −98.088 | 492.774 | −5.477 |
| 4800 | 82.921 | 471.387 | 396.057 | 361.581 | −96.494 | 505.328 | −5.499 |
| 4900 | 82.930 | 473.096 | 397.612 | 369.873 | −94.857 | 517.849 | −5.520 |
| 5000 | 82.938 | 474.772 | 399.139 | 378.167 | −93.177 | 530.337 | −5.540 |
| 5100 | 82.946 | 476.414 | 400.638 | 386.461 | −91.457 | 542.790 | −5.559 |
| 5200 | 82.954 | 478.025 | 402.110 | 394.756 | −89.697 | 555.209 | −5.577 |
| 5300 | 82.961 | 479.605 | 403.558 | 403.052 | −87.898 | 567.594 | −5.594 |
| 5400 | 82.967 | 481 156 | 404.980 | 411.348 | −86.062 | 579.945 | −5.610 |
| 5500 | 82.974 | 482.678 | 406.379 | 419.645 | −84.190 | 592.261 | −5.625 |
| 5600 | 82.980 | 484.174 | 407.755 | 427.943 | −82.283 | 604.543 | −5.639 |
| 5700 | 82.985 | 485.642 | 409.109 | 436.241 | −80.342 | 616.790 | −5.652 |
| 5800 | 82.991 | 487.086 | 410.441 | 444.540 | −78.369 | 629.003 | −5.665 |
| 5900 | 82.996 | 488.504 | 411.752 | 452.839 | −76.364 | 641.183 | −5.677 |
| 6000 | 83.001 | 489.899 | 413.043 | 461.139 | −74.329 | 653.327 | −5.688 |

PREVIOUS· June 1977 (1 atm) CURRENT· June 1977 (1 bar)

**Nitrogen Fluoride Oxide ($NF_3O$)** **IDEAL GAS** **$M_r$ = 87.001309** **Nitrogen Fluoride Oxide ($NF_3O$)** **$F_3N_1O_1(g)$**

$\Delta_fH°(0\ K) = -154.926 \pm 20.9\ kJ{\cdot}mol^{-1}$
$S°(298.15\ K) = 278.490 \pm 0.21\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = -163.176 \pm 20.9\ kJ{\cdot}mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, $cm^{-1}$ | <br>$\nu$, $cm^{-1}$ |
|---|---|
| 1687(1) | 887(2) |
| 743(1) | 528(2) |
| 558(1) | 398(2) |

Ground State Quantum Weight: 1 $\sigma = 3$
Point Group: $C_{3v}$
Bond Distances: N–O = [1.15]Å; N–F = 1.48 ± 0.1Å
Bond Angles: O–N–F = [109° 28′], F–N–F = [109° 28′]
Product of the Moments of Inertia: $I_AI_BI_C = [4.064027 \times 10^{-114}]\ g^3{\cdot}cm^6$

## Enthalpy of Formation

Bougon *et al.*[1] determined equilibrium constants for the reaction $NOF(g) + F_2(g) \rightleftarrows NOF_3(g)$ as a function of temperature and total pressure. 2nd and 3rd law analyses of these equilibrium data are given below:

|  | Data Points | T/K | $\Delta_rH°$(298.15 K), kcal·mol$^{-1}$ 2nd law | 3rd law | Drift cal K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| Set I | 7 | 533–643 | −17.1 | −18.7 | −2.4 ± 2.1 |
| Set II | 1 | 533.2 |  | −18.2 | . |

Set I contains their equilibrium data as a function of temperature, while Set II is their adopted equilibrium constant, $K_p°$ (553.2 K) = 0.015 ± 0.005 atm$^{-1}$, corresponding to the lowest pressure (103 atm.) that was studied. Estimated corrections for nonideality are small and neglected. Adopting $\Delta_rH°(298.15\ K) = -18.7 \pm 1.0\ kcal{\cdot}mol^{-1}$, we derive $\Delta_fH°(NOF_3, g, 298.15\ K) = -34.4 \pm 1.4\ kcal{\cdot}mol^{-1}$ with $\Delta_fH°(NOF, g, 298.15\ K) = -15.7 \pm 0.4\ kcal{\cdot}mol^{-1}$.[2]

Armstrong and King [3] determined $\Delta_rH°(304\ K) = -253.7 \pm 0.6\ kcal{\cdot}mol^{-1}$ for the reaction $NOF_3(g) + 5/2\ H_2(g) + 122\ H_2O(l) \rightarrow 1/2\ N_2(g) + [3\ HF123{\cdot}H_2O](l)$ in a constant pressure flame calorimeter. Combining this result with their earlier enthalpy data for reduction reactions involving $F_2(g)$ and $O_2(g)$ with $H_2(g)$, they obtained $\Delta_fH°(NOF_3, g, 304\ K) = -44.7 \pm 1.5\ kcal{\cdot}mol^{-1}$.

Very recently, Dibeler and Walker[4] investigated the photoionization of $NOF_3$ by mass spectrometry. From their ionization threshold data, they determined $\Delta_fH°(NOF_3, g, 0\ K) = -69.6 \pm 1.2\ kcal{\cdot}mol^{-1}$.

The value for the enthalpy of formation of gaseous $NOF_3$ is tentatively selected as $-39.0 \pm 5.0\ kcal{\cdot}mol^{-1}$.

## Heat Capacity and Entropy

Several recent infrared[5 6, 7] and Raman[8] studies of $NOF_3$ have been reported in the literature. The fundamental vibrational frequencies observed in the infrared spectrum of the molecule by the various investigators are in good agreement, although the assignment of the $\nu_3$ and $\nu_5$ bending modes has varied. Fox *et al.*[6] assigned $\nu_3 = 558\ cm^{-1}$ and $\nu_5 = 528\ cm^{-1}$, while Curtis *et al.*[7] reversed the assignments. Very recently, Abramowitz and Levin[8] investigated the Raman spectrum of polycrystalline film of $NOF_3$ at 78 K and assigned $\nu_3 = 535\ cm^{-1}$ and $\nu_5 = 522\ cm^{-1}$ consistent with the infrared work of Fox *et al.*[6] The fundamental vibrational frequencies and assignments given by Fox *et al.*[6] are adopted here.

Fox *et al.*[9] also investigated the nuclear magnetic resonance spectrum of $NOF_3$ which indicated that the molecule contained three equivalent fluorine atoms. This result, along with the general appearance of the infrared spectrum, clearly establishes that the molecule has $C_{3v}$ symmetry. The N–O bond distance and bond angles are estimated quantities from the work of Curtis *et al.*[7] These estimated data have been used in calculating the N–F bond distance from the rotational constants given by Curtis *et al.*[7] Individual moments of inertia calculated from the structural data given above are: $I_A = I_B = 14.8502 \times 10^{-39}$ and $I_C = 18.4285 \times 10^{-39}\ g{\cdot}cm^2$.

## References

[1] R. Bougon, J. Chatelet, J. P. Desmoulin, and P. Plurien, Compt. Rend. 226c, 760 (1968).
[2] JANAF Thermochemical Tables: NOF(g), 6–30–61.
[3] G. T. Armstrong and R. C. King, U. S. Nat. Bur. Stand., AFOSR 69–2154 TR, (July 1, 1969).
[4] V. H. Dibeler and J. A. Walker, Inorg. Chem. 8, 1728 (1969).
[5] N. Bartlett, J. Passmore, and E. J. Wells, Chem. Commun., 213, (1966).
[6] W. B. Fox, J. S. MacKenzie, N. Vanderkooi, B. S. Sukornick, C. A. Wamser, J. R. Holmes, R. E. Eibeck, and B. B. Stewart, J. Amer. Chem. Soc. 88, 2604 (1966).
[7] E. C. Curtis, D. Pilipovich, and W. H. Moberly, J. Chem. Phys. 46, 2904 (1967).
[8] S. Abramowitz and I. W. Levin, J. Chem. Phys. 51, 463 (1969).
[9] W. B. Fox, J. S. MacKenzie, E. R. McCarthy, J. R. Holmes, R. F. Stahl, and R. Juurik, Inorg. Chem. 7, 2064 (1968).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ (J·K$^{-1}$mol$^{-1}$) | $S°$ (J·K$^{-1}$mol$^{-1}$) | $-[G°-H°(T_r)]/T$ (J·K$^{-1}$mol$^{-1}$) | $H°-H°(T_r)$ (kJ·mol$^{-1}$) | $\Delta_fH°$ (kJ·mol$^{-1}$) | $\Delta_fG°$ (kJ·mol$^{-1}$) | log $K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0. | 0. | INFINITE | −13.664 | −154.926 | −154.926 | INFINITE |
| 100 | 35.733 | 225.011 | 327.998 | −10.299 | −158.825 | −139.114 | 72.666 |
| 200 | 52.446 | 254.510 | 284.237 | −5.945 | −161.776 | −118.135 | 30.854 |
| 250 | 60.935 | 267.147 | 279.570 | −3.106 | −162.646 | −107.116 | 22.381 |
| 298.15 | 67.862 | 278.490 | 278.490 | 0. | −163.176 | −96.369 | 16.883 |
| 300 | 68.103 | 278.911 | 278.492 | 0.126 | −163.191 | −95.954 | 16.707 |
| 350 | 73.975 | 289.865 | 279.343 | 3.683 | −163.484 | −84.722 | 12.644 |
| 400 | 78.762 | 300.067 | 281.304 | 7.505 | −163.585 | −73.461 | 9.593 |
| 450 | 82.682 | 309.577 | 283.923 | 11.545 | −163.538 | −62.197 | 7.220 |
| 500 | 85.920 | 318.462 | 286.937 | 15.762 | −163.376 | −50.945 | 5.322 |
| 600 | 90.882 | 334.592 | 293.564 | 24.617 | −162.803 | −28.508 | 2.482 |
| 700 | 94.429 | 348.882 | 300.465 | 33.892 | −162.004 | −6.186 | 0.462 |
| 800 | 97.033 | 361.670 | 307.331 | 43.471 | −161.062 | 16.010 | −1.045 |
| 900 | 98.988 | 373.217 | 314.021 | 53.277 | −160.029 | 38.083 | −2.210 |
| 1000 | 100.486 | 383.727 | 320.474 | 63.254 | −158.937 | 60.037 | −3.136 |
| 1100 | 101.654 | 393.362 | 326.668 | 73.363 | −157.811 | 81.880 | −3.888 |
| 1200 | 102.579 | 402.248 | 332.601 | 83.576 | −156.666 | 103.620 | −4.510 |
| 1300 | 103.324 | 410.489 | 338.279 | 93.873 | −155.511 | 125.264 | −5.033 |
| 1400 | 103.930 | 418.169 | 343.714 | 104.236 | −154.357 | 146.819 | −5.478 |
| 1500 | 104.430 | 425.357 | 348.920 | 114.655 | −153.209 | 168.291 | −5.860 |
| 1600 | 104.846 | 432.110 | 353.911 | 125.120 | −152.071 | 189.687 | −6.193 |
| 1700 | 105.197 | 438.478 | 358.700 | 135.622 | −150.945 | 211.013 | −6.484 |
| 1800 | 105.494 | 444.499 | 363.301 | 146.157 | −149.832 | 232.272 | −6.740 |
| 1900 | 105.748 | 450.210 | 367.726 | 156.720 | −148.732 | 253.470 | −6.968 |
| 2000 | 105.967 | 455.640 | 371.987 | 167.306 | −147.643 | 274.610 | −7.172 |
| 2100 | 106.157 | 460.815 | 376.095 | 177.912 | −146.563 | 295.696 | −7.355 |
| 2200 | 106.323 | 465.757 | 380.059 | 188.536 | −145.487 | 316.731 | −7.520 |
| 2300 | 106.469 | 470.486 | 383.888 | 199.176 | −144.411 | 337.717 | −7.670 |
| 2400 | 106.597 | 475.021 | 387.592 | 209.830 | −143.332 | 358.656 | −7.806 |
| 2500 | 106.711 | 479.374 | 391.176 | 220.495 | −142.244 | 379.550 | −7.930 |
| 2600 | 106.812 | 483.562 | 394.650 | 231.171 | −141.142 | 400.400 | −8.044 |
| 2700 | 106.903 | 487.595 | 398.018 | 241.857 | −140.023 | 421.207 | −8.149 |
| 2800 | 106.984 | 491.484 | 401.287 | 252.552 | −138.881 | 441.973 | −8.245 |
| 2900 | 107.058 | 495.239 | 404.462 | 263.254 | −137.712 | 462.697 | −8.334 |
| 3000 | 107.124 | 498.870 | 407.549 | 273.963 | −136.513 | 483.380 | −8.416 |
| 3100 | 107.184 | 502.383 | 410.552 | 284.678 | −135.280 | 504.023 | −8.493 |
| 3200 | 107.239 | 505.787 | 413.475 | 295.399 | −134.011 | 524.625 | −8.564 |
| 3300 | 107.289 | 509.088 | 416.323 | 306.126 | −132.703 | 545.188 | −8.630 |
| 3400 | 107.334 | 512.292 | 419.098 | 316.857 | −131.355 | 565.710 | −8.691 |
| 3500 | 107.376 | 515.404 | 421.806 | 327.593 | −129.964 | 586.191 | −8.748 |
| 3600 | 107.415 | 518.429 | 424.448 | 338.332 | −128.529 | 606.633 | −8.802 |
| 3700 | 107.450 | 521.372 | 427.028 | 349.075 | −127.050 | 627.034 | −8.852 |
| 3800 | 107.483 | 524.238 | 429.548 | 359.822 | −125.525 | 647.394 | −8.899 |
| 3900 | 107.513 | 527.031 | 432.012 | 370.572 | −123.955 | 667.714 | −8.943 |
| 4000 | 107.541 | 529.753 | 434.422 | 381.325 | −122.340 | 687.993 | −8.984 |
| 4100 | 107.567 | 532.409 | 436.780 | 392.080 | −120.680 | 708.230 | −9.023 |
| 4200 | 107.591 | 535.001 | 439.087 | 402.838 | −118.975 | 728.427 | −9.059 |
| 4300 | 107.614 | 537.533 | 441.348 | 413.598 | −117.226 | 748.583 | −9.093 |
| 4400 | 107.635 | 540.007 | 443.562 | 424.361 | −115.434 | 768.697 | −9.126 |
| 4500 | 107.655 | 542.427 | 445.732 | 435.125 | −113.600 | 788.771 | −9.156 |
| 4600 | 107.673 | 544.793 | 447.860 | 445.892 | −111.724 | 808.802 | −9.184 |
| 4700 | 107.691 | 547.109 | 449.947 | 456.660 | −109.808 | 828.794 | −9.211 |
| 4800 | 107.707 | 549.376 | 451.995 | 467.430 | −107.853 | 848.743 | −9.236 |
| 4900 | 107.722 | 551.597 | 454.005 | 478.201 | −105.860 | 868.652 | −9.260 |
| 5000 | 107.736 | 553.774 | 455.979 | 488.974 | −103.832 | 888.520 | −9.282 |
| 5100 | 107.750 | 555.907 | 457.917 | 499.748 | −101.769 | 908.346 | −9.303 |
| 5200 | 107.763 | 558.000 | 459.822 | 510.524 | −99.672 | 928.132 | −9.323 |
| 5300 | 107.775 | 560.052 | 461.694 | 521.301 | −97.544 | 947.877 | −9.342 |
| 5400 | 107.786 | 562.067 | 463.534 | 532.079 | −95.385 | 967.582 | −9.359 |
| 5500 | 107.797 | 564.045 | 465.343 | 542.858 | −93.198 | 987.246 | −9.376 |
| 5600 | 107.807 | 565.987 | 467.123 | 553.638 | −90.984 | 1006.871 | −9.392 |
| 5700 | 107.817 | 567.896 | 468.875 | 564.420 | −88.745 | 1026.455 | −9.406 |
| 5800 | 107.826 | 569.771 | 470.598 | 575.202 | −86.482 | 1046.000 | −9.420 |
| 5900 | 107.835 | 571.614 | 472.295 | 585.985 | −84.197 | 1065.506 | −9.433 |
| 6000 | 107.843 | 573.427 | 473.965 | 596.769 | −81.892 | 1084.973 | −9.446 |

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

**Nitrogen Fluoride Oxide ($NF_3O$)** **$F_3N_1O_1(g)$**

## Phosphoryl Fluoride ($POF_3$) IDEAL GAS $M_r = 103.968369$ Phosphoryl Fluoride ($POF_3$) $F_3O_1P_1(g)$

$S°(298.15\ K) = 285.413 \pm 0.30\ J\ K^{-1}\cdot mol^{-1}$

$\Delta_fH°(0\ K) = -1245.468 \pm 8.0\ kJ\cdot mol^{-1}$

$\Delta_fH°(298.15\ K) = -1254.250 \pm 8.0\ kJ\cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|
| 1417.7(1) | 994 (2) |
| 872.8(1) | 488.2(2) |
| 473.2(1) | 335.6(2) |

Ground State Quantum Weight: [1] $\sigma = 3$

Point Group: $C_{3v}$

Bond Distances P–O = 1.45 ± 0.03 Å, P–F = 1.52 ± 0.02 Å

Bond Angles: F–P–F = 102.5 ± 2°, F–P–O = 115.8 ± 2°

Product of the Moments of Inertia: $I_AI_BI_C = 5.907318 \times 10^{-114}\ g^3\ cm^6$

### Enthalpy of Formation

Ebel and Bretscher[1] measured the enthalpy change for the following reaction: $PF_3(g) + 1/2\ O_2(g) \rightarrow POF_3(g)$. They reported a heat of reaction of $-70.6 \pm 1$ kcal·mol$^{-1}$. Combining this result with the enthalpy of formation of $PF_3$, $\Delta_fH°(298.15\ K) = -224.9 \pm 0.9$ kcal mol$^{-1}$,[2] we derive, $\Delta_fH°(POF_3, g, 298.15\ K) = -295.6 \pm 1.9$ kcal·mol$^{-1}$.

### Heat Capacity and Entropy

The vibrational frequencies are from the infrared studies of Selig and Claasen[3] and are in good agreement with the Raman and infrared studies of Gutowsky and Liehr.[4] Several microwave studies[5,6,7,8] of $POF_3$ have been reported. As pointed out by Williams *et al.*,[7] the rotational constant calculated from their microwave studies leads to a moment of inertia, $I_B$, which is in disagreement with the moment of inertia calculated from the molecular constants obtained from electron–diffraction studies by Brockway and Beach.[9] Since insufficient microwave data were available for an independent determination, Williams *et al.*[7] sought to find parameters which were consistent with both measurements. Their molecular constants are adopted for this tabulation. Individual moments of inertia are $I_A = 17.7329 \times 10^{-39}$, $I_B = I_C = 18.2518 \times 10^{-39}$ g·cm$^2$.

### References

[1] F. Ebel and E. Bretscher, Helv. Chim. Acta. **12**, 450 (1929).

[2] JANAF Thermochemical Tables: $PF_3(g)$, 12–31–69.

[3] H. Selig and H. H. Claassen, J. Chem. Phys. **44**, 1404 (1966).

[4] H. S. Gutowsky and A. D. Liehr, J. Chem. Phys. **20**, 1652 (1952).

[5] S. J. Senatore, Phys. Rev. **78**, 293 (1950).

[6] N. J. Hawkins, V. W. Cohen, and W. S. Koski, J. Chem. Phys. **20**, 528 (1952).

[7] Q. Williams, J. Sheridan, and W. Gordy, J. Chem. Phys. **20**, 164 (1952).

[8] C. A. Burrus and W. Gordy, J. Chem. Phys. **26**, 391 (1957).

[9] L. O. Brockway and J. Y. Beach, J. Amer. Chem. Soc. **60**, 1836 (1938).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0 | 0. | INFINITE | −14.157 | −1245.468 | −1245 468 | INFINITE |
| 100 | 37.612 | 229.302 | 336.796 | −10.749 | −1248.761 | −1235.701 | 645.464 |
| 200 | 55.073 | 260.721 | 291.294 | −6.115 | −1252.238 | −1221.413 | 319.000 |
| 250 | 62.605 | 273.841 | 286.512 | −3.168 | −1253.366 | −1213.571 | 253.562 |
| 298.15 | 68.815 | 285.413 | 285.413 | 0. | −1254.250 | −1205.824 | 211.255 |
| 300 | 69.034 | 285.839 | 285.414 | 0.128 | −1254.281 | −1205.523 | 209.900 |
| 350 | 74.490 | 296.902 | 286.275 | 3 719 | −1255.746 | −1197.265 | 178 682 |
| 400 | 79.094 | 307.158 | 288.252 | 7.562 | −1256.413 | −1188.863 | 155.250 |
| 450 | 82.962 | 316.704 | 290.890 | 11.617 | −1256.934 | −1180.387 | 137.016 |
| 500 | 86.209 | 325.618 | 293.922 | 15.848 | −1257.337 | −1171.859 | 122.423 |
| 600 | 91.231 | 341.806 | 300.582 | 24 735 | −1257.873 | −1154.708 | 100.526 |
| 700 | 94.821 | 356.154 | 307.516 | 34.047 | −1258.148 | −1137.489 | 84.880 |
| 800 | 97 435 | 368.995 | 314.412 | 43.666 | −1258.244 | −1120.243 | 73.144 |
| 900 | 99.378 | 380.589 | 321.132 | 53.512 | −1258.215 | −1102.994 | 64.016 |
| 1000 | 100.853 | 391.139 | 327.613 | 63.527 | −1258 099 | −1085.753 | 56.714 |
| 1100 | 101.993 | 400.807 | 333.834 | 73.671 | −1257.921 | −1068.526 | 50 740 |
| 1200 | 102.890 | 409 722 | 339.791 | 83.917 | −1321.273 | −1050.239 | 45.716 |
| 1300 | 103.607 | 417 987 | 345.492 | 94.243 | −1320.251 | −1027 695 | 41.293 |
| 1400 | 104.188 | 425.687 | 350.948 | 104.634 | −1319.215 | −1005.229 | 37.506 |
| 1500 | 104.664 | 432.892 | 356.174 | 115 077 | −1318.175 | −982.838 | 34.225 |
| 1600 | 105 060 | 439.660 | 361.182 | 125.564 | −1317.135 | −960.516 | 31.358 |
| 1700 | 105.391 | 446.039 | 365.988 | 136.087 | −1316.100 | −938.259 | 28.829 |
| 1800 | 105 672 | 452.071 | 370.604 | 146.641 | −1315.070 | −916.063 | 26.583 |
| 1900 | 105.911 | 457.791 | 375.044 | 157.220 | −1314 047 | −893.924 | 24.576 |
| 2000 | 106.117 | 463.229 | 379.318 | 167.822 | −1313.030 | −871.838 | 22.770 |
| 2100 | 106.295 | 468.411 | 383.438 | 178.443 | −1312.015 | −849 804 | 21.138 |
| 2200 | 106.451 | 473.360 | 387.414 | 189 080 | −1311.002 | −827.817 | 19.655 |
| 2300 | 106.587 | 478.095 | 391.255 | 199.732 | −1309.985 | −805.877 | 18.302 |
| 2400 | 106.707 | 482.633 | 394.968 | 210.397 | −1308.961 | −783.981 | 17.063 |
| 2500 | 106.813 | 486.992 | 398.562 | 221.073 | −1307.925 | −762.128 | 15.924 |
| 2600 | 106.907 | 491.183 | 402.045 | 231.759 | −1306.873 | −740.317 | 14.873 |
| 2700 | 106.992 | 495.219 | 405 421 | 242.454 | −1305.800 | −718.547 | 13 901 |
| 2800 | 107.067 | 499.112 | 408.698 | 253.157 | −1304.703 | −696.817 | 12.999 |
| 2900 | 107.135 | 502.870 | 411.881 | 263.867 | −1303.578 | −675.126 | 12.160 |
| 3000 | 107.197 | 506.503 | 414.975 | 274.584 | −1302.420 | −653.475 | 11.378 |
| 3100 | 107.253 | 510.019 | 417.985 | 285.306 | −1301.227 | −631.863 | 10.647 |
| 3200 | 107.303 | 513.425 | 420.914 | 296.034 | −1299.997 | −610.291 | 9.962 |
| 3300 | 107.350 | 516.727 | 423.768 | 306.767 | −1298.726 | −588.757 | 9.319 |
| 3400 | 107.392 | 519.933 | 426.549 | 317.504 | −1297.414 | −567.262 | 8.715 |
| 3500 | 107.431 | 523.046 | 429.262 | 328.245 | −1296.058 | −545.807 | 8 146 |
| 3600 | 107.466 | 526.073 | 431.909 | 338.990 | −1294 657 | −524.390 | 7.609 |
| 3700 | 107.499 | 529.018 | 434.494 | 349.738 | −1293.211 | −503 014 | 7.101 |
| 3800 | 107.530 | 531.885 | 437.020 | 360 490 | −1291.720 | −481.677 | 6.621 |
| 3900 | 107.558 | 534 679 | 439.488 | 371.244 | −1290.182 | −460.380 | 6.166 |
| 4000 | 107.583 | 537.402 | 441.902 | 382.001 | −1288.598 | −439.123 | 5.734 |
| 4100 | 107 608 | 540.059 | 444.264 | 392.761 | −1286.968 | −417.907 | 5.324 |
| 4200 | 107.630 | 542.653 | 446.576 | 403.523 | −1285.294 | −396.730 | 4 934 |
| 4300 | 107.651 | 545.185 | 448.840 | 414.287 | −1283.574 | −375.594 | 4.563 |
| 4400 | 107.670 | 547 660 | 451.058 | 425.053 | −1281.811 | −354.499 | 4.208 |
| 4500 | 107.689 | 550.080 | 453.231 | 435.821 | −1280.006 | −333 444 | 3.871 |
| 4600 | 107.706 | 552.447 | 455.362 | 446.591 | −1278.158 | −312.430 | 3.548 |
| 4700 | 107.722 | 554.764 | 457.453 | 457.362 | −1276.270 | −291.455 | 3 239 |
| 4800 | 107.737 | 557.032 | 459.504 | 468 135 | −1274.343 | −270.522 | 2.944 |
| 4900 | 107 751 | 559.254 | 461.517 | 478.909 | −1272.377 | −249.629 | 2.661 |
| 5000 | 107.764 | 561.431 | 463.494 | 489.685 | −1270.375 | −228.777 | 2.390 |
| 5100 | 107.776 | 563.565 | 465.435 | 500.462 | −1268.338 | −207.965 | 2.130 |
| 5200 | 107.788 | 565.658 | 467.342 | 511.240 | −1266.268 | −187.194 | 1.880 |
| 5300 | 107.799 | 567 711 | 469.217 | 522.020 | −1264.165 | −166.462 | 1.641 |
| 5400 | 107.810 | 569.726 | 471.059 | 532.800 | −1262.032 | −145.771 | 1 410 |
| 5500 | 107.820 | 571 704 | 472.871 | 543.582 | −1259.869 | −125.120 | 1.188 |
| 5600 | 107.829 | 573.647 | 474.654 | 554.364 | −1257.679 | −104.507 | 0.975 |
| 5700 | 107.838 | 575.556 | 476.407 | 565.147 | −1255.464 | −83 935 | 0.769 |
| 5800 | 107.847 | 577 431 | 478.133 | 575.932 | −1253.223 | −63.401 | 0.571 |
| 5900 | 107.855 | 579.275 | 479.831 | 586 717 | −1250.961 | −42.907 | 0.380 |
| 6000 | 107.862 | 581.088 | 481.504 | 597.503 | −1248.677 | −22.450 | 0.195 |

PREVIOUS: December 1969 (1 atm) CURRENT December 1969 (1 bar)

## Phosphorus Fluoride ($PF_3$) IDEAL GAS $M_r = 87.968969$ Phosphorus Fluoride ($PF_3$) $F_3P_1(g)$

$S°(298.15\ K) = 273\,064 \pm 0.13\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -952.782 \pm 3.8\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -958.441 \pm 3.8\ kJ{\cdot}mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, cm $^{-1}$ | $\nu$, cm $^{-1}$ |
|---|---|
| 892 (1) | 860 (2) |
| 487 (1) | 344 (2) |

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: $C_{3v}$
Bond Distances: P–F = 1.5700 ± 0.0012 Å; F....F = 2.3643 ± 0.0028 Å
Bond Angle: F–P–F = 97.8 ± 0.2°
Product of the Moments of Inertia: $I_A I_B I_C = 2.070369 \times 10^{-114}\ g^3{\cdot}cm^6$

### Enthalpy of Formation

Berthelot[1] measured the enthalpy of hydrolysis of $PF_3(g)$ and $PCl_3(l)$. These results can be combined to give, $\Delta_r H° = 24.5\ kcal{\cdot}mol^{-1}$ for the reaction

$$PF_3(g) + 3\ KCl{\cdot}157\ H_2O \rightarrow PCl_3(l) + 3\ KF{\cdot}112\ H_2O.$$

Combining this result with the following enthalpy of formation data,

$$\Delta_f H°(PCL_3,\ l,\ 298.15\ K) = -72.2\ kcal{\cdot}mol^{-1}\ {}^{2}$$
$$\Delta_f H°(KCl{\cdot}157\ H_2O,\ 298.15\ K) = -100.0\ kcal{\cdot}mol^{-1}\ {}^{3}$$
$$\Delta_f H°(KF{\cdot}112\ H_2O,\ 298.15\ K) = -138.5\ kcal{\cdot}mol^{-1}\ {}^{3}$$

we derive, $\Delta_f H°(PF_3,\ g,\ 298.15\ K) = -212.2\ kcal{\cdot}mol^{-1}$.

Duus and Mykytink[4] reported an enthalpy of reaction of − 2.361 kcal·mol⁻¹ (corrected to 25°C) for the following reaction

$$PCl_3(g) + 3/2\ CaF_2(cr) \rightarrow PF_3(g) + 3/2\ CaCl_2(cr).$$

Combining this result with the following enthalpy of formation data,

$$\Delta_f H°(PCl_3,\ g,\ 298.15\ K) = -64.4\ kcal{\cdot}mol^{-1}\ {}^{2}$$
$$\Delta_f H°(CaF_2,\ cr,\ 298.15\ K) = 293.0 \pm 1.5\ kcal{\cdot}mol^{-1}\ {}^{5}$$
$$\Delta_f H°(CaCl_2,\ cr,\ 298.15\ K) = -190.0\ kcal{\cdot}mol^{-1}\ {}^{3}$$

we derive, $\Delta_f H°(PF_3,\ g,\ 298.15\ K) = -221.9\ kcal{\cdot}mol^{-1}$.

Recently, Rudzitis *et al.*[6] measured the enthalpy of combustion of $PF_3$ in fluorine in a two-chambered bomb calorimeter at 25°C. They reported an enthalpy of combustion of $-152.0 \pm 0.2\ kcal{\cdot}mol^{-1}$ for the reaction

$$PF_3(g) + F_2(g) \rightarrow PF_5(g)$$

Combining this result with $\Delta_f H°(PF_5,\ g,\ 298.15\ K) = -376.9 \pm 0.7\ kcal{\cdot}mol^{-1}$,[5] we derive $\Delta_f H°(PF_3,\ g,\ 298.15\ K) = -224.9 \pm 0.9\ kcal{\cdot}mol^{-1}$. This result is adopted for this tabulation.

### Heat Capacity and Entropy

The vibrational frequencies are those reported by Wilson and Palo.[8] Several different values for the P–F bond length and F–P–F bond angle have been reported in the literature. This problem was recently discussed by Morino *et al.*[9] who also reported new data obtained from electron–diffraction studies. Their results are adopted for this tabulation. Individual moments of inertia calculated according to their structure are: $I_A = I_B = 10.8265 \times 10^{-39}$ and $I_C = 17.6633 \times 10^{-39}\ g{\cdot}cm^2$.

### References

[1] M. Berthelot, Compt. Rend. 100, 81 (1885). M. Berthelot and W. Lounginine, Ann Chim. Phys. [5], 6, 305 (1875).
[2] U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).
[3] U. S. Nat. Bur. Stand. Circ. 500, (1952).
[4] H. C. Duus and D. P. Mykytink, J. Chem. Eng. Data 9, 585 (1964).
[5] JANAF Thermochemical Tables: $CaF_2$(cr), 12–31–68.
[6] E. Rudzitis, Argonne National Laboratory, personal communication, (1969).
[7] M. Kent Wilson and S. R. Palo, J. Chem. Phys. 20, 1716 (1952).
[8] Y. Morino, K. Kuchitsu, and T. Moritani, Inorg. Chem. 8, 867 (1969).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| $T/K$ | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −12.938 | −952.782 | −952.782 | INFINITE |
| 100 | 36.571 | 222.647 | 318.125 | −9.548 | −954.640 | −949.580 | 496.010 |
| 200 | 48.620 | 251.683 | 278.127 | −5.289 | −957.038 | −943.753 | 246.483 |
| 250 | 54 098 | 263.132 | 274.006 | −2.718 | −957.812 | −940.340 | 196.473 |
| 298.15 | 58.691 | 273.064 | 273.064 | 0. | −958.441 | −936.916 | 164.144 |
| 300 | 58.853 | 273.428 | 273.065 | 0.109 | −958.464 | −936.782 | 163.108 |
| 350 | 62.825 | 282.808 | 273.797 | 3.154 | −959.738 | −933.052 | 139.250 |
| 400 | 66 071 | 291.417 | 275.469 | 6.379 | −960.274 | −929.202 | 121.341 |
| 450 | 68.700 | 299.356 | 277.688 | 9.751 | −960.720 | −925.291 | 107.405 |
| 500 | 70.827 | 306.708 | 280.227 | 13.241 | −961.094 | −921.334 | 96.251 |
| 600 | 73.966 | 319.918 | 285.767 | 20.491 | −961.686 | −913.323 | 79.512 |
| 700 | 76.094 | 331.490 | 291.489 | 28.001 | −962.137 | −905.225 | 67.549 |
| 800 | 77.584 | 341.754 | 297.143 | 35.689 | −962.495 | −897.070 | 58.573 |
| 900 | 78.658 | 350.957 | 302.620 | 43.504 | −962.794 | −888.873 | 51.589 |
| 1000 | 79.455 | 359.288 | 307.877 | 51.411 | −963.054 | −880.646 | 46.000 |
| 1100 | 80.061 | 366.891 | 312.901 | 59.388 | −963.290 | −872.393 | 41.427 |
| 1200 | 80.531 | 373.878 | 317.695 | 67.419 | −1027.083 | −863.042 | 37.567 |
| 1300 | 80.902 | 380.339 | 322.269 | 75.491 | −1026.522 | −849.394 | 34.129 |
| 1400 | 81.201 | 386.346 | 326.634 | 83.597 | −1025.965 | −835.790 | 31.184 |
| 1500 | 81.444 | 391.957 | 330.804 | 91.729 | −1025.415 | −822.225 | 28.632 |
| 1600 | 81.644 | 397.219 | 334.792 | 99.884 | −1024.874 | −808.697 | 26.401 |
| 1700 | 81.811 | 402.174 | 338.611 | 108.057 | −1024.342 | −795.202 | 24.434 |
| 1800 | 81.952 | 406.855 | 342.274 | 116.245 | −1023.820 | −781.739 | 22.685 |
| 1900 | 82.072 | 411.289 | 345 790 | 124.447 | −1023.305 | −768.304 | 21.122 |
| 2000 | 82.175 | 415.501 | 349.171 | 132.659 | −1022.795 | −754.896 | 19.716 |
| 2100 | 82.264 | 419.513 | 352.426 | 140.881 | −1022.287 | −741.514 | 18.444 |
| 2200 | 82.341 | 423.341 | 355.563 | 149.112 | −1021.777 | −728.155 | 17.289 |
| 2300 | 82.408 | 427.003 | 358.590 | 157.349 | −1021.259 | −714.820 | 16.234 |
| 2400 | 82.468 | 430.512 | 361.515 | 165.593 | −1020.729 | −701.508 | 15.268 |
| 2500 | 82.520 | 433.879 | 364.342 | 173.843 | −1020.183 | −688.218 | 14.380 |
| 2600 | 82.567 | 437.117 | 367.079 | 182.097 | −1019.614 | −674.951 | 13.560 |
| 2700 | 82.608 | 440.234 | 369.731 | 190.356 | −1019.019 | −661.706 | 12.801 |
| 2800 | 82.646 | 443.239 | 372.303 | 198.618 | −1018.394 | −648.483 | 12.098 |
| 2900 | 82.679 | 446.139 | 374.800 | 206.885 | −1017.733 | −635.284 | 11.443 |
| 3000 | 82.709 | 448.943 | 377.225 | 215.154 | −1017.034 | −622.108 | 10.832 |
| 3100 | 82.737 | 451.655 | 379.582 | 223.426 | −1016.294 | −608.956 | 10.261 |
| 3200 | 82.762 | 454.282 | 381.876 | 231.701 | −1015.509 | −595.828 | 9.726 |
| 3300 | 82.784 | 456.829 | 384.109 | 239.979 | −1014.679 | −582.726 | 9.224 |
| 3400 | 82.805 | 459.301 | 386.284 | 248.258 | −1013.800 | −569.650 | 8.752 |
| 3500 | 82.824 | 461.702 | 388.405 | 256.540 | −1012.872 | −556.600 | 8.307 |
| 3600 | 82.841 | 464 035 | 390.473 | 264.823 | −1011.893 | −543.577 | 7.887 |
| 3700 | 82.858 | 466.305 | 392.492 | 273.108 | −1010.864 | −530.582 | 7.490 |
| 3800 | 82.872 | 468.515 | 394.464 | 281.394 | −1009.782 | −517.616 | 7.115 |
| 3900 | 82.886 | 470.668 | 396.390 | 289.682 | −1008.650 | −504.679 | 6.759 |
| 4000 | 82.899 | 472.767 | 398.274 | 297.972 | −1007.466 | −491.771 | 6.422 |
| 4100 | 82.911 | 474.814 | 400.116 | 306.262 | −1006.232 | −478.895 | 6.101 |
| 4200 | 82.921 | 476.812 | 401.918 | 314.554 | −1004.947 | −466.048 | 5.796 |
| 4300 | 82.932 | 478.763 | 403.683 | 322.846 | −1003.612 | −453.233 | 5.506 |
| 4400 | 82.941 | 480.670 | 405.411 | 331.140 | −1002.228 | −440.449 | 5.229 |
| 4500 | 82.950 | 482.534 | 407.104 | 339.435 | −1000.797 | −427.697 | 4.965 |
| 4600 | 82.958 | 484.357 | 408.764 | 347.730 | −999.318 | −414.978 | 4.712 |
| 4700 | 82.966 | 486.141 | 410.391 | 356.026 | −997.794 | −402.291 | 4.471 |
| 4800 | 82.973 | 487.888 | 411.987 | 364.323 | −996.225 | −389.637 | 4.240 |
| 4900 | 82.980 | 489.599 | 413.554 | 372.621 | −994.613 | −377.017 | 4.019 |
| 5000 | 82.987 | 491.275 | 415.092 | 380.919 | −992.958 | −364.430 | 3.807 |
| 5100 | 82.993 | 492.919 | 416.602 | 389.218 | −991.262 | −351.876 | 3.604 |
| 5200 | 82.999 | 494.530 | 418.085 | 397.518 | −989.526 | −339.356 | 3.409 |
| 5300 | 83.004 | 496.112 | 419.542 | 405.818 | −987.750 | −326.869 | 3.221 |
| 5400 | 83.009 | 497.663 | 420.974 | 414.119 | −985.938 | −314.417 | 3.041 |
| 5500 | 83.014 | 499.186 | 422.383 | 422.420 | −984.088 | −301.999 | 2.868 |
| 5600 | 83.019 | 500.682 | 423.768 | 430.721 | −982.204 | −289.613 | 2.701 |
| 5700 | 83.023 | 502.152 | 425.130 | 439.024 | −980.285 | −277.263 | 2.541 |
| 5800 | 83.027 | 503.595 | 426.470 | 447.326 | −978.333 | −264.947 | 2.386 |
| 5900 | 83.031 | 505.015 | 427.790 | 455 629 | −976.349 | −252.663 | 2.237 |
| 6000 | 83.035 | 506.410 | 429.088 | 463.932 | −974.334 | −240.415 | 2.093 |

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

Phosphorus Fluoride ($PF_3$) $F_3P_1(g)$

## Thiophosphoryl Fluoride ($PSF_3$) IDEAL GAS $M_r = 120.028969$ Thiophosphoryl Fluoride ($PSF_3$) $F_3P_1S_1(g)$

$\Delta_f H°(0\ K) = [-1001.318 \pm 62.8]\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 298.139 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [-1009.068 \pm 62.8]\ kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|
| 981(1) | 945(2) |
| 442(1) | 275(2) |
| 695(1) | 402(2) |

Ground Quantum Weight: [1] $\sigma = 3$
Point Group: $C_{3v}$
Bond Distances: P–S = 1.87 ± 0.03 Å; P–F = 1.53 ± 0.02 Å
Bond Angles: F–P–F = 100.3 ± 2°; F–P–S = 117.6 ± 2°
Product of the Moments of Inertia: $I_A I_B I_C = 1.731454 \times 10^{-113}\ g^3 \cdot cm^6$

### Enthalpy of Formation

The enthalpy of formation of $PSF_3$ is calculated from the enthalpy of formation of $POF_3$ and estimated P=O and P=S bond strengths. Mortimer[1] calculated several P=O and P=S bond dissociation energies from enthalpy of reaction data reported in the literature. Some of these data are given below.

| Reaction | D(P=O) | D(P=S) |
|---|---|---|
| | kcal·mol$^{-1}$ | |
| $\Delta H$ oxidation $PF_3$ to $POF_3$ | 130.3 | |
| $\Delta H$ oxidation $P(OEt)_3$ to $PS(OEt)_3$ | | 81.6 |
| $\Delta H$ oxidation $PPr_3$ to $PSPr_3$ | | 82.6 |

Mole and McCoubrey[2] reported the following enthalpy of reaction:

$$PCl_3(l) + Si(cr) \rightarrow PSCl_3(l).\ \Delta_r H = -5.6\ kcal \cdot mol^{-1}.$$

Combining this result with enthalpy of vaporization data for $PCl_3$[3] and $PSCl_3$,[4] along with the enthalpy of sublimation of S,[3] we derive D(P=S) = 71 kcal·mol$^{-1}$. Averaging this result with the two values given above, we obtain D(P=S) = 78.4 kcal·mol$^{-1}$. We assume that this result represents the enthalpy change for reaction $PSF_3(g) \rightarrow PF_3(g) + S(g)$. Combining this result with similar data for $POF_3$, namely D(P=O) = 130.3 kcal·mol$^{-1}$ and $\Delta_f H°(POF_3, g, 298.15\ K) = -295.6 \pm 1.9$ kcal·mol$^{-1}$,[3] we derive $\infty_f H°(PSF_3, g, 298.15\ K) = -237 \pm 15$ kcal·mol$^{-1}$, from the relationship $\infty_f H°(PSF_3, g, 298.15\ K) = \infty_f H°(POF_3, g, 298.15\ K) + \infty_f H°(S, g, 298.15\ K) - \infty_f H°(O, g, 298.15\ K) - D(P=O) + D(P=S)$.

### Heat Capacity and Entropy

Several recent infrared and Raman studies[7 8, 9 10] of $PSF_3$ have been reported. These data are in good agreement, except for the $\tau_1$ fundamental. Dewaulle and Francois[11] assigned this fundamental to the 869 cm$^{-1}$ band observed in their spectra. The recent work indicates that this fundamental should be assigned to the 981 cm$^{-1}$ band. Average values of the vibrational frequencies reported by[8 9 10] are adopted for this tabulation. The molecular structure of this molecule was determined by Williams *et al.*[12] and Hawkins and Cohen[13] from microwave studies. The individual moments of inertia calculated from the constants given by Williams *et al.*[12] are $I_A = 1.74111 \times 10^{-39}$, $I_B = I_C = 31.5349 \times 10^{-39}\ g \cdot cm^2$.

### References

[1] C. T. Mortimer, Pure Appl. Chem. 2, 71 (1961).
[2] M. F. Mole and J. C. McCoubrey, Nature 202, 450 (1964).
[3] JANAF Thermochemical Tables: $PCl_3$(l), 9–30–62; S(cr), 12–31–65; $POF_3$(g), 12–31–69.
[4] D. E Rogers and G. Nickless in "Inorganic Sulphur Chemistry," G. Nickless, Ed., Elsevier Publishing Co., New York, N. Y., Chapter 9, (1968).
[5] H. H. Horn, A. Muller and O. Glemser, Z. Naturforsch 20a, 746 (1965).
[6] R. G. Cavell, Spectrochim. Acta 23a, 249 (1967).
[7] A. Muller, B. Krebs, E. Niecke, and A. Ruoff, Ber Bunsenges Phys. Chem. 71 (6), 571 (1967).
[8] J. R. Durig and J. W. Clark, J. Chem. Phys. 46, 3057 (1967).
[9] M. L. Dewaulle and F. Francois, Compt. Rend. 226, 894 (1948).
[10] Q. Williams, J. Sheridan and W. Gordy, J. Chem. Phys. 20, 164 (1952).
[11] N. J. Hawkins, V. W. Cohen and W S. Koski, J. Chem. Phys. 20, 528 (1952).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −15.260 | −1001.318 | −1001.318 | INFINITE |
| 100 | 40.782 | 236.647 | 354.315 | −11.767 | −1003.763 | −998.851 | 521.746 |
| 200 | 60.470 | 271.207 | 304.539 | −6.666 | −1006.961 | −992.854 | 259.307 |
| 250 | 68.259 | 285.562 | 299.333 | −3.443 | −1008.103 | −989.192 | 206.680 |
| 298.15 | 74.551 | 298.139 | 298.139 | 0. | −1009.068 | −985.461 | 172.649 |
| 300 | 74.771 | 298.601 | 298.140 | 0.138 | −1009.103 | −985.314 | 171.558 |
| 350 | 80.142 | 310.544 | 299.071 | 4.015 | −1010.711 | −981.207 | 146.437 |
| 400 | 84.525 | 321.542 | 301.202 | 8.136 | −1013.783 | −976.844 | 127.563 |
| 450 | 88.085 | 331.710 | 304.034 | 12.454 | −1015.207 | −972.149 | 112.844 |
| 500 | 90.978 | 341.146 | 307.279 | 16.933 | −1016.595 | −967.287 | 101.052 |
| 600 | 95.275 | 358.139 | 314.372 | 26.260 | −1018.696 | −957.218 | 83.333 |
| 700 | 98.210 | 373.059 | 321.712 | 35.943 | −1020.319 | −946.838 | 70.654 |
| 800 | 100.276 | 386.316 | 328.975 | 45.873 | −1021.647 | −936.247 | 61.131 |
| 900 | 101.774 | 398.218 | 336.018 | 55.980 | −1075.911 | −924.422 | 53.652 |
| 1000 | 102.888 | 409.001 | 342.786 | 66.215 | −1075.699 | −907.600 | 47.408 |
| 1100 | 103.737 | 418.849 | 349.260 | 76.548 | −1075.450 | −890.802 | 42.301 |
| 1200 | 104.396 | 427.905 | 355.441 | 86.956 | −1138.753 | −872.950 | 37.999 |
| 1300 | 104.919 | 436.282 | 361.342 | 97.423 | −1137.700 | −850.842 | 34.187 |
| 1400 | 105.339 | 444.074 | 366.976 | 107.937 | −1136.653 | −828.815 | 30.923 |
| 1500 | 105.682 | 451.353 | 372.361 | 118.488 | −1135.617 | −806.863 | 28.097 |
| 1600 | 105.965 | 458.183 | 377.514 | 129.071 | −1134.596 | −784.980 | 25.627 |
| 1700 | 106.201 | 464.615 | 382.450 | 139.680 | −1133.592 | −763.159 | 23.449 |
| 1800 | 106.400 | 470.691 | 387.185 | 150.310 | −1132.604 | −741.398 | 21.515 |
| 1900 | 106.569 | 476.448 | 391.733 | 160.959 | −1131.632 | −719.691 | 19.786 |
| 2000 | 106.714 | 481.918 | 396.107 | 171.623 | −1130.672 | −698.034 | 18.231 |
| 2100 | 106.840 | 487.128 | 400.318 | 182.301 | −1129.720 | −676.426 | 16.825 |
| 2200 | 106.949 | 492.101 | 404.378 | 192.990 | −1128.773 | −654.863 | 15.548 |
| 2300 | 107.045 | 496.857 | 408.296 | 203.690 | −1127.825 | −633.343 | 14.384 |
| 2400 | 107.128 | 501.414 | 412.082 | 214.399 | −1126.871 | −611.864 | 13.317 |
| 2500 | 107.203 | 505.789 | 415.743 | 225.116 | −1125.906 | −590.425 | 12.336 |
| 2600 | 107.269 | 509.995 | 419.288 | 235.839 | −1124.924 | −569.025 | 11.432 |
| 2700 | 107.328 | 514.045 | 422.723 | 246.569 | −1123.920 | −547.663 | 10.595 |
| 2800 | 107.380 | 517.949 | 426.054 | 257.305 | −1122.889 | −526.339 | 9.819 |
| 2900 | 107.428 | 521.718 | 429.288 | 268.045 | −1121.828 | −505.053 | 9.097 |
| 3000 | 107.471 | 525.360 | 432.430 | 278.790 | −1120.732 | −483.803 | 8.424 |
| 3100 | 107.510 | 528.885 | 435.485 | 289.539 | −1119.599 | −462.591 | 7.795 |
| 3200 | 107.545 | 532.299 | 438.458 | 300.292 | −1118.424 | −441.416 | 7.205 |
| 3300 | 107.577 | 535.609 | 441.352 | 311.048 | −1117.207 | −420.278 | 6.652 |
| 3400 | 107.606 | 538.821 | 444.172 | 321.807 | −1115.944 | −399.178 | 6.133 |
| 3500 | 107.633 | 541.940 | 446.921 | 332.569 | −1114.636 | −378.115 | 5.643 |
| 3600 | 107.658 | 544.973 | 449.602 | 343.334 | −1113.281 | −357.091 | 5.181 |
| 3700 | 107.681 | 547.923 | 452.220 | 354.101 | −1111.877 | −336.105 | 4.745 |
| 3800 | 107.702 | 550.795 | 454.776 | 364.870 | −1110.426 | −315.157 | 4.332 |
| 3900 | 107.721 | 553.593 | 457.274 | 375.641 | −1108.928 | −294.248 | 3.941 |
| 4000 | 107.739 | 556.320 | 459.717 | 386.414 | −1107.382 | −273.379 | 3.570 |
| 4100 | 107 756 | 558.981 | 462.105 | 397.189 | −1105.789 | −252.549 | 3.218 |
| 4200 | 107.771 | 561.578 | 464.443 | 407.965 | −1104.151 | −231.757 | 2.882 |
| 4300 | 107.786 | 564.114 | 466.732 | 418.743 | −1102.467 | −211.006 | 2.563 |
| 4400 | 107.799 | 566.592 | 468.973 | 429.522 | −1100.740 | −190.294 | 2.259 |
| 4500 | 107 812 | 569.014 | 471.169 | 440.303 | −1098.969 | −169.622 | 1.969 |
| 4600 | 107.824 | 571.384 | 473.322 | 451.085 | −1097.157 | −148.990 | 1.692 |
| 4700 | 107.835 | 573.703 | 475.433 | 461.868 | −1095.305 | −128.397 | 1.427 |
| 4800 | 107.845 | 575.974 | 477.504 | 472.652 | −1093.414 | −107.845 | 1.174 |
| 4900 | 107.855 | 578.197 | 479.537 | 483.437 | −1091.485 | −87.332 | 0.931 |
| 5000 | 107.864 | 580.376 | 481.532 | 494.223 | −1089.521 | −66.859 | 0.698 |
| 5100 | 107.873 | 582.512 | 483.491 | 505.010 | −1087.521 | −46.425 | 0.475 |
| 5200 | 107 881 | 584.607 | 485.415 | 515.797 | −1085.488 | −26.031 | 0.261 |
| 5300 | 107.889 | 586.662 | 487.306 | 526.586 | −1083.423 | −5.677 | 0.056 |
| 5400 | 107.896 | 588.679 | 489.165 | 537.375 | −1081.327 | 14.638 | −0.142 |
| 5500 | 107.903 | 590.659 | 490.993 | 548.165 | −1079.202 | 34.914 | −0.332 |
| 5600 | 107.909 | 592.603 | 492.790 | 558.955 | −1077.048 | 55.152 | −0.514 |
| 5700 | 107.916 | 594.513 | 494.558 | 569.747 | −1074.867 | 75.350 | −0.691 |
| 5800 | 107.921 | 596.390 | 496.297 | 580.539 | −1072.661 | 95.510 | −0.860 |
| 5900 | 107 927 | 598.235 | 498.009 | 591.331 | −1070.429 | 115.632 | −1.024 |
| 6000 | 107 932 | 600.049 | 499.695 | 602.124 | −1068.174 | 135.715 | −1 182 |

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

**Sulfur Fluoride ($SF_3$)** **IDEAL GAS** $M_r = 89.055209$ **Sulfur Fluoride ($SF_3$)** **$F_3S_1(g)$**

$S°(298.15\ K) = [286.174 \pm 4.2]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -498\,980 \pm 33.5\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -503\,030 \pm 33.5\ kJ\ mol^{-1}$

| Electronic Levels and Quantum Weights | |
|---|---|
| $\epsilon_i$, cm$^{-1}$ | $g_i$ |
| 0 | [2] |
| [25000] | [2] |

| Vibrational Frequencies and Degeneracies | |
|---|---|
| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
| [850](1) | [725](1) |
| [550](1) | [450](1) |
| [300] | [350](1) |

Point Group: $C_{2v}$ $\sigma = 2$
Bond Distances: S–F* = [1.545] Å; S–F** = [1.646] Å
Bond Angles: F*–S–F** = [89]°; F**–S–F** = [178]°
(* – equatorial ** – axial)
Product of the Moments of Inertia: $I_AI_BI_C = [2.272514 \times 10^{-114}]\ g^3{\cdot}cm^6$

## Enthalpy of Formation

$\Delta_fH°(0\ K) = -119.26 \pm 8.0\ kcal{\cdot}mol^{-1}$ is calculated from the primary bond dissociation energy for $SF_4$ of $D_0^\circ\ (SF_3-F) = 80.0 \pm 3.0\ kcal{\cdot}mol^{-1}$ with JANAF[1] $\Delta_fH°$ data for F(g) and $SF_4(g)$. The value of $D_0^\circ$ is taken to be equal to one–fourth the enthalpy of atomization of $SF_4$.[1] We calculate the heat of atomization, $\Delta_aH°(0\ K)$, and mean bond dissocation energy ($D_0^\circ$) for $SF_3$ to be 240.1 kcal·mol$^{-1}$ and 80.0 kcal·mol$^{-1}$, respectively. $\Delta_fH°$ is $-120.227\ kcal{\cdot}mol^{-1}$ at 298.15 K.

Several pieces of information are available which are relatively imprecise but do support our assumption that $D_0^\circ\ (SF_3-F) = \Delta_aH°(SF_4)/4$. Bott[2] has reported the results of shock–tube experiments on the dissociation of $SF_4$ over the temperature range 1650–1950 K. Rate constants based on spectroscopic measurements were correlated with the Rice–Ramsperger–Kassel (RRK) theory. This study strongly suggests that $D_0^\circ\ (SF_3-F) = 79.0 \pm 3.0\ kcal{\cdot}mol^{-1}$.

Electron–impact threshold measurements for $SF_3^+$ from $SF_4$ have been reported by Hildenbrand[3] and Glemser *et al.*[4] The measured appearance potentials (AP) are in good agreement and indicate $AP(SF_3^+/SF_4) = 12.67 \pm 0.1\ eV$. Combining this value with an upper limit for the ionization potential of $SF_3(IP \leqslant 9.25\ eV,\ 5)$, we obtain a lower limit for $D_0^\circ\ (SF_3-F)$ of 78.9 kcal·mol$^{-1}$.

Two upper limit values for $D_0^\circ\ (SF_3-F)$ can be obtained from threshold measurements by Harland and Thynne[6] on dissociative attachment in $SF_6$ and $SF_4$. We combine their $AP(F^-/SF_4) = 0.20 \pm 0.05\ eV$ with the electron affinity of F(EA = 3.399 eV,)[1] to obtain $D_0^\circ\ (SF_3-F) \leqslant 83.0\ kcal{\cdot}mol^{-1}$. In addition, their appearance potentials[6] for the formation of $F^-$ from $SF_6$ by two distinct processes are combined directly to give $D_0^\circ\ (SF_3-F) \leqslant 80.7\ kcal{\cdot}mol^{-1}$.

The AP of $SF_3^+$ from $SF_6$ has been measured by electron–impact[3,7] and photoelectron spectroscopy.[8] These three threshold values are in agreement with $AP(SF_3^+/SF_6) = 19.97 \pm 0.1\ eV$ Assuming the ionization process to be $SF_6(g) + e^- = SF_3^+(g) + 3\ F(g) + 2\ e^-$, we combine the mean AP value with $IP(SF_3) \leqslant 9.25\ eV$[5] to obtain $\Delta_fH°(SF_3,\ g,\ 0\ K) < -96.3\ kcal{\cdot}mol^{-1}$. This result conflicts with all of the other available information; thus, we are led to conclude that the formation of $SF_3^+$ from $SF_6$ probably involves significant kinetic and/or excitation energies.

## Heat Capacity and Entropy

We assume a molecular structure in which the four atoms form a slightly distorted T–shaped molecule having bond angles similar to those for $ClF_3$.[1] We eliminate a nonplanar pyramid ($C_{3v}$ symmetry) as a plausible structure since recent ESR studies[9] show that the radical has only two equivalent fluorine nuclei. The equatorial and axial S–F bond lengths are assumed to be equal to those for $SF_4$.[1] The principal moments of inertia are: $I_A = 5.8076 \times 10^{-39}$, $I_B = 17.0895 \times 10^{-39}$, and $I_C = 22.8971 \times 10^{-39}\ g{\cdot}cm^2$.

The vibrational representation for the adopted structure is $3A_1 + 2B_1 + B_2$. We estimate the six fundamentals according to symmetry species by analogy with the frequencies and assignments for $ClF_3$ and $SF_4$.[1,10] Since several of the assignments for $SF_4$[11] are uncertain, more weight is given to the results for $ClF_3$. Bott[2] detected IR radiation in emission at 11.0–12.6 μ in $SF_4$/Ar mixtures which were shock–heated to temperatures above 2050 K. He attributed this radiation to $SF_3$, indicating that at least one fundamental lies in the region 794–909 cm$^{-1}$. We assume that the unpaired electron will form all doublet states, and we include an excited level at 25000 cm$^{-1}$ by analogy with that which has been observed for $SF_4^+$.[8]

Wilkins[12] has previously reported thermal functions for $SF_3$ which cover an extended temperature range (0–6000 K). These functions are based on a pyramidal structure and vibrational frequencies obtained from estimated force constants Since this structure now appears to be incorrect, our functions are believed to be more reliable.

## References

[1] JANAF Thermochemical Tables: F(g), 9-30-65, $SF_4(g)$ and $SF_6(g)$, 6-30-76; $F^-(g)$, 12-31-71; $ClF_3(g)$, 9-30-65.
[2] J. F. Bott, J. Chem. Phys. 54, 181 (1971).
[3] D. L. Hildenbrand, J. Phys. Chem. 77, 897 (1973).
[4] O. Glemser, A. Muller, D. Bohler and B. Krebs, Z. Anorg. Allg. Chem. 357, 184 (1968).
[5] F. C. Fehsenfeld, J. Chem. Phys. 54, 438 (1971).

Continued from page 1216

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0 | INFINITE | −13.599 | −498.980 | −498.980 | INFINITE |
| 100 | 37.533 | 232.606 | 334.474 | −10.187 | −500.617 | −497.070 | 259.643 |
| 200 | 52.232 | 263.155 | 291.624 | −5.694 | −502.160 | −492.868 | 128.724 |
| 250 | 58.316 | 275.488 | 287.187 | −2.925 | −502.664 | −490.483 | 102.481 |
| 298 15 | 62.978 | 286.174 | 286.174 | 0. | −503.030 | −488.103 | 85.514 |
| 300 | 63.136 | 286.564 | 286.176 | 0.117 | −503.042 | −488.010 | 84.970 |
| 350 | 66.875 | 296.590 | 286.959 | 3.371 | −503.337 | −485.480 | 72.454 |
| 400 | 69.763 | 305.717 | 288.742 | 6.790 | −505.795 | −482.825 | 63.050 |
| 450 | 72.006 | 314.069 | 291.099 | 10.336 | −506.674 | −479.909 | 55.706 |
| 500 | 73.764 | 321 750 | 293.785 | 13.982 | −507.579 | −476.884 | 49.820 |
| 600 | 76.276 | 335 437 | 299 615 | 21.494 | −508.863 | −470.617 | 40.971 |
| 700 | 77.927 | 347.328 | 305.600 | 29.209 | −509.821 | −464.163 | 34.636 |
| 800 | 79 060 | 357.812 | 311.484 | 37.062 | −510.594 | −457.586 | 29.877 |
| 900 | 79.867 | 367.173 | 317.161 | 45.010 | −564.383 | −449.839 | 26.108 |
| 1000 | 80 460 | 375.620 | 322.592 | 53.028 | −563.757 | −437.145 | 22.834 |
| 1100 | 80.907 | 383.311 | 327.767 | 61.098 | −563.139 | −424.514 | 20.159 |
| 1200 | 81.252 | 390.366 | 332.694 | 69.206 | −562.536 | −411.939 | 17.931 |
| 1300 | 81.524 | 396.881 | 337.384 | 77.346 | −561.953 | −399.413 | 16 049 |
| 1400 | 81.742 | 402.930 | 341.852 | 85.509 | −561.393 | −386.931 | 14.437 |
| 1500 | 81.918 | 408.576 | 346.115 | 93.693 | −560.859 | −374.488 | 13.041 |
| 1600 | 82.064 | 413.868 | 350.185 | 101.892 | −560.351 | −362.080 | 11.821 |
| 1700 | 82.185 | 418.847 | 354.079 | 110.105 | −559.869 | −349.703 | 10.745 |
| 1800 | 82.287 | 423.547 | 357.809 | 118.328 | −559.411 | −337.354 | 9.790 |
| 1900 | 82.374 | 427 999 | 361.387 | 126.562 | −558.975 | −325.029 | 8.936 |
| 2000 | 82.448 | 432.226 | 364 825 | 134.803 | −558.557 | −312.727 | 8.168 |
| 2100 | 82.512 | 436.250 | 368 131 | 143.051 | −558.152 | −300.446 | 7.473 |
| 2200 | 82.568 | 440.090 | 371.315 | 151.305 | −557.755 | −288.183 | 6.842 |
| 2300 | 82 616 | 443.761 | 374.386 | 159.564 | −557.360 | −275.939 | 6.267 |
| 2400 | 82.659 | 447.278 | 377.350 | 167.828 | −556.962 | −263.712 | 5.740 |
| 2500 | 82.698 | 450.654 | 380.215 | 176.096 | −556.555 | −251.501 | 5.255 |
| 2600 | 82.732 | 453.898 | 382.987 | 184.367 | −556.132 | −239 307 | 4.808 |
| 2700 | 82.762 | 457.021 | 385.672 | 192.642 | −555.689 | −227 130 | 4.394 |
| 2800 | 82.790 | 460.031 | 388.274 | 200.920 | −555.221 | −214.970 | 4.010 |
| 2900 | 82.816 | 462.937 | 390.799 | 209.200 | −554.722 | −202.826 | 3.653 |
| 3000 | 82.840 | 465.745 | 393.250 | 217.483 | −554.190 | −190.701 | 3.320 |
| 3100 | 82.862 | 468.461 | 395.633 | 225.768 | −553.620 | −178.594 | 3.009 |
| 3200 | 82.884 | 471 092 | 397.950 | 234.055 | −553.010 | −166.506 | 2.718 |
| 3300 | 82.905 | 473.643 | 400.205 | 242.345 | −552.356 | −154.438 | 2.445 |
| 3400 | 82.925 | 476.118 | 402.402 | 250.636 | −551.657 | −142.390 | 2.188 |
| 3500 | 82.945 | 478.523 | 404.543 | 258.930 | −550.911 | −130.364 | 1.946 |
| 3600 | 82.965 | 480.859 | 406.630 | 267.225 | −550.118 | −118.359 | 1.717 |
| 3700 | 82.986 | 483.133 | 408.667 | 275.523 | −549.276 | −106.377 | 1.502 |
| 3800 | 83.007 | 485.346 | 410.656 | 283.823 | −548.385 | −94.419 | 1.298 |
| 3900 | 83.029 | 487.503 | 412.599 | 292.124 | −547.445 | −82.484 | 1.105 |
| 4000 | 83.052 | 489.605 | 414.498 | 300.428 | −546.456 | −70.575 | 0.922 |
| 4100 | 83.076 | 491.656 | 416.355 | 308.735 | −545.419 | −58.691 | 0.748 |
| 4200 | 83.101 | 493.658 | 418.172 | 317.044 | −544.333 | −46.832 | 0.582 |
| 4300 | 83.127 | 495.614 | 419.950 | 325.355 | −543.200 | −35.001 | 0.425 |
| 4400 | 83.155 | 497.526 | 421.692 | 333.669 | −542.021 | −23.195 | 0.275 |
| 4500 | 83.185 | 499.395 | 423.398 | 341.986 | −540.796 | −11.417 | 0.133 |
| 4600 | 83.215 | 501.223 | 425.070 | 350.306 | −539.526 | 0.332 | −0.004 |
| 4700 | 83.248 | 503.013 | 426.709 | 358.629 | −538.213 | 12.055 | −0.134 |
| 4800 | 83.282 | 504.766 | 428.317 | 366.956 | −536.858 | 23.748 | −0.258 |
| 4900 | 83.317 | 506.484 | 429.895 | 375.286 | −535.461 | 35.413 | −0.378 |
| 5000 | 83.354 | 508.167 | 431.444 | 383.619 | −534.024 | 47.049 | −0.492 |
| 5100 | 83.393 | 509.818 | 432.964 | 391.957 | −532.549 | 58.656 | −0.601 |
| 5200 | 83.433 | 511.438 | 434.458 | 400.298 | −531.036 | 70.234 | −0.706 |
| 5300 | 83.475 | 513.028 | 435.925 | 408.643 | −529.486 | 81.782 | −0.806 |
| 5400 | 83.518 | 514.588 | 437.368 | 416.993 | −527.901 | 93.300 | −0.903 |
| 5500 | 83.563 | 516.121 | 438.786 | 425.347 | −526.281 | 104.789 | −0.995 |
| 5600 | 83 609 | 517.627 | 440.180 | 433.706 | −524.628 | 116.248 | −1.084 |
| 5700 | 83.657 | 519.108 | 441.552 | 442.069 | −522.942 | 127.677 | −1.170 |
| 5800 | 83.706 | 520.563 | 442.902 | 450.437 | −521.226 | 139.076 | −1.253 |
| 5900 | 83.756 | 521.994 | 444.230 | 458.810 | −519.479 | 150.447 | −1.332 |
| 6000 | 83.807 | 523.403 | 445.538 | 467.188 | −517.703 | 161.786 | −1.408 |

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

**Sulfur Fluoride, Ion ($SF_3^+$)** **IDEAL GAS** **$M_r$ = 89.054660** **Sulfur Fluoride, Ion ($SF_3^+$)** **$F_3S_1^+(g)$**

$S°(298.15 K) = 268.972 \pm 2.1\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0 K) = 392.632 \pm 33.5\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15 K) = 393.589 \pm 33.5\ kJ \cdot mol^{-1}$

| Electronic Levels and Quantum Weights | |
|---|---|
| $\epsilon_i$, cm$^{-1}$ | $g_i$ |
| 0 | 1 |
| 21777 | 1 |

| Vibrational Frequencies and Degeneracies | |
|---|---|
| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
| 938 (1) | 914 (2) |
| 530 (1) | 411 (2) |

Point Group: $C_{3v}$ $\sigma = 3$
Bond Distance. S–F = 1 497 ± 0.03Å
Bond Angle: F–S–F = 97.51 ± 0.5°
Product of the Moments of Inertia: $I_A I_B I_C = 1.5584 \times 10^{-114}\ g^3 \cdot cm^6$

## Enthalpy of Formation

Glemser *et al.*[1] determined $AP(SF_3^+) = 12\,70 \pm 0.03$ eV from electron–impact measurements on $SF_4$ Their results[1] are confirmed by the subsequent measurements of Hildenbrand[2] who reported AP values of 12.63 ± 0 1 eV (from $SF_4$) and 12.8 eV (from $SF_4$ formed as a reaction product in $SF_6 + C$) From these results we arrive at a $\Delta_r H°(0 K) = 293.1 \pm 2.3$ kcal·mol$^{-1}$ (mean AP value) for the process $SF_4(g) + e^- = SF_3^+(g) + F(g) + 2e^-$. Assuming that the products are formed with no excess energies, we combine the value of $\Delta_r H°(0 K)$ with JANAF enthalpy of formation[3] for $SF_4$ and F to obtain the result, $\Delta_f H°(SF_3^+, g, 0 K) = 93.84 \pm 8.0$ kcal·mol$^{-1}$ which is adopted. Our $\Delta_f H°$ value corresponds to $IP(SF_3) = 213.1 \pm 16.0$ kcal mol$^{-1}$ (9 24 ± 0 7 eV) This value is consistent with the observations of Fehsenfeld[4] who found no charge transfer reaction between NO and $SF_3^+$, suggesting that $IP(SF_3) < 9.25$ eV In addition, we predict that $IP(SF_3) << IP(SF_2)$ due to a stabilization of the positive charge in the even–electron $SF_3^+$ cation by resonance structures such as $F_2S{=}F^+$. JANAF data[3] gives $IP(SF_2) - IP(SF_3) = 1.05$ eV which compares favorably with the 1–2 eV lowerings[5] observed in other di– and tri–fluoride molecules and radicals.

Paulett and Lustig [6] reported appearance potentials for $SF_3^+$ and $SF_4$+ from $SF_5NF_2$. We combine their results to arrive at $\Delta_r H°(0 K) = 2.31 \pm 4.6$ kcal·mol$^{-1}$ for the process $SF_4^+(g) + NF_3(g) = SF_3^+(g) + NF_2(g) + F_2(g)$ which leads to $\Delta_f H°(SF_3^+, g, 0 K) = 61.5$ kcal·mol$^{-1}$ This value is in poor agreement with the adopted result, suggesting that the fragmentation processes involving $SF_5NF_2$ probably include unknown excess energy terms. Other reported fragment–ion appearance potentials for $SF^+$ have been previously analyzed (refer to $SF_3(g)$ and $SF_4(g)$ tables) and were shown to be seriously in error.

$\Delta_f H°(298\ 15 K)$ is calculated to be 94 07 kcal·mol$^{-1}$. Using JANAF data.[3] we find that the primary bond dissociation energy $D_0^\circ(SF_2^+{-}F)$ is 91.4 kcal·mol$^{-1}$ which when compared with $D_0^\circ$ values for $SF_3$ (67 3 kcal·mol$^{-1}$) and $SF_3^-$ (106.4 kcal mol$^{-1}$) indicates that the trend is $D_0^\circ(SF_3^-) > D_0^\circ(SF_3^+) >> D_0^\circ(SF_3)$. The observed increased bond strengths in both ions relative to the $SF_3$ radical provide additional support to the view that the positive and negative charges are delocalized in the even–electron ions. Furthermore, available structural information shows that the bond length in $SF_3^+$ is the shortest S–F bond that has so far been reported. The heat of atomization, $\Delta_a H°(0 K)$, and average bond dissociation energy are 265.9 kcal·mol$^{-1}$ and 88.6 kcal·mol$^{-1}$, respectively.

## Heat Capacity and Entropy

The molecular structure and vibrational frequencies are those measured by Gibler *et al.*[7] for the $SF_3^+$ ion in the solid $SF_4BF_3$ adduct. We adopt average values of the bond lengths and angles reported by Gibler *et al.*[7] since spectroscopic evidence[8] indicates that in crystal adducts the $SF_3^+$ symmetry is lowered somewhat as a result of flourine bridging with the anion. The adopted bond length is estimated to be within ±2.0% of the true gas–phase value, based on a comparison of structural data for gaseous and crystalline $ClF_3$.[9] The adopted bond angle (97.51°) is close to the gas–phase value (97.8 ± 0.2°) found for the isoelectronic molecule $PF_3$,[3] suggesting that the gas–phase bond angle for $SF_3^+$ is probably within ±0.5° of the adopted solid–state value. Our frequencies show good agreement with those determined by Azeem *et al.*[8] in their infrared and Raman studies of solid adducts of $SF_4$ with several fluoride acceptors Their results[8] indicate that the $SF_3^+$ frequencies are relatively independent of the anion and are not significantly different when measured in the liquid state Thus, we believe that the error introduced in the $SF_3^+$ thermal functions by use of solid–state frequencies is probably small The individual moments of inertia are: $I_A = 1.5987 \times 10^{-38}$, $I_B = 9\,8733 \times 10^{-39}$, and $I_C = 9.8733 \times 10^{-39}$ g cm$^2$.

Delwiche[10] has reported an ionization efficiency curve for $SF_3^+$ which was obtained by retarded potential difference (RPD) measurements. This curve reveals the existence of an excited state, lying 2177 cm$^{-1}$ above the ground state We include this level and assume that the ground and excited states are both singlets since $SF_3^+$ has no unpaired electrons.

## References

[1] O. Glemser, A. Muller, D. Bohler, and B. Krebs, Z. anorg allg. Chem. 357, 184 (1968).
[2] D. L. Hildenbrand, J. Phys. Chem. 77, 897 (1973).
[3] JANAF Thermochemical Tables. $SF_4(g)$ and $SF_3(g)$, 6–30–76, F(g), 9–30–65; $SF_3^+(g)$, 12–31–76; $PF_3(g)$, 12–31–69.
[4] F. C. Fehsenfeld, J. Chem. Phys. 54, 438 (1971).

Continued on page 1216

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p^\circ$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
|---|---|---|---|---|---|---|---|
| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
| 0 | 0. | 0 | INFINITE | −12.409 | 392.632 | | |
| 100 | 35.082 | 221.200 | 311 734 | −9.053 | | | |
| 200 | 45 909 | 248.643 | 273.799 | −5.031 | | | |
| 250 | 51 457 | 259.492 | 269.872 | −2.595 | | | |
| 298.15 | 56.223 | 268.972 | 268.972 | 0. | 393.589 | 407.390 | −71.373 |
| 300 | 56.393 | 269.321 | 268.974 | 0.104 | 393.603 | 407.476 | −70.948 |
| 350 | 60.593 | 278.339 | 269.676 | 3.032 | 394.020 | 409.756 | −61.153 |
| 400 | 64.076 | 286.665 | 271.286 | 6.151 | 392.303 | 412.059 | −53.809 |
| 450 | 66.931 | 294.382 | 273 429 | 9.429 | 392.193 | 414.526 | −48.117 |
| 500 | 69.262 | 301.559 | 275.887 | 12.836 | 392.089 | 417.016 | −43.565 |
| 600 | 72.739 | 314.515 | 281.270 | 19.947 | 392.484 | 421.974 | −36.736 |
| 700 | 75.120 | 325 917 | 286.850 | 27.347 | 393.288 | 426.830 | −31.850 |
| 800 | 76 797 | 336.064 | 292.379 | 34.948 | 394.342 | 431.552 | −28.177 |
| 900 | 78.014 | 345.183 | 297.748 | 42.691 | 342.426 | 437.213 | −25.375 |
| 1000 | 78.919 | 353.452 | 302.912 | 50.540 | 344.963 | 447.609 | −23.381 |
| 1100 | 79.609 | 361.008 | 307.855 | 58.468 | 347.518 | 457.750 | −21.737 |
| 1200 | 80 145 | 367.958 | 312.578 | 66.457 | 350.079 | 467.658 | −20.357 |
| 1300 | 80.570 | 374.391 | 317.088 | 74.493 | 352.638 | 477.352 | −19.180 |
| 1400 | 80.911 | 380.375 | 321.397 | 82.568 | 355.187 | 486.850 | −18.165 |
| 1500 | 81.189 | 385.967 | 325.518 | 90.673 | 357.722 | 496.166 | −17.278 |
| 1600 | 81.419 | 391.214 | 329.461 | 98.804 | 360.240 | 505.313 | −16.497 |
| 1700 | 81.611 | 396.156 | 333.241 | 106.956 | 362.740 | 514.304 | −15.803 |
| 1800 | 81 773 | 400.825 | 336.867 | 115.125 | 365.222 | 523.148 | −15.181 |
| 1900 | 81.911 | 405.250 | 340.351 | 123.310 | 367.688 | 531.854 | −14.622 |
| 2000 | 82.029 | 409.455 | 343.702 | 131.507 | 370.140 | 540.431 | −14.115 |
| 2100 | 82.131 | 413.460 | 346.929 | 139.715 | 372.584 | 548.885 | −13.653 |
| 2200 | 82.220 | 417.283 | 350.040 | 147.933 | 375 023 | 557.223 | −13.230 |
| 2300 | 82.299 | 420 939 | 353.044 | 156.159 | 377 464 | 565.451 | −12.842 |
| 2400 | 82.368 | 424 443 | 355 947 | 164.392 | 379.910 | 573.571 | −12.483 |
| 2500 | 82.430 | 427.807 | 358.754 | 172.632 | 382.368 | 581.590 | −12.152 |
| 2600 | 82 486 | 431.041 | 361.473 | 180.878 | 384.843 | 589.510 | −11.843 |
| 2700 | 82.537 | 434.155 | 364.107 | 189.129 | 387.341 | 597.335 | −11.556 |
| 2800 | 82.584 | 437.158 | 366.663 | 197.385 | 389.867 | 605.066 | −11.288 |
| 2900 | 82.628 | 440.056 | 369 144 | 205.646 | 392.424 | 612.707 | −11 036 |
| 3000 | 82.670 | 442.858 | 371.555 | 213 911 | 395.017 | 620.259 | −10.800 |
| 3100 | 82.709 | 445.570 | 373 899 | 222.180 | 397.649 | 627.723 | −10.577 |
| 3200 | 82.748 | 448 196 | 376.180 | 230 453 | 400.324 | 635.102 | −10.367 |
| 3300 | 82 786 | 450.743 | 378.401 | 238.729 | 403.044 | 642.397 | −10.168 |
| 3400 | 82.824 | 453.215 | 380.565 | 247.010 | 405.810 | 649.609 | −9.980 |
| 3500 | 82.862 | 455.616 | 382.675 | 255.294 | 408.625 | 656.739 | −9.801 |
| 3600 | 82.900 | 457 951 | 384.734 | 263.582 | 411 490 | 663.788 | −9.631 |
| 3700 | 82.939 | 460.223 | 386.744 | 271.874 | 414.405 | 670.756 | −9.469 |
| 3800 | 82.979 | 462 436 | 388.707 | 280.170 | 417.370 | 677.644 | −9.315 |
| 3900 | 83 021 | 464.592 | 390.625 | 288.470 | 420.387 | 684.455 | −9.167 |
| 4000 | 83 063 | 466.694 | 392.500 | 296.774 | 423.455 | 691 187 | −9.026 |
| 4100 | 83 108 | 468 746 | 394.335 | 305.083 | 426.573 | 697.841 | −8.891 |
| 4200 | 83.154 | 470.749 | 396.131 | 313.396 | 429.742 | 704.420 | −8 761 |
| 4300 | 83.201 | 472 706 | 397.889 | 321.714 | 432.960 | 710.921 | −8.636 |
| 4400 | 83.250 | 474.619 | 399.611 | 330.036 | 436.226 | 717.348 | −8.516 |
| 4500 | 83.301 | 476.491 | 401.299 | 338.364 | 439.540 | 723.700 | −8.400 |
| 4600 | 83.354 | 478.322 | 402.953 | 346 696 | 442 901 | 729.978 | −8.289 |
| 4700 | 83 408 | 480.115 | 404.576 | 355.034 | 446.308 | 736.182 | −8.182 |
| 4800 | 83 464 | 481.872 | 406.168 | 363.378 | 449.759 | 742.313 | −8.078 |
| 4900 | 83.522 | 483.594 | 407.731 | 371.727 | 453.253 | 748.372 | −7.978 |
| 5000 | 83.580 | 485.282 | 409.265 | 380.082 | 456.790 | 754.359 | −7.881 |
| 5100 | 83.641 | 486.937 | 410.772 | 388.443 | 460.368 | 760.275 | −7.787 |
| 5200 | 83.702 | 488.562 | 412.252 | 396.811 | 463.986 | 766.120 | −7 696 |
| 5300 | 83 765 | 490 157 | 413.707 | 405.184 | 467.642 | 771.896 | −7.607 |
| 5400 | 83.829 | 491 723 | 415.137 | 413.564 | 471.336 | 777.602 | −7.522 |
| 5500 | 83 894 | 493.262 | 416.544 | 421.950 | 475.066 | 783.239 | −7.439 |
| 5600 | 83.960 | 494.774 | 417.927 | 430.343 | 478.832 | 788.808 | −7.358 |
| 5700 | 84 026 | 496.261 | 419.289 | 438.742 | 482.632 | 794.309 | −7.279 |
| 5800 | 84.093 | 497.723 | 420.628 | 447.148 | 486.465 | 799 744 | −7.202 |
| 5900 | 84.161 | 499.161 | 421.947 | 455.560 | 490.330 | 805.113 | −7.128 |
| 6000 | 84.228 | 500.576 | 423.246 | 463.980 | 494 226 | 810.415 | −7.055 |

PREVIOUS December 1976 (1 atm)    CURRENT· December 1976 (1 bar)

**Sulfur Fluoride, Ion ($SF_3^+$)** **$F_3S_1^+(g)$**

**Sulfur Fluoride, Ion ($SF_3^-$)** **IDEAL GAS** **$M_r$ = 89.055758** **Sulfur Fluoride, Ion ($SF_3^-$)** **$F_3S_1^-(g)$**

$S°(298.15\ K) = [280.198 \pm 4.2]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -766.148 \pm 29.3\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -776.396 \pm 29.3\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies

| $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ |
|---|---|---|
| [850](1) | [300](1) | [450](1) |
| [550](1) | [725](1) | [350](1) |

Ground State Quantum Weight: [1] $\sigma = [2]$
Point Group: [$C_{2v}$]
Bond Distances S–F* = [1.545] Å; S–F** = [1.646] Å
Bond Angles: F*–S–F** = [87]°; F**–S–F** = [174]°
(* – equatorial ** – axial)
Product of the Moments of Inertia: $I_AI_BI_C = [2.158616 \times 10^{-114}]\ g^3{\cdot}cm^6$

| Enthalpy Reference Temperature = $T_r$ = 298.15 K | | | | | | Standard State Pressure = $p°$ = 0.1 MPa | |
|---|---|---|---|---|---|---|---|
| | $J{\cdot}K^{-1}mol^{-1}$ | | | $kJ{\cdot}mol^{-1}$ | | | |
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −13.599 | −766.148 | | |
| 100 | 37.533 | 226.630 | 328.497 | −10.187 | | | |
| 200 | 52.232 | 257.178 | 285 647 | −5.694 | | | |
| 250 | 58.316 | 269.511 | 281.210 | −2.925 | | | |
| 298.15 | 62.978 | 280.198 | 280 198 | 0. | −776.396 | −753.432 | 131.998 |
| 300 | 63.136 | 280.588 | 280 199 | 0.117 | −776.446 | −753.289 | 131.159 |
| 350 | 66.875 | 290.613 | 280 982 | 3.371 | −777.781 | −749.323 | 111.830 |
| 400 | 69.763 | 299.740 | 282.765 | 6.790 | −781.277 | −745.082 | 97.298 |
| 450 | 72.006 | 308.092 | 285.122 | 10.336 | −783.196 | −740.451 | 85.949 |
| 500 | 73.764 | 315.773 | 287.808 | 13.982 | −785 140 | −735.594 | 76.847 |
| 600 | 76.276 | 329.461 | 293.638 | 21 494 | −788.503 | −725.362 | 63 148 |
| 700 | 77.927 | 341.351 | 299.623 | 29.209 | −791.540 | −714.595 | 53.324 |
| 800 | 79.060 | 351.835 | 305.508 | 37 062 | −794.391 | −703.406 | 45.928 |
| 900 | 79 867 | 361.196 | 311.184 | 45.010 | −850.259 | −690.787 | 40.092 |
| 1000 | 80 460 | 369.643 | 316.615 | 53.028 | −851.711 | −672.990 | 35 153 |
| 1100 | 80.907 | 377.334 | 321.790 | 61.098 | −853.172 | −655.047 | 31 106 |
| 1200 | 81.252 | 384.389 | 326.717 | 69.206 | −854.647 | −636.971 | 27.727 |
| 1300 | 81.524 | 390.904 | 331.407 | 77.346 | −856.143 | −618.771 | 24 863 |
| 1400 | 81.742 | 396.954 | 335.876 | 85.509 | −857.662 | −600.455 | 22.403 |
| 1500 | 81.918 | 402.599 | 340.138 | 93.693 | −859.206 | −582.029 | 20.268 |
| 1600 | 82.064 | 407.891 | 344.209 | 101.892 | −860.777 | −563.499 | 18.396 |
| 1700 | 82.185 | 412.870 | 348.103 | 110.105 | −862.374 | −544.871 | 16.742 |
| 1800 | 82.287 | 417.571 | 351.833 | 118.328 | −863.995 | −526.147 | 15.268 |
| 1900 | 82.374 | 422 022 | 355.411 | 126.562 | −865.637 | −507.334 | 13 948 |
| 2000 | 82.448 | 426.249 | 358.848 | 134.803 | −867.298 | −488.432 | 12.757 |
| 2100 | 82.512 | 430.273 | 362.154 | 143.051 | −868.971 | −469 448 | 11.677 |
| 2200 | 82.568 | 434 113 | 365.338 | 151.305 | −870.653 | −450.384 | 10 693 |
| 2300 | 82.616 | 437 785 | 368.409 | 159.564 | −872.336 | −431.243 | 9.794 |
| 2400 | 82.659 | 441.302 | 371.373 | 167.828 | −874.017 | −412.029 | 8.968 |
| 2500 | 82.697 | 444.677 | 374.238 | 176.096 | −875.688 | −392.745 | 8.206 |
| 2600 | 82.730 | 447 921 | 377.010 | 184.367 | −877.345 | −373.395 | 7.502 |
| 2700 | 82.760 | 451.044 | 379.695 | 192.642 | −878.980 | −353.981 | 6.848 |
| 2800 | 82.787 | 454 054 | 382.297 | 200.919 | −880.591 | −334.507 | 6.240 |
| 2900 | 82.811 | 456.959 | 384.822 | 209.199 | −882.172 | −314.976 | 5.673 |
| 3000 | 82.833 | 459.767 | 387.273 | 217.481 | −883.719 | −295.391 | 5.143 |
| 3100 | 82.852 | 462 484 | 389.656 | 225.765 | −885.228 | −275.755 | 4.646 |
| 3200 | 82 870 | 465 114 | 391.973 | 234.051 | −886.697 | −256.071 | 4.180 |
| 3300 | 82.886 | 467.665 | 394.228 | 242.339 | −888.124 | −236.342 | 3.741 |
| 3400 | 82.901 | 470.139 | 396.425 | 250.629 | −889.505 | −216.570 | 3.327 |
| 3500 | 82.915 | 472.543 | 398.566 | 258.920 | −890.841 | −196.758 | 2.936 |
| 3600 | 82.927 | 474.878 | 400.653 | 267.212 | −892.130 | −176.909 | 2.567 |
| 3700 | 82.939 | 477 151 | 402.690 | 275.505 | −893.371 | −157 024 | 2.217 |
| 3800 | 82.950 | 479.363 | 404.679 | 283.799 | −894.564 | −137.107 | 1.885 |
| 3900 | 82.959 | 481.518 | 406.621 | 292.095 | −895.709 | −117.159 | 1.569 |
| 4000 | 82.968 | 483.618 | 408.520 | 300.391 | −896.806 | −97.182 | 1.269 |
| 4100 | 82.977 | 485.667 | 410.377 | 308.689 | −897.856 | −77.178 | 0.983 |
| 4200 | 82.985 | 487.666 | 412.193 | 316.987 | −898.860 | −57.149 | 0 711 |
| 4300 | 82.992 | 489.619 | 413.971 | 325.285 | −899.818 | −37.098 | 0.451 |
| 4400 | 82.999 | 491.527 | 415.712 | 333.585 | −900.732 | −17.024 | 0.202 |
| 4500 | 83.005 | 493.393 | 417 418 | 341.885 | −901.602 | 3.071 | −0.036 |
| 4600 | 83.011 | 495.217 | 419.090 | 350.186 | −902.430 | 23.184 | −0.263 |
| 4700 | 83.017 | 497.002 | 420.728 | 358.487 | −903.218 | 43.315 | −0.481 |
| 4800 | 83.022 | 498.750 | 422.336 | 366.789 | −903.965 | 63.462 | −0.691 |
| 4900 | 83.027 | 500 462 | 423.913 | 375.092 | −904.675 | 83.624 | −0.891 |
| 5000 | 83.032 | 502.139 | 425.460 | 383.395 | −905.347 | 103.800 | −1.084 |
| 5100 | 83.036 | 503.784 | 426.980 | 391.698 | −905.984 | 123.989 | −1.270 |
| 5200 | 83.040 | 505.396 | 428.473 | 400.002 | −906.587 | 144.191 | −1.448 |
| 5300 | 83.044 | 506.978 | 429.939 | 408.306 | −907.157 | 164.404 | −1.620 |
| 5400 | 83.048 | 508.530 | 431.380 | 416.611 | −907.696 | 184.627 | −1.786 |
| 5500 | 83.051 | 510.054 | 432.797 | 424.916 | −908.204 | 204.859 | −1.946 |
| 5600 | 83.054 | 511.551 | 434.190 | 433.221 | −908.683 | 225.102 | −2.100 |
| 5700 | 83 057 | 513.021 | 435.560 | 441.526 | −909.134 | 245.351 | −2.248 |
| 5800 | 83.060 | 514.465 | 436.908 | 449.832 | −909.558 | 265.609 | −2.392 |
| 5900 | 83.063 | 515.885 | 438.235 | 458.139 | −909.957 | 285.875 | −2.531 |
| 6000 | 83.066 | 517.281 | 439.540 | 466.445 | −910.331 | 306.146 | −2.665 |

PREVIOUS: December 1976 (1 atm) CURRENT· December 1976 (1 bar)

## Enthalpy of Formation

Using time-of-flight measurements, Harland and Thynne[1 2] have identified $SF_3^-$ in the negative ion mass spectra of $SF_4$, $SF_6$, and $SF_5Cl$. Ionization efficiency curves obtained for a dissociative resonance capture process involving $SF_4$ were analyzed by a deconvolution procedure to give an appearance potential (AP) for $SF_3^-$ of 0.70 ± 0.05 eV. Harland and Thynne[1] suggested that the process responsible for ion formation was $SF_4(g) + e^- = SF_3^-(g) + F(g)$. Assuming that the products are formed with no excess energies, we assign the measured value of AP to $\Delta_rH°$ of the proposed ion-formation process, and we obtain the adopted value, $\Delta_fH°(SF_3^-, g, 0\ K) = -183.1 \pm 7.0\ kcal{\cdot}mol^{-1}$ by combining $\Delta_rH°(0\ K)$ with JANAF enthalpies of formation[3] for $SF_4$ and F. Using this $\Delta_fH°$ value, we calculate $EA(SF_3) = 2.72 \pm 0.65$ eV and a fluoride-ion affinity (IA) of $IA(SF_2) = 52.7\ kcal{\cdot}mol^{-1}$. This value of EA is in excellent agreement with the result (EA = 2.71 eV) obtained by a magnetron technique,[4] suggesting that the electron-impact data are reliable and that the interpretation is correct.

The electron-impact AP for $SF_3^-$ from $SF_5Cl$ has been reported[2] as 7 0 ± 0.2 eV. Harland and Thynne[1 2] have suggested two ion formation processes; namely, (A) $SF_5Cl(g) + e^- = SF_3^-(g) + F(g) + FCl(g)$ and (B) $SF_5Cl(g) + e^- = SF_3^-(g) + 2\ F(g) + Cl(g)$. We eliminate (A) as a plausible process since it leads to $EA(SF_3) = -2.1$ eV. We are unable to reproduce the result (EA = 2.9 ± 0.1 eV) obtained for process (A) by Harland and Thynne[1] and believe their calculations to be in error. Process (B) leads to $EA(SF_3) = 0.5$ eV which suggests that $EA(SF_3) < EA(SF_4)$. We believe that this is very unlikely based on trends in the electron affinities for S–F species.[3] We conclude that process (B) very likely involves excess energy terms, amounting to about 2.2 eV.

$\Delta_fH°(298.15\ K)$ is calculated to be $-185.6\ kcal{\cdot}mol^{-1}$ at 298.15 K. In addition, we find that the primary bond dissociation energy $D_0°(SF_2^- - F)$ is $108.0\ kcal{\cdot}mol^{-1}$ which when compared with JANAF $D_0°$ values for $SF_3^+(91.4\ kcal{\cdot}mol^{-1})$ and $SF_3(67.3\ kcal{\cdot}mol^{-1})$ indicates that the trend is $D_0°(SF_3^-) > D_0°(SF_3^+) >> D_0°(SF_3)$. The observed increased bond strengths in both ions relative to the $SF_3$ radical suggest that the positive and negative charges are delocalized in the even-electron ions. Further evidence supporting this view is presented on the $SF_3^+$ (g) table.[3] The enthalpy of atomization and average bond dissociation energy are $225.6\ kcal{\cdot}mol^{-1}$ and $75.2\ kcal{\cdot}mol^{-1}$, respectively.

## Heat Capacity and Entropy

$SF_3^-$ has 28 valence electrons, and according to the Walsh correlation diagram,[5] the ion should have a planar structure. We predict that this planar structure will have a slightly distorted T-shape ($C_{2v}$ symmetry) by analogy with that for the isoelectronic molecule $ClF_3$.[3] As pointed out by Frey *et al.*,[6] the slightly distorted T-shaped structure of $ClF_3$ is closely related to the trigonal bipyramidal structure of $SF_4$. We estimate structural data for $SF_3^-$ from that for $SF_4$[3] by considering the effects of removing one of its equatorial fluorine atoms. We assume that this removal process would produce no change in the S–F bond lengths and only minor changes in the bond angles. The structural data obtained in this way appear reasonable in comparison with that for $ClF_3$.[3] The individual moments of inertia are· $I_A = 5.5926 \times 10^{-39}$, $I_B = 17.0479 \times 10^{-39}$, and $I_C = 22.6406 \times 10^{-39}\ g{\cdot}cm^2$.

The vibrational representation for the adopted structure of $SF_3^-$ is $3A_1 + 2B_1 + B_2$. We estimate the fundamentals according to symmetry species by analogy with the frequencies and assignments for $ClF_3$ and $SF_4$.[3 6] Since several of the assignments for $SF_4$[7] are uncertain, more weight is given to the results for $ClF_3$. We assume a singlet ground state (no unpaired electrons) and neglect excited states.

## References

[1] P. W. Harland and J. C. J. Thynne, J. Phys. Chem. 75, 3517 (1971).
[2] P Harland and J. C. J. Thynne, J. Phys. Chem. 73, 4031 (1969).
[3] JANAF Thermochemical Tables $SF_4(g)$ and $SF_3(g)$, 6–30–76; F(g) and $ClF_3(g)$, 9–30–65, $SF_3^+(g)$, $SF^-(g)$, $SF_2^-$, $SF_4^-(g)$, $SF_5^-(g)$, 12–31–76; $SF_6^-(g)$, 6–30–77.
[4] F. M. Page and G. C. Goode, "Negative Ions and the Magnetron," Wiley, New York, N.Y., (1970).
[5] A. D. Walsh, J. Chem. Soc. 1953, 2301 (1953).
[6] R A. Frey, R. L. Redington, and A. L. K. Aljibury, J. Chem. Phys. 54, 344 (1971).
[7] I. W. Levin, J. Chem. Phys. 55, 5393 (1971).

## Trifluorosilyl (SiF$_3$) IDEAL GAS $M_r$ = 85.080709 Trifluorosilyl (SiF$_3$) F$_3$Si$_1$(g)

$\Delta_a H°(0\ K) = 1758.954 \pm 16.7\ kJ\cdot mol^{-1}$
$S°(298.15\ K) = [282.381 \pm 0.4]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1082.273 \pm 16.7\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1085.330 \pm 16.7\ kJ\cdot mol^{-1}$

| Electronic Levels and Quantum Weights | | |
|---|---|---|
| State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
| X[$^2$A$_1$] | 0 | [2] |
| [$^2$E] | 44120 | [2] |

| Vibratonal Frequencies and Degeneracies $\nu$, cm$^{-1}$ |
|---|
| 832 (1) |
| 406 (1) |
| 954 (2) |
| 290 (2) |

Point Group: C$_{3v}$ $\sigma = 3$
Bond Distance: Si–F = [1.5624] Å
Bond Angle. F–Si–F = 109.4712°
Product of the Moments of Inertia: $I_A I_B I_C = [2.537436 \times 10^{-114}]\ g^3\cdot cm^6$

### Enthalpy of Formation

$\Delta_f H°(SiF_3, g, 298.15\ K) = -259.4 \pm 2\ kcal\cdot mol^{-1}$ is derived from the mass spectrometric equilibrium constants determined by Farber[9] for the reaction $SiF_4(g) + SiF_2(g) = 2SiF_3(g)$. Our 2nd and 3rd law analysis of the ten points in the 1590 to 1782 K range, using auxiliary data,[1] gives $\Delta_r H°(298.15\ K) = 7.47 \pm 0.19\ kcal\cdot mol^{-1}$ (2nd law) and $\Delta_r H°(298.15\ K) = 7.61 \pm 0.04\ kcal\cdot mol^{-1}$ (3rd law) with a drift of $0.09 \pm 0.11$ cal K$^{-1}\cdot$mol$^{-1}$ (3rd law). The 3rd law heat of reaction leads to the adopted enthalpy of formation. The adopted value is consistent with the total pressure data above the silicon–magnesium fluoride system observed by Layne.[2] The value of $\Delta_f H° = -235 \pm 20\ kcal\cdot mol^{-1}$, derived by McDonald *et al.*[3] from appearance and ionization potentials and by Wang *et al.*[4] from appearance potentials and translational energies, appears to be too positive. A later paper by Franklin[10] suggests that the assumption of the fraction of active vibrations as a constant may have caused a bias of 15 kcal·mol$^{-1}$ or more in the derived enthalpy of formation.

$\Delta_f H°(0\ K) = -258.7\ kcal\ mol^{-1}$ corresponds to $\Delta_a H°(0\ K) = 420.4\ kcal\cdot mol^{-1}$, using auxiliary data.[1] The average bond energies in SiF$_2$(g), SiF$_3$(g), and SiF$_4$(g) are all within ~2 kcal·mol$^{-1}$.

### Heat Capacity and Entropy

The electronic levels are those tentatively assigned by Wang *et al*[5] from emission spectral observations. The first excited state is designated as $^2$E, rather than $^2$B, as stated by So[11] based on ab initio Hartree–Fock calculations and group theory arguments. The vibrational frequencies are derived from matrix–isolation UV and IR spectra of Milligan *et al.*[6] They also determined the angle between the Si–F bonds and the three–fold axis to be 71 ± 2° which is consistent with the adopted tetrahedral F–Si–F bond angle. Theoretical calculations[7,8,11] indicate that this angle should be somewhat less than the tetrahedral angle. Calculations based on a bond angle of 108° decrease $S°(298.15\ K)$ by 0.029 cal K$^{-1}\cdot$mol$^{-1}$. As suggested by Milligan *et al.*,[6] the Si–F bond length is assumed to be that in SiHF$_3$.[1] The C$_{3v}$ structure is well established by ESR studies.[12,13] The principal moments of inertia are $I_A = I_B = 11.1156 \times 10^{-39}$ and $I_C = 20.5365 \times 10^{-39}\ g\cdot cm^2$.

### References

[1] JANAF Thermochemical Tables. SiHF$_3$(g) and SiF$_4$(g), 6–30–76, F(g), 9–30–65; Si(g), 3–31–67; SiF$_2$(g), 12–31–77.
[2] G. S. Layne, The Dow Chemical Company, personal communication, (August 1969).
[3] J. D. McDonald, C. H. Williams, J. C. Thompson, and J. L Margrave, Advan. Chem. Ser. No. **72**, 261 (1968).
[4] J. Ling–Fai Wang, J. L. Margrave, and J. L. Franklin, J. Chem. Phys. **58**, 5417 (1973).
[5] J. Ling–Fai Wang, C. N. Krishnan, and J. L. Margrave, J. Mol. Spectrosc. **48**, 346 (1973).
[6] D. E. Milligan, M. E. Jacox, and W. A. Guillory, J. Chem. Phys. **49**, 5330 (1968)
[7] L. J. Aarons, I. H. Hillier, and M. F. Guest, J. Chem. Soc. Faraday Trans. II **70**, 167 (1974).
[8] Y. I. Gorlov, I. I. Ukrainskii and V. V. Pen'Kovskii, Theor. Chim. Acta **34**, 31 (1974).
[9] M. Farber, Space Sciences, Inc , personal communication, (October 18, 1976).
[10] J. L. Franklin, Science **193**, 725 (1976).
[11] S. P. So, J. Mol. Struct. **39**, 133 (1977).
[12] A Hasegawa, K. Sogabe, and M. Miura, Mol. Phys. **30**, 1889 (1975).
[13] M. V. Merritt and R. W. Fessenden, J. Chem Phys. **56**, 2353 (1972).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log K$_f$ |
| 0 | 0. | 0 | INFINITE | −13.399 | −1082.273 | −1082.273 | INFINITE |
| 100 | 38.701 | 229.583 | 329.089 | −9 951 | −1083.451 | −1080.471 | 564.380 |
| 200 | 50.816 | 260.374 | 287.566 | −5.438 | −1084.512 | −1077.058 | 281.299 |
| 250 | 55.586 | 272.237 | 283.340 | −2.776 | −1084.953 | −1075.143 | 224.639 |
| 298.15 | 59.625 | 282.381 | 282.381 | 0. | −1085.330 | −1073.218 | 188.023 |
| 300 | 59.769 | 282.750 | 282.382 | 0.110 | −1085.343 | −1073.143 | 186.851 |
| 350 | 63.348 | 292.240 | 283.123 | 3.191 | −1085.681 | −1071.082 | 159.850 |
| 400 | 66.341 | 300.901 | 284.812 | 6.435 | −1085.968 | −1068.976 | 139.594 |
| 450 | 68.812 | 308.862 | 287.048 | 9.816 | −1086.212 | −1066.837 | 123.835 |
| 500 | 70.843 | 316.221 | 289.602 | 13.309 | −1086.421 | −1064.673 | 111.226 |
| 600 | 73.891 | 329.424 | 295.164 | 20.556 | −1086.761 | −1060.290 | 92.306 |
| 700 | 75.992 | 340.982 | 300.901 | 28.056 | −1087.036 | −1055.855 | 78.789 |
| 800 | 77.478 | 351.231 | 306.564 | 35.734 | −1087.281 | −1051.384 | 68 648 |
| 900 | 78.559 | 360.423 | 312.047 | 43.538 | −1087.520 | −1046.883 | 60.759 |
| 1000 | 79.365 | 368.743 | 317.307 | 51.436 | −1087.768 | −1042.354 | 54.447 |
| 1100 | 79.980 | 376.338 | 322.333 | 59.405 | −1088.035 | −1037.800 | 49.281 |
| 1200 | 80.458 | 383.318 | 327.128 | 67.428 | −1088.330 | −1033.221 | 44.975 |
| 1300 | 80.838 | 389.774 | 331.702 | 75.493 | −1088.659 | −1028.615 | 41.330 |
| 1400 | 81.143 | 395.776 | 336.067 | 83.593 | −1089.027 | −1023.983 | 38.205 |
| 1500 | 81.392 | 401.383 | 340.237 | 91 720 | −1089 440 | −1019.323 | 35.496 |
| 1600 | 81.598 | 406.643 | 344.224 | 99.870 | −1089.899 | −1014 634 | 33.124 |
| 1700 | 81 770 | 411.595 | 348.043 | 108 039 | −1140.584 | −1009.467 | 31.017 |
| 1800 | 81.915 | 416.273 | 351 705 | 116.223 | −1140.909 | −1001.745 | 29.070 |
| 1900 | 82.038 | 420.705 | 355.221 | 124 421 | −1141.238 | −994.005 | 27.327 |
| 2000 | 82.144 | 424.916 | 358.601 | 132.630 | −1141.570 | −986.247 | 25.758 |
| 2100 | 82.235 | 428.926 | 361.855 | 140.849 | −1141.901 | −978.473 | 24.338 |
| 2200 | 82.314 | 432.754 | 364.992 | 149.077 | −1142.228 | −970.683 | 23.047 |
| 2300 | 82.384 | 436.414 | 368.018 | 157.312 | −1142.545 | −962.878 | 21.868 |
| 2400 | 82.445 | 439.922 | 370.941 | 165.553 | −1142.848 | −955.060 | 20.786 |
| 2500 | 82.499 | 443.289 | 373.768 | 173.800 | −1143.132 | −947.230 | 19 791 |
| 2600 | 82.547 | 446.525 | 376.505 | 182.053 | −1143.393 | −939.388 | 18.873 |
| 2700 | 82.590 | 449.641 | 379 156 | 190.310 | −1143.625 | −931.538 | 18.022 |
| 2800 | 82.629 | 452.646 | 381 728 | 198.571 | −1143.825 | −923.679 | 17.231 |
| 2900 | 82.663 | 455.546 | 384.223 | 206.835 | −1143.988 | −915 813 | 16.496 |
| 3000 | 82.695 | 458.349 | 386.648 | 215.103 | −1144.112 | −907.943 | 15.809 |
| 3100 | 82.723 | 461.061 | 389.005 | 223.374 | −1144.193 | −900.070 | 15.166 |
| 3200 | 82.749 | 463.688 | 391.298 | 231.648 | −1144.227 | −892.194 | 14.564 |
| 3300 | 82.772 | 466.234 | 393.530 | 239.924 | −1144.215 | −884.318 | 13 998 |
| 3400 | 82.793 | 468.706 | 395.705 | 248.202 | −1144.152 | −876.443 | 13 465 |
| 3500 | 82.813 | 471.106 | 397.825 | 256.482 | −1144.039 | −868.571 | 12.963 |
| 3600 | 82.831 | 473.439 | 399.893 | 264.765 | −1528.026 | −850.241 | 12.337 |
| 3700 | 82.848 | 475.709 | 401 912 | 273.049 | −1527.395 | −831.423 | 11.738 |
| 3800 | 82.863 | 477 918 | 403 883 | 281.334 | −1526.713 | −812.622 | 11.170 |
| 3900 | 82.877 | 480 071 | 405.809 | 289.621 | −1525.979 | −793.839 | 10.632 |
| 4000 | 82.891 | 482.169 | 407.692 | 297.910 | −1525.194 | −775.076 | 10.121 |
| 4100 | 82.903 | 484.216 | 409.534 | 306.199 | −1524.357 | −756.334 | 9.636 |
| 4200 | 82.914 | 486.214 | 411.336 | 314.490 | −1523.469 | −737.612 | 9 174 |
| 4300 | 82.925 | 488.165 | 413.100 | 322.782 | −1522.531 | −718.912 | 8.733 |
| 4400 | 82.935 | 490.072 | 414.828 | 331.075 | −1521.542 | −700.235 | 8.313 |
| 4500 | 82.945 | 491.936 | 416.520 | 339.369 | −1520.504 | −681.580 | 7.912 |
| 4600 | 82.954 | 493.759 | 418.180 | 347.664 | −1519.418 | −662.949 | 7.528 |
| 4700 | 82.962 | 495.543 | 419.807 | 355.960 | −1518.284 | −644.342 | 7.161 |
| 4800 | 82.970 | 497.290 | 421.403 | 364.256 | −1517.104 | −625.760 | 6.810 |
| 4900 | 82.978 | 499.001 | 422 969 | 372.554 | −1515.878 | −607.203 | 6.473 |
| 5000 | 82.985 | 500.677 | 424.507 | 380.852 | −1514.608 | −588.672 | 6.150 |
| 5100 | 82.993 | 502.320 | 426.016 | 389.151 | −1513.296 | −570 166 | 5.840 |
| 5200 | 83.000 | 503.932 | 427.499 | 397.450 | −1511.942 | −551.686 | 5.542 |
| 5300 | 83.007 | 505.513 | 428 956 | 405.751 | −1510.547 | −533.233 | 5.255 |
| 5400 | 83 014 | 507.065 | 430.389 | 414.052 | −1509.114 | −514.807 | 4.980 |
| 5500 | 83.020 | 508.588 | 431 797 | 422.353 | −1507.642 | −496.407 | 4.714 |
| 5600 | 83.027 | 510 084 | 433.181 | 430.656 | −1506.134 | −478 034 | 4 459 |
| 5700 | 83.034 | 511.554 | 434.543 | 438.959 | −1504.591 | −459.690 | 4.213 |
| 5800 | 83 041 | 512.998 | 435.884 | 447.263 | −1503.015 | −441.372 | 3.975 |
| 5900 | 83 048 | 514 417 | 437.203 | 455.567 | −1501.405 | −423.081 | 3.746 |
| 6000 | 83 055 | 515 813 | 438 501 | 463 872 | −1499 764 | −404.818 | 3.524 |

PREVIOUS December 1977 (1 atm) CURRENT December 1977 (1 bar)

## Titanium Fluoride ($TiF_3$) CRYSTAL $M_r$ = 104.875209 Titanium Fluoride ($TiF_3$) $F_3Ti_1(cr)$

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K) = [87.864 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -1435.530 \pm 41.8\ kJ \cdot mol^{-1}$

### Enthalpy of Formation

Blocher and Hall[1] have reported vapor pressure data for the process 1/2 $Hg_2F_2 + TiF_3(cr) = TiF_4(g) + Hg(l)$. 2nd and 3rd law analyses of their data give a 2nd law $\Delta_f H°(298.15\ K)$ of 23.7 $kcal \cdot mol^{-1}$, a 3rd law $\Delta_f H°(298.15\ K)$ of 29.864, and a 3rd law drift of 11.9 ± 1.0 cal $K^{-1} \cdot mol^{-1}$ The 3rd law value is combined with the JANAF values for the enthalpy of formation of $Hg_2F_2(cr)$ and $TiF_4(g)$ to give a $\Delta_f H°(298.15\ K)$ of $-343.1 \pm 10.0\ kcal \cdot mol^{-1}$. The large uncertainty on $\Delta_f H°(298\ 15\ K)$ is assigned because Blocher and Hall were not able to identify $TiF_3(cr)$ as the reaction product in the above process. They reported that the X-ray pattern of the products contained lines corresponding to $Hg_2F_2(cr)$ plus others that did not correspond to $TiF_3(cr)$.

### Heat Capacity and Entropy

The heat capacity of $TiF_3(cr)$ is estimated from the heat capacities of $ZrF_4$ and $TiF_4$. The entropy, $S°(298.15\ K)$, is estimated from $CrF_3$ and from ionic entropy contributions. Both methods give values which are within ±0.5 cal $K^{-1} \cdot mol^{-1}$ of the chosen value of 21 ± 3 cal $K^{-1} \cdot mol^{-1}$.

### Sublimation Data

The heat of sublimation is calculated from the vapor pressure data of Zmbov and Margrave.[2] Refer to $TiF_3(g)$ table for details. The sublimation temperature is taken as temperature at which the fugacity is one atmosphere for the process $TiF_3(cr) = TiF_3(g)$.

### References

[1] J. N. Blocher, Jr. and E. N Hall, J. Phys. Chem. 63, 127 (1959).

[2] K. F. Zmbov and J. L. Margrave, J. Phys. Chem. 71, 2893 (1967).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | $J \cdot K^{-1} mol^{-1}$ | | | $kJ \cdot mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T/K$ | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 92.023 | 87.864 | 87.864 | 0. | −1435.530 | −1361.864 | 238.593 |
| 300 | 92.048 | 88 433 | 87.866 | 0.170 | −1435.494 | −1361.407 | 237.042 |
| 400 | 93.303 | 115.049 | 91.486 | 9.425 | −1433.682 | −1336.992 | 174.593 |
| 500 | 96.106 | 136.170 | 98.379 | 18.895 | −1432.000 | −1313.014 | 137.170 |
| 600 | 98.475 | 153.900 | 106.194 | 28.624 | −1430.307 | −1289.376 | 112.250 |
| 700 | 100.952 | 169.264 | 114.130 | 38.594 | −1428.552 | −1266.025 | 94.472 |
| 800 | 103.537 | 182.912 | 121.890 | 48.817 | −1426.668 | −1242.933 | 81.155 |
| 900 | 106.232 | 195.262 | 129.367 | 59.305 | −1424.653 | −1220.086 | 70.812 |
| 1000 | 109.035 | 206.598 | 136.531 | 70.067 | −1422.546 | −1197.469 | 62.549 |
| 1100 | 111.947 | 217.126 | 143.385 | 81 116 | −1420.393 | −1175.066 | 55 799 |
| 1200 | 114.968 | 226.996 | 149.945 | 92.461 | −1422.162 | −1152.740 | 50 177 |
| 1300 | 118.098 | 236.321 | 156.234 | 104.113 | −1419.144 | −1130.409 | 45.420 |
| 1400 | 121.336 | 245.191 | 162.274 | 116.084 | −1415.918 | −1108.319 | 41.352 |
| 1500 | 124.683 | 253 691 | 168.087 | 128.406 | −1412.462 | −1086.467 | 37.834 |
| 1600 | 125.520 | 261 764 | 173.692 | 140.916 | −1408.949 | −1064.849 | 34.764 |
| 1700 | 126.357 | 269.399 | 179.099 | 153.510 | −1405.496 | −1043.448 | 32.061 |
| 1800 | 127.194 | 276.645 | 184.319 | 166.187 | −1402.112 | −1022.249 | 29.665 |
| 1900 | 128.030 | 283.544 | 189.361 | 178.948 | −1398.807 | −1001.237 | 27.526 |
| 2000 | 128.867 | 290.133 | 194.236 | 191 793 | −1410.275 | −979.942 | 25.593 |

PREVIOUS· December 1967 CURRENT: June 1968

## Titanium Fluoride ($TiF_3$) IDEAL GAS $M_r$ = 104.895209 Titanium Fluoride ($TiF_3$) $F_3Ti_1(g)$

$S°(298.15\ K) = [291.440 \pm 4.2]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1184.510 \pm 41.8\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1188.674 \pm 41.8\ kJ\cdot mol^{-1}$

| Electronic Levels and Quantum Weights | |
|---|---|
| $\epsilon_i$, cm-1 | $g_i$ |
| 0 | [2] |
| [600] | [2] |
| [1500] | [2] |
| [4000] | [2] |
| [10000] | [2] |

| Vibrational Frequencies and Degeneracies |
|---|
| $\nu$, cm $^{-1}$ |
| [800](1) |
| [450](1) |
| [750](2) |
| [300](2) |

Ground State Quantum Weight: [2] $\sigma = 3$

Point Group: $C_{3v}$

Bond Distance: Ti–F = [1.9]Å

Bond Angle: F–Ti–F = [100]°

Product of the Moments of Inertia: $I_A I_B I_C = [7.509460 \times 10^{-114}]\ g^3\cdot cm^6$

### Enthalpy of Formation

The enthalpy of formation of $TiF_3(g)$ is calculated from that of $TiF_3(cr)$ and the enthalpy of sublimation determined from the mass spectrometric vapor pressure data of Zmbov and Margrave.[1] Their data give nine points over the temperature range 759–865 K.

2nd and 3rd law analyses of their data give a 2nd law $\Delta_{sub}H°(298.15\ K)$ of 61.2 ± 0.4 $kcal\cdot mol^{-1}$ and a 3rd law $\Delta_{sub}H°(298.15\ K)$ of 59.0 $kcal\cdot mol^{-1}$ with an entropy drift of −2.7 ± 0.5 units. The 3rd law value is used to calculate $\Delta_f H°(298.15\ K)$.

### Heat Capacity and Entropy

The interatomic distance is estimated from those of $TiF_4(g)$, and $TiCl_4(g)$, and $TiCl_3(g)$. The pyramidal bond angle is estimated assuming $TiF_3(g)$ similar to the group V trihalides. The principal moments of inertia are $I_A = I_B = 16.7602 \times 10^{-39}$ and $I_C = 26.7330 \times 10^{-39}\ g\cdot cm^2$. The vibrational frequencies are estimated from those of $PF_3$ and $AsF_3$. The electronic levels are estimated from the levels of $Ti^{+3}$.[2]

### References

[1] K. F. Zmbov and J. L. Margrave, J. Phys. Chem. 71, 2893 (1967).

[2] C. E. Moore, U. S. Nat. Bur. Stand. Circ. 467, (1949).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −13.903 | −1184.510 | −1184.510 | INFINITE |
| 100 | 38.206 | 236.501 | 341.197 | −10.470 | −1185.998 | −1183.266 | 618.075 |
| 200 | 53.531 | 267.655 | 297.086 | −5.886 | −1187.725 | −1179.815 | 308.136 |
| 250 | 60.296 | 280.349 | 292.491 | −3.035 | −1188.291 | −1177.768 | 246.081 |
| 298.15 | 65.585 | 291 440 | 291.440 | 0. | −1188.674 | −1175.704 | 205.978 |
| 300 | 65.764 | 291.846 | 291.441 | 0.121 | −1188.687 | −1175.623 | 204.694 |
| 350 | 70.016 | 302.317 | 292.258 | 3.521 | −1188.958 | −1173.423 | 175.124 |
| 400 | 73.278 | 311.889 | 294.123 | 7.107 | −1189 144 | −1171 191 | 152.942 |
| 450 | 75.772 | 320.671 | 296.591 | 10.836 | −1189.273 | −1168.938 | 135.687 |
| 500 | 77.684 | 328.757 | 299.409 | 14.674 | −1189.365 | −1166 673 | 121.882 |
| 600 | 80.293 | 343.172 | 305.531 | 22.584 | −1189 491 | −1162.122 | 101 172 |
| 700 | 81.878 | 355.678 | 311.822 | 30.699 | −1189.591 | −1157.553 | 86.378 |
| 800 | 82.877 | 366.681 | 318.006 | 38.940 | −1189.689 | −1152.970 | 75.281 |
| 900 | 83.536 | 376.483 | 323.968 | 47.263 | −1189.839 | −1148.372 | 66.650 |
| 1000 | 83.989 | 385.309 | 329.669 | 55.641 | −1190.117 | −1143.751 | 59.743 |
| 1100 | 84.314 | 393.330 | 335.097 | 64.057 | −1190.596 | −1139.093 | 54.091 |
| 1200 | 84.554 | 400.678 | 340.260 | 72.501 | −1195.265 | −1134.262 | 49.373 |
| 1300 | 84.733 | 407.453 | 345.172 | 80.966 | −1195.435 | −1129.172 | 45.371 |
| 1400 | 84.869 | 413 738 | 349.847 | 89.446 | −1195.699 | −1124.066 | 41.939 |
| 1500 | 84.973 | 419.597 | 354.304 | 97.938 | −1196.073 | −1118.937 | 38.965 |
| 1600 | 85.052 | 425.083 | 358.558 | 106.440 | −1196.569 | −1113.779 | 36.361 |
| 1700 | 85.112 | 430.241 | 362.625 | 114.948 | −1197.202 | −1108.586 | 34 063 |
| 1800 | 85.157 | 435.108 | 366.518 | 123.462 | −1197.981 | −1103.351 | 32.018 |
| 1900 | 85.192 | 439.713 | 370.250 | 131.979 | −1198.920 | −1098 070 | 30.188 |
| 2000 | 85.218 | 444.083 | 373.833 | 140.500 | −1214.713 | −1092.280 | 28.527 |
| 2100 | 85.238 | 448.241 | 377.278 | 149.023 | −1216.744 | −1086.109 | 27.015 |
| 2200 | 85.253 | 452.207 | 380.595 | 157.547 | −1218.778 | −1079.840 | 25.639 |
| 2300 | 85.265 | 455.997 | 383.791 | 166.073 | −1220.808 | −1073.479 | 24.379 |
| 2400 | 85.273 | 459.626 | 386.876 | 174.600 | −1222.830 | −1067.030 | 23.223 |
| 2500 | 85.280 | 463.107 | 389.856 | 183.128 | −1224.838 | −1060.497 | 22.158 |
| 2600 | 85.285 | 466.452 | 392.738 | 191.656 | −1226.827 | −1053.884 | 21.173 |
| 2700 | 85.288 | 469.671 | 395.528 | 200.184 | −1228 791 | −1047 195 | 20.259 |
| 2800 | 85.290 | 472.773 | 398.232 | 208.713 | −1230.728 | −1040.434 | 19.410 |
| 2900 | 85.291 | 475.765 | 400.854 | 217.242 | −1232.631 | −1033.604 | 18.617 |
| 3000 | 85.290 | 478.657 | 403.400 | 225.771 | −1234.497 | −1026.709 | 17.877 |
| 3100 | 85.289 | 481.454 | 405.873 | 234.300 | −1236.324 | −1019.753 | 17.183 |
| 3200 | 85.287 | 484.161 | 408.277 | 242.829 | −1238.108 | −1012.738 | 16.531 |
| 3300 | 85.283 | 486.786 | 410.617 | 251.358 | −1239.847 | −1005.668 | 15.918 |
| 3400 | 85.279 | 489.332 | 412.895 | 259.886 | −1241.539 | −998.546 | 15.341 |
| 3500 | 85.274 | 491.804 | 415.114 | 268.413 | −1243.183 | −991.376 | 14.795 |
| 3600 | 85.268 | 494.206 | 417.278 | 276.941 | −1244.777 | −984.158 | 14.280 |
| 3700 | 85.260 | 496.542 | 419.389 | 285.467 | −1655.420 | −969 109 | 13.681 |
| 3800 | 85.252 | 498.816 | 421.449 | 293.993 | −1655.680 | −950.557 | 13.066 |
| 3900 | 85.243 | 501.030 | 423.461 | 302.517 | −1655.944 | −931.997 | 12.483 |
| 4000 | 85.234 | 503.188 | 425.428 | 311.041 | −1656.213 | −913.431 | 11.928 |
| 4100 | 85.223 | 505.292 | 427.350 | 319.564 | −1656.484 | −894.859 | 11.401 |
| 4200 | 85.212 | 507.346 | 429.230 | 328.086 | −1656.756 | −876.279 | 10.898 |
| 4300 | 85.199 | 509.351 | 431.070 | 336.606 | −1657.030 | −857.693 | 10.419 |
| 4400 | 85.187 | 511.309 | 432.872 | 345.126 | −1657.302 | −839.101 | 9.961 |
| 4500 | 85.173 | 513.224 | 434.636 | 353.644 | −1657.574 | −820.502 | 9.524 |
| 4600 | 85.159 | 515.096 | 436.365 | 362.160 | −1657.844 | −801.897 | 9.106 |
| 4700 | 85.144 | 516.927 | 438.060 | 370.675 | −1658.110 | −783.287 | 8.705 |
| 4800 | 85.129 | 518.719 | 439.722 | 379.189 | −1658.373 | −764.671 | 8.321 |
| 4900 | 85.113 | 520.474 | 441.352 | 387.701 | −1658.630 | −746.049 | 7.953 |
| 5000 | 85.097 | 522.194 | 442.951 | 396.212 | −1658.883 | −727 423 | 7.599 |
| 5100 | 85.080 | 523.879 | 444.522 | 404.721 | −1659.128 | −708.791 | 7.260 |
| 5200 | 85.063 | 525.531 | 446.064 | 413.228 | −1659.367 | −690.154 | 6.933 |
| 5300 | 85.046 | 527.151 | 447.579 | 421 733 | −1659.597 | −671.513 | 6.618 |
| 5400 | 85.028 | 528.740 | 449.067 | 430.237 | −1659.819 | −652.869 | 6.315 |
| 5500 | 85.010 | 530.300 | 450.530 | 438.739 | −1660.031 | −634.220 | 6.023 |
| 5600 | 84.992 | 531.832 | 451.968 | 447.239 | −1660.233 | −615.566 | 5.742 |
| 5700 | 84.974 | 533.336 | 453.382 | 455.737 | −1660.424 | −596.910 | 5.470 |
| 5800 | 84.955 | 534.814 | 454.774 | 464.234 | −1660.603 | −578.251 | 5.208 |
| 5900 | 84.937 | 536.266 | 456.142 | 472.728 | −1660.770 | −559.587 | 4.954 |
| 6000 | 84.918 | 537.693 | 457.490 | 481.221 | −1660.924 | −540.922 | 4.709 |

PREVIOUS: June 1968 (1 atm) CURRENT. June 1968 (1 bar)

# Zirconium Fluoride ($ZrF_3$) CRYSTAL $M_r = 148.215209$ Zirconium Fluoride ($ZrF_3$) $F_3Zr_1(cr)$

$S°(298.15\ K) = [87.864 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = $ Unknown
$\Delta_f H°(298.15\ K) = [-1401.640 \pm 83.7]\ kJ \cdot mol^{-1}$

## Enthalpy of Formation

The enthalpy of formation at 298.15 K for $ZrF_3$(cr) was reported as $-350$ kcal·mol$^{-1}$[1] which was estimated by Brewer.[2] Based on this $\Delta_f H°$(298.15 K) value, the crystal lattice energy (U) of $ZrF_3$(cr) is calculated to be 1371 kcal·mol$^{-1}$ by the Born–Haber cycle method.[3] For the evaluation of U from the relation $\Delta_f H°(ZrF_3, cr, 298.15\ K) = \Sigma\ I_i + L - 3(E - D/2) - U$, the following values (kcal mol$^{-1}$) are used. $\Sigma\ I_i$ (the sum of the successive three ionization potentials of Zr metal) = 1055[4] L (the enthalpy of sublimation of Zr metal) = 148.3[5] E (the electron affinity of fluorine) = 79.5[6] and D (the enthalpy of dissociation of fluorine) = 37.7).[5] The derived value of U($ZrF_3$, cr is of the same order of magnitude of the value, U($TiF_3$, cr) = 1376 kcal·mol$^{-1}$, calculated by Cavell and Clark[3] using the same method.

From $\Delta_f H°$($ZrF_3$, cr, 298.15 K) = $-350$ kcal·mol$^{-1}$, the derived $\Delta_f G$($ZrF_3$, cr) values indicate that $ZrF_3$(cr) is thermodynamically more stable than the system $ZrF_4$(cr) + Zr(cr). For example, in the temperature range 298–1200 K, the Gibbs energy changes for the reaction $3\ ZrF_4(cr) + Zr(cr) = 4\ ZrF_3(cr)$ are about $-29 \pm 1$ kcal·mol$^{-1}$. However, this product $ZrF_3$(cr) has never been prepared successfully from this reaction in many laboratories.[7] In order to make the $\Delta_f G°$($ZrF_3$, cr, 298.15 K) values consistent with the experimental observations, the enthalpy of formation of $ZrF_3$(cr) is arbitrarily adjusted to be 15 kcal·mol$^{-1}$ less negative, or $\Delta_f H°$($ZrF_3$, cr, 298.15 K) = $-335$ kcal·mol$^{-1}$ with uncertainty as high as $\pm 20$ kcal·mol$^{-1}$. This value is tentatively adopted.

The Gibbs energy changes for the reaction $3\ ZrF_4(g) + Zr(cr) = 4\ ZrF_3(cr)$ are evaluated to be very favorable at temperatures below 900 K, e.g., $\Delta_r G° = -93.9$ and $-6.7$ kcal·mol$^{-1}$ at 298 and 900 K, respectively. But according to Larsen and Leddy[8] this reaction does not occur in the temperature range 473–973 K, and pressure range 5–15 atm. One possible explanation is that these heterogeneous reactants may require very high activation energy to initiate the reaction. In other words, this reaction is unfavorable at these temperatures probably due to kinetic rather than thermodynamic reasons.

## Heat Capacity and Entropy

The heat capacities of $ZrF_3$(cr) are not available in the literature. They are estimated from the $C_p°$ values of $ZrF_4$(cr) by deduction of one F atom $C_p°$ contributions which are calculated as $1/4[C_p°(ZrF_4, cr) - C_p°(Zr, cr)]$. The $S°$(298.15 K) is taken to be $1/2[S°(ZrF_4, cr, 298.15\ K) + S°(ZrF_2, cr, 298.15\ K)]$ of which the value $S°$($ZrF_2$, cr, 298.15 K) is estimated; refer to $ZrF_2$(cr) table for details.

## Sublimation Data

The difference between $\Delta_f H°$(298.15 K) for $ZrF_3$(g) and $ZrF_3$(cr) is $\Delta_{sub}H°$(298.15 K). Actually $ZrF_3$(cr) is thermodynamically unstable, e.g., the Gibbs energy changes for the reaction $4\ ZrF_3(cr) = 3\ ZrF_4(cr) + Zr(cr)$ are about $-30$ kcal·mol$^{-1}$ in the temperature range 298–1400 K. In other words, $ZrF_3$(cr) decomposes into $ZrF_4$(cr) + Zr(cr) before sublimation occurs.

## References

[1] U. S. Nat. Bur. Stand. Circ. 500, (1952).
[2] L. Brewer, University of California, Berkeley, California, personal communication; cited in reference 1.
[3] R. G. Cavell and H. C. Clark, J. Chem. Soc. 1965, 444 (1965).
[4] C. E. Moore, U. S. Nat. Bur. Stand. Circ. 467, Vol. III, (1958).
[5] JANAF Thermochemical Tables. Zr(cr), 12–31–67; F(g), 9–30–65.
[6] U. S. Nat. Bur. Stand. Report 8628, (1965).
[7] T. B. Douglas, U. S. Nat. Bur. Stand., personal communication, (July 10, 1961).
[8] E. M. Larsen and J. J. Leddy, J. Amer. Chem. Soc. 78, 5983 (1956).

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 83.680 | 87.864 | 87.864 | 0. | −1401.640 | −1325.555 | 232.232 |
| 300 | 84.308 | 88.384 | 87.866 | 0.155 | −1401.618 | −1325.083 | 230.718 |
| 400 | 91.839 | 113.729 | 91.270 | 8.984 | −1400.178 | −1299.777 | 169.733 |
| 500 | 96.860 | 134.789 | 97.927 | 18.431 | −1398.404 | −1274.876 | 133.185 |
| 600 | 100.416 | 152.778 | 105.606 | 28.303 | −1396.433 | −1250.353 | 108.853 |
| 700 | 102.926 | 168.451 | 113.489 | 38.474 | −1394.357 | −1226.170 | 91.498 |
| 800 | 105.018 | 182.339 | 121.244 | 48.876 | −1392.218 | −1202.289 | 78.501 |
| 900 | 106.483 | 194.795 | 128.736 | 59.453 | −1390.070 | −1178.677 | 68.409 |
| 1000 | 107.738 | 206.083 | 135.915 | 70.168 | −1387.946 | −1155.303 | 60.347 |
| 1100 | 108.491 | 216.390 | 142.769 | 80.983 | −1385.882 | −1132.139 | 53.761 |
| 1200 | 108.868 | 225.847 | 149.304 | 91.851 | −1387.635 | −1108.937 | 48.271 |
| 1300 | 109.202 | 234.574 | 155.532 | 102.755 | −1385.253 | −1085.809 | 43.628 |
| 1400 | 109.495 | 242.678 | 161.471 | 113.690 | −1382.915 | −1062.863 | 39.656 |
| 1500 | 109.746 | 250.241 | 167.139 | 124.653 | −1380.632 | −1040.082 | 36.219 |

PREVIOUS: June 1968 (1 atm)    CURRENT June 1968 (1 bar)

## Zirconium Fluoride ($ZrF_3$) IDEAL GAS $M_r = 148.215209$ Zirconium Fluoride ($ZrF_3$) $F_3Zr_1(g)$

$S°(298.15\ K) = [305.742 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1101\ 784 \pm 20.9\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1105\ 413 \pm 20.9\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

| $\epsilon_i$, $cm^{-1}$ | $g_i$ |
|---|---|
| 0 | [2] |
| [1800] | [2] |
| [4500] | [2] |
| [12000] | [2] |
| [30000] | [2] |

Vibrational Frequencies and Degeneracies

| $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ |
|---|---|
| [611](1) | [655](2) |
| [203](1) | [240](2) |

Ground State Quantum Weight: [2] $\sigma = [3]$
Point Group: $C_{3v}$
Bond Distance: Zr–F = [1.93]Å
Bond Angle: F–Zr–F = [105]°
Product of the Moments of Inertia. $I_A I_B I_C = [9.87893 \times 10^{-114}]\ g^3 \cdot cm^6$

### Enthalpy of Formation

Murad and Hildenbrand[1] studied the gaseous equilibria involving $ZrF_4$, $ZrF_3$, $ZrF_2$, Ca and CaF. These species were generated at high temperatures in a graphite Knudsen cell containing powdered calcium fluoride and elemental zirconium. Ion intensities were measured 3 eV above threshold over the temperature range 1665–1747 K and the equilibrium constants were calculated for the following isomolecular reaction: $Ca(g) + ZrF_4(g) = CaF(g) + ZrF_3(g)$ Based on the reported equilibrum constants the enthalpy change of this reaction is evaluated by the 2nd and 3rd law methods to be $-8.0 \pm 25$ and $28.0 \pm 2\ kcal \cdot mol^{-1}$, respectively. The 3rd law entropy drift is $20 \pm 15\ cal\ K^{-1} \cdot mol^{-1}$ Using the 3rd law value and $\Delta_f H°(298.15\ K) = 42.85 \pm 0.3$, $-400.0 \pm 0.5$, and $-65.0 \pm 2\ kcal \cdot mol^{-1}$ for Ca(g), $ZrF_4(g)$, and CaF(g) we obtain $\Delta_f H°(ZrF_3,\ g,\ 298\ 15\ K) = -264.2 \pm 5\ kcal \cdot mol^{-1}$ which is adopted. Employing slightly different Gibbs energy functions and $\Delta_f H°(298.15\ K)$ values for the products and reactants, Murad and Hildenbrand[1] evaluated the 3rd law enthalpy change of the above reaction as $29.4 \pm 5$ and $\Delta_f H°(ZrF_3,\ g,\ 298.15\ K) = -262 \pm 5\ kcal \cdot mol^{-1}$ which are in reasonable agreement with the values adopted here.

### Heat Capacity and Entropy

The molecular structure is assumed to be the same as that of $TiF_3(g)$. The Zr–F bond distance is estimated by comparison with those for $ZrF_4(g)$ and $ZrF_2(g)$. The F–Zr–F bond angle is taken to be slightly bigger than the F–Ti–F bond angle in $TiF_3(g)$ molecule. The vibrational frequencies are calculated by the valence force method[2] using force constants transferred from those for the $ZrF_2(g)$ molecule. The three principal moments of inertia are: $I_A = I_B = 18.2815x\ 10^{-39}$ and $I_C = 29.5856x\ 10^{-39}\ g \cdot cm^2$ The electronic levels are estimated to be three times higher than those of $TiF_3(g)$, based on the ratio of the first splitting interval between Ti(IV) and Zr(IV), given by Moore.[3] The quantum weights are assumed to be the same as those of $TiF_3(g)$.

### References

[1] E. Murad and D. L Hildenbrand, J Chem. Phys. 45, 4751 (1966).
[2] G. Herzberg, "Infrared and Raman Spectra," D Van Nostrand Co., Inc., New York, (1945).
[3] C. E. Moore, U S. Nat. Bur. Stand. Circ. 467, Vol. III, (1958).

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −15.106 | −1101.784 | −1101.784 | INFINITE |
| 100 | 44.437 | 244.931 | 359.453 | −11.452 | −1103.377 | −1100.909 | 575.056 |
| 200 | 58.700 | 280.460 | 311.683 | −6.245 | −1104.756 | −1097.842 | 286.727 |
| 250 | 63.889 | 294.138 | 306.838 | −3.175 | −1105.156 | −1096.064 | 229.010 |
| 298.15 | 67.832 | 305.742 | 305.742 | 0. | −1105.413 | −1094.288 | 191.715 |
| 300 | 67.965 | 306 162 | 305.743 | 0.126 | −1105.421 | −1094.219 | 190.521 |
| 350 | 71.158 | 316.888 | 306.583 | 3.607 | −1105.594 | −1092.338 | 163.022 |
| 400 | 73.704 | 326.562 | 308.486 | 7.231 | −1105.704 | −1090 436 | 142.396 |
| 450 | 75.781 | 335.367 | 310.991 | 10.969 | −1105 770 | −1088.523 | 126.352 |
| 500 | 77.506 | 343.444 | 313.838 | 14.803 | −1105.805 | −1086.604 | 113.517 |
| 600 | 80.188 | 357.825 | 320.000 | 22.695 | −1105.814 | −1082.762 | 94.263 |
| 700 | 82.126 | 370.340 | 326.317 | 30.816 | −1105 787 | −1078.922 | 80.510 |
| 800 | 83.534 | 381.403 | 332.525 | 39.103 | −1105.765 | −1075.086 | 70.196 |
| 900 | 84.561 | 391.304 | 338.515 | 47.510 | −1105.786 | −1071.251 | 62.174 |
| 1000 | 85.314 | 400.255 | 344.249 | 56.006 | −1105.881 | −1067.409 | 55.756 |
| 1100 | 85.869 • | 408.413 | 349.717 | 64.566 | −1106.072 | −1063.554 | 50.504 |
| 1200 | 86.277 | 415.903 | 354.924 | 73.175 | −1110.084 | −1059.454 | 46.117 |
| 1300 | 86.576 | 422.822 | 359.885 | 81.818 | −1109.963 | −1055.240 | 42.400 |
| 1400 | 86.791 | 429.246 | 364.612 | 90.487 | −1109.891 | −1051.034 | 39.215 |
| 1500 | 86.941 | 435.239 | 369.123 | 99.174 | −1109.883 | −1046.831 | 36.454 |
| 1600 | 87.040 | 440.854 | 373.433 | 107.873 | −1109.954 | −1042.625 | 34.038 |
| 1700 | 87.100 | 446.132 | 377.556 | 116.581 | −1110.115 | −1038 413 | 31.907 |
| 1800 | 87.129 | 451.112 | 381.505 | 125.292 | −1110.379 | −1034.188 | 30.011 |
| 1900 | 87.134 | 455.823 | 385.294 | 134.006 | −1110 754 | −1029.946 | 28.315 |
| 2000 | 87.122 | 460.292 | 388.933 | 142.719 | −1111.250 | −1025.680 | 26.788 |
| 2100 | 87.097 | 464.542 | 392.433 | 151 430 | −1111.873 | −1021.387 | 25.406 |
| 2200 | 87.062 | 468.593 | 395.803 | 160.138 | −1133.952 | −1016.315 | 24.130 |
| 2300 | 87.021 | 472.462 | 399.053 | 168.842 | −1135.264 | −1010.938 | 22.959 |
| 2400 | 86.976 | 476 165 | 402.189 | 177.542 | −1136.573 | −1005.505 | 21.884 |
| 2500 | 86.928 | 479.715 | 405.220 | 186.237 | −1137.874 | −1000.017 | 20 894 |
| 2600 | 86.880 | 483.123 | 408.151 | 194.927 | −1139.161 | −994.477 | 19.979 |
| 2700 | 86.832 | 486.401 | 410.989 | 203.613 | −1140.429 | −988.888 | 19 131 |
| 2800 | 86.784 | 489.558 | 413.739 | 212.294 | −1141.674 | −983.253 | 18.343 |
| 2900 | 86.738 | 492.602 | 416.406 | 220.970 | −1142.890 | −977.573 | 17 608 |
| 3000 | 86.693 | 495.542 | 418.995 | 229 641 | −1144.074 | −971.853 | 16.921 |
| 3100 | 86.651 | 498.384 | 421.511 | 238.309 | −1145.223 | −966.093 | 16.279 |
| 3200 | 86.610 | 501 135 | 423.956 | 246 972 | −1146.333 | −960.297 | 15.675 |
| 3300 | 86.570 | 503.799 | 426.335 | 255.631 | −1147.402 | −954.467 | 15.108 |
| 3400 | 86.533 | 506.383 | 428.652 | 264.286 | −1148.427 | −948.605 | 14.574 |
| 3500 | 86.497 | 508.891 | 430.909 | 272.937 | −1149.407 | −942.713 | 14.069 |
| 3600 | 86.463 | 511.327 | 433.109 | 281.585 | −1150.341 | −936.794 | 13.593 |
| 3700 | 86.431 | 513.696 | 435.255 | 290.230 | −1151.227 | −930.850 | 13.141 |
| 3800 | 86.400 | 516.000 | 437.350 | 298.871 | −1152.066 | −924.883 | 12.713 |
| 3900 | 86.370 | 518.244 | 439.395 | 307.510 | −1152.856 | −918.893 | 12.307 |
| 4000 | 86.341 | 520.430 | 441.394 | 316 145 | −1153.598 | −912.885 | 11.921 |
| 4100 | 86.313 | 522.562 | 443.348 | 324.778 | −1154.291 | −906.859 | 11.554 |
| 4200 | 86.287 | 524.642 | 445.259 | 333.408 | −1154.937 | −900.815 | 11.203 |
| 4300 | 86.261 | 526.672 | 447.129 | 342.036 | −1155.536 | −894.758 | 10.869 |
| 4400 | 86.236 | 528.655 | 448.959 | 350.660 | −1156.088 | −888.687 | 10.550 |
| 4500 | 86.212 | 530.592 | 450.752 | 359.283 | −1156.595 | −882.603 | 10.245 |
| 4600 | 86.189 | 532.487 | 452.508 | 367.903 | −1157.056 | −876.510 | 9 953 |
| 4700 | 86.166 | 534.340 | 454.229 | 376.521 | −1157.474 | −870.406 | 9.673 |
| 4800 | 86.144 | 536.154 | 455.917 | 385 136 | −1718.785 | −852.677 | 9.279 |
| 4900 | 86.123 | 537.930 | 457.573 | 393.749 | −1718.770 | −834.633 | 8.897 |
| 5000 | 86.102 | 539.670 | 459.198 | 402.361 | −1718.730 | −816.590 | 8.531 |
| 5100 | 86.082 | 541.375 | 460.792 | 410 970 | −1718.667 | −798.548 | 8.179 |
| 5200 | 86.062 | 543 046 | 462.358 | 419.577 | −1718.579 | −780.507 | 7.840 |
| 5300 | 86.043 | 544.685 | 463.896 | 428.182 | −1718.467 | −762.468 | 7.515 |
| 5400 | 86.024 | 546.293 | 465 407 | 436 786 | −1718.330 | −744.432 | 7.201 |
| 5500 | 86.006 | 547.872 | 466.892 | 445.387 | −1718.168 | −726.399 | 6.899 |
| 5600 | 85.989 | 549.421 | 468.352 | 453.987 | −1717.980 | −708.368 | 6 607 |
| 5700 | 85.971 | 550.943 | 469.788 | 462.585 | −1717 767 | −690.341 | 6.326 |
| 5800 | 85 955 | 552.438 | 471.200 | 471 181 | −1717.528 | −672.318 | 6.055 |
| 5900 | 85.938 | 553 907 | 472.589 | 479.776 | −1717.264 | −654.299 | 5 793 |
| 6000 | 85.923 | 555.351 | 473.957 | 488.369 | −1716.974 | −636 286 | 5.539 |

PREVIOUS December 1969 (1 atm)    CURRENT. December 1969 (1 bar)

## Hydrogen Fluoride ($H_4F_4$) IDEAL GAS $M_r = 80.025372$ Hydrogen Fluoride ($H_4F_4$) $F_4H_4(g)$

$\Delta_fH°(0\ K) = -1171.786 \pm -20.9\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = [349.210 \pm 16.7]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = -1183.821 \pm 20.9\ kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ |
|---|
| [202](4) |
| [53](2) |
| [962](4) |
| [552](4) |
| [3060](4) |

Ground State Quantum Weight: 1 $\sigma = [4]$
Point Group. $C_4$
Bond Distance: F–F = [2.5] Å
Product of the Moments of Inertia: $I_AI_BI_C = [1.790364 \times 10^{-113}]\ g^3 \cdot cm^6$

### Enthalpy of Formation

The enthalpy of 4 HF(g) → $H_4F_4$(g) was taken as the mean of 3rd law values which were determined from the equilibrium data of two investigations. Briegleb and Strohmeier[1] measured the vapor density of associated HF between 20 and 60°C and between 50 and 650 torr. Franck and Meyer[2] measured $C_p°$ between −20 and 100 °C and between 100 and 700 torr. Each investigation evaluated $K_p$ at $n = 2, 3, 4, ...$ for the reactions n(HF) → $(HF)_n$ and reported 2nd law values of $\Delta H°$ and $\Delta S°$. At $n = 4$ their 2nd law values differed by 4.2 kcal·mol$^{-1}$, which was taken as an estimate of error, while the calculated 3rd law values differed by 1.5 kcal·mol$^{-1}$. Using $\Delta_fH°(298.15\ K) = -22.38\ kcal \cdot mol^{-1}$ and auxiliary JANAF data[3] gives the enthalpy of formation of $H_4F_4$(g).

### Heat Capacity and Entropy

The molecular structure of $H_4F_4$ was assumed as planar with the F atoms forming the vertices of a square and with the H atoms also lying in the circumscribed circle. That rings are more stable than open chains was confirmed by Del Bene and Pople's[4] theoretical molecular–orbital studies on HF polymers. The length of side (F–F axis) was taken from Atoji and Lipscomb's[5] X–ray studies of solid HF (F–F = 2.49 Å) and agrees with the 2.52Å which Janzen and Bartell[6] determined for the gaseous polymers by electron diffraction. The low F–bending frequency (53 cm$^{-1}$) was taken from Boutin *et al.*[7] The other vibrational frequencies were taken from Kittelberger and Hornig's[8] work on crystalline HF. Huong and Couzi[9] and Smith[10] have made spectral studies of the gas phase in the range from 350 to 4000 cm$^{-1}$.

National Bureau of Standards prepared this table[11] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_fH°$ selected by NBS,[11] we recalculate the table in terms of 1973 fundamental constants,[12] 1975 atomic weights,[13] and current JANAF reference states for the elements.

### References

[1] G. Briegleb and W. Strohmeier, Z. Elektrochem. 57, 668 (1953).
[2] E. U. Franck and F. Meyer, Z. Elektrochem. 63, 571 (1959).
[3] JANAF Thermochemical Tables: HF(g), 6–30–77.
[4] J. E. Del Bene and J. A. Pople, J. Chem. Phys. 55, 2296 (1971).
[5] M. Atoji and W. N. Lipscomb, Acta Cryst. 7, 173 (1954).
[6] J. Janzen and L. S. Bartell, J. Chem. Phys. 50, 3611 (1969).
[7] H. Boutin, G. J. Stafford, and V. Brajovic, J. Chem. Phys. 39, 3135 (1963).
[8] J. S. Kittelberger and D. F. Hornig, J. Chem. Phys. 46, 3099 (1967).
[9] P. V. Huong and M. Couzi, J. Chim. Phys. 66, 1309 (1969).
[10] D. F. Smith, J. Chem. Phys. 28, 1040 (1958); 48, 1429 (1968).
[11] S. Abramowitz et al., U. S. Nat. Bur. Stand, Report 10904, 239, (1972).
[12] CODATA Task Group on Fundamental Constants, CODATA Bulletin 11, (December 1973).
[13] IUPAC Commission on Atomic Weights, Pure Appl. Chem. 47, 75 (1976).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −22.549 | −1171.786 | −1171.786 | INFINITE |
| 100 | 67.044 | 256.376 | 431.836 | −17.546 | −1178.595 | −1150.013 | 600.705 |
| 200 | 89.508 | 310.130 | 358.442 | −9.662 | −1181.957 | −1119.957 | 292.503 |
| 250 | 98.807 | 331.124 | 350.923 | −4.950 | −1183.042 | −1104.326 | 230.736 |
| 298.15 | 106.585 | 349.210 | 349.210 | 0. | −1183.821 | −1089.090 | 190.804 |
| 300 | 106.860 | 349.870 | 349.212 | 0.197 | −1183.846 | −1088.502 | 189.525 |
| 350 | 113.638 | 366.868 | 350.539 | 5.715 | −1184.404 | −1072.565 | 160.072 |
| 400 | 119.262 | 382.421 | 353.566 | 11.542 | −1184.752 | −1056.562 | 137.973 |
| 450 | 123.931 | 396.746 | 357.578 | 17.625 | −1184.923 | −1040.526 | 120.781 |
| 500 | 127.857 | 410.012 | 362.167 | 23.923 | −1184.948 | −1024.479 | 107.027 |
| 600 | 134.181 | 433.907 | 372.177 | 37.038 | −1184.637 | −992.407 | 86.397 |
| 700 | 139.264 | 454.985 | 382.530 | 50.718 | −1183.937 | −960.419 | 71.667 |
| 800 | 143.630 | 473.872 | 392.788 | 64.868 | −1182.911 | −928.555 | 60.628 |
| 900 | 147.504 | 491.017 | 402.764 | 79.428 | −1181.609 | −896.835 | 52.051 |
| 1000 | 150.977 | 506.741 | 412.386 | 94.355 | −1180.069 | −865.275 | 45.197 |
| 1100 | 154.091 | 521.280 | 421.633 | 109.611 | −1178.330 | −833.878 | 39.598 |
| 1200 | 156.873 | 534.809 | 430.507 | 125.162 | −1176.428 | −802.647 | 34.938 |
| 1300 | 159.350 | 547.465 | 439.022 | 140.976 | −1174.394 | −771.580 | 31.002 |
| 1400 | 161.549 | 559.356 | 447.197 | 157.023 | −1172.257 | −740.674 | 27.635 |
| 1500 | 163.500 | 570.570 | 455.052 | 173.277 | −1170.039 | −709.924 | 24.722 |
| 1600 | 165.229 | 581.178 | 462.606 | 189.715 | −1167.761 | −679.323 | 22.178 |
| 1700 | 166.762 | 591.242 | 469.880 | 206.316 | −1165.437 | −648.867 | 19.937 |
| 1800 | 168.124 | 600.813 | 476.890 | 223.062 | −1163.079 | −618.548 | 17.950 |
| 1900 | 169.336 | 609.937 | 483.654 | 239.936 | −1160.695 | −588.362 | 16.175 |
| 2000 | 170.416 | 618.650 | 490.188 | 256.925 | −1158.288 | −558.300 | 14.581 |
| 2100 | 171.382 | 626.989 | 496.505 | 274.016 | −1155.862 | −528.361 | 13.142 |
| 2200 | 172.246 | 634.982 | 502.619 | 291.198 | −1153.417 | −498.537 | 11.837 |
| 2300 | 173.023 | 642.656 | 508.542 | 308.462 | −1150.951 | −468.825 | 10.647 |
| 2400 | 173.722 | 650.035 | 514.285 | 325.800 | −1148.462 | −439.221 | 9.559 |
| 2500 | 174.353 | 657.139 | 519.858 | 343.204 | −1145.947 | −409.720 | 8.561 |
| 2600 | 174.924 | 663.989 | 525.270 | 360.669 | −1143.403 | −380.322 | 7.641 |
| 2700 | 175.442 | 670.600 | 530.531 | 378.187 | −1140.826 | −351.021 | 6.791 |
| 2800 | 175.913 | 676.990 | 535.648 | 395.755 | −1138.211 | −321.817 | 6.004 |
| 2900 | 176.343 | 683.170 | 540.629 | 413.369 | −1135.557 | −292.706 | 5.272 |
| 3000 | 176.736 | 689.155 | 545.481 | 431.023 | −1132.860 | −263.689 | 4.591 |
| 3100 | 177.095 | 694.956 | 550.210 | 448.715 | −1130.117 | −234.762 | 3.956 |
| 3200 | 177.425 | 700.584 | 554.821 | 466.441 | −1127.327 | −205.924 | 3.361 |
| 3300 | 177.728 | 706.048 | 559.322 | 484.199 | −1124.487 | −177.173 | 2.804 |
| 3400 | 178.008 | 711.358 | 563.716 | 501.986 | −1121.598 | −148.510 | 2.282 |
| 3500 | 178.266 | 716.522 | 568.008 | 519.799 | −1118.657 | −119.933 | 1.790 |
| 3600 | 178.504 | 721.547 | 572.204 | 537.638 | −1115.665 | −91.439 | 1.327 |
| 3700 | 178.726 | 726.441 | 576.306 | 555.500 | −1112.622 | −63.031 | 0.890 |
| 3800 | 178.931 | 731.210 | 580.320 | 573.383 | −1109.529 | −34.705 | 0.477 |
| 3900 | 179.122 | 735.861 | 584.249 | 591.285 | −1106.386 | −6.460 | 0.087 |
| 4000 | 179.299 | 740.398 | 588.096 | 609.207 | −1103.193 | 21.702 | −0.283 |
| 4100 | 179.465 | 744.827 | 591.865 | 627.145 | −1099.953 | 49.784 | −0.634 |
| 4200 | 179.620 | 749.154 | 595.559 | 645.099 | −1096.667 | 77.788 | −0.967 |
| 4300 | 179.765 | 753.382 | 599.180 | 663.069 | −1093.336 | 105.711 | −1.284 |
| 4400 | 179.900 | 757.516 | 602.732 | 681.052 | −1089.961 | 133.557 | −1.586 |
| 4500 | 180.027 | 761.561 | 606.217 | 699.048 | −1086.543 | 161.326 | −1.873 |
| 4600 | 180.147 | 765.519 | 609.637 | 717.057 | −1083.085 | 189.018 | −2.146 |
| 4700 | 180.259 | 769.394 | 612.995 | 735.077 | −1079.588 | 216.635 | −2.408 |
| 4800 | 180.364 | 773.191 | 616.293 | 753.109 | −1076.052 | 244.178 | −2.657 |
| 4900 | 180.464 | 776.911 | 619.533 | 771.150 | −1072.480 | 271.644 | −2.896 |
| 5000 | 180.558 | 780.557 | 622.717 | 789.201 | −1068.871 | 299.040 | −3.124 |
| 5100 | 180.647 | 784.134 | 625.847 | 807.262 | −1065.228 | 326.361 | −3.343 |
| 5200 | 180.730 | 787.642 | 628.925 | 825.330 | −1061.551 | 353.612 | −3.552 |
| 5300 | 180.810 | 791.086 | 631.952 | 843.407 | −1057.841 | 380.791 | −3.753 |
| 5400 | 180.885 | 794.466 | 634.931 | 861.492 | −1054.098 | 407.900 | −3.946 |
| 5500 | 180.956 | 797.786 | 637.862 | 879.584 | −1050.323 | 434.938 | −4.131 |
| 5600 | 181.023 | 801.047 | 640.747 | 897.683 | −1046.515 | 461.910 | −4.309 |
| 5700 | 181.088 | 804.252 | 643.587 | 915.789 | −1042.676 | 488.812 | −4.479 |
| 5800 | 181.149 | 807.402 | 646.384 | 933.901 | −1038.806 | 515.646 | −4.644 |
| 5900 | 181.207 | 810.499 | 649.140 | 952.018 | −1034.903 | 542.414 | −4.802 |
| 6000 | 181.262 | 813.545 | 651.855 | 970.142 | −1030.968 | 569.114 | −4.955 |

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

## Magnesium Fluoride (($MgF_2)_2$) IDEAL GAS $M_r = 124.603612$ Magnesium Fluoride (($MgF_2)_2$) $F_4Mg_2(g)$

$\Delta_fH°(0\ K) = -1711.866 \pm 20.9$ (or ± 37.7) $kJ \cdot mol^{-1}$

$S°(298.15\ K) = [337.014 \pm 20.9]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = -1718.369 \pm 20.9$ (or ± 37.7) $kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies | | |
|---|---|---|
| $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ |
| 585(1) | [235](1) | 487(1) |
| 353(1) | [220](1) | [220](1) |
| [400](1) | [240](1) | 747(1) |
| [508](1) | [200](1) | 450(1) |

Ground State Quantum Weight: [1] $\sigma = 4$

Point Group: [$D_{2h}$]

Bond Distances: Mg–F = [1.77] Å; Mg–F' = [1.96] Å

Bond Angles: Mg–F'–Mg = [90]°; F–Mg–F' = [90]°; F–Mg–F' = [135]°

(F' = Ring Fluorine)

Product of Moments of Inertia: $I_AI_BI_C = [8.5873 \times 10^{-113}]\ g^3 \cdot cm^6$

### Enthalpy of Formation

Berkowitz and Marquart[1] have found approximately 1% dimer in the equilibrium vapor over $MgF_2(cr)$ at about 1400 K by mass spectrometry. Independent measurements which are discussed elsewhere (See $MgF_2(g)$ table) support their results. Berkowitz and Marquart[1] reported a 2nd law $\Delta_rH°(1440\ K)$ of 30 $kcal \cdot mol^{-1}$ for the reaction $MgF_2(cr) + MgF_2(g) = Mg_2F_2(g)$. This value corrected to 298.15 K gives $\Delta_rH° = 31.7\ kcal \cdot mol^{-1}$ which leads to $\Delta_fH°(Mg_2F_4, g, 298.15\ K) = -410.7\ kcal \cdot mol^{-1}$. The corresponding heat of dimerization at 298.15 K is $-63.3\ kcal \cdot mol^{-1}$. Berkowitz and Marquart[1] also reported approximate absolute pressures for $MgF_2(g)$ and $Mg_2F_4(g)$ at 1429 K. A 3rd law analysis of these reported pressures gives $\Delta_rH°(298.15\ K)$ of $-69.5\ kcal \cdot mol^{-1}$ for the process $2MgF_2(g) = Mg_2F_4(g)$, or $\Delta_fH°(Mg_2F_4, g, 298.15\ K) = -416.9\ kcal \cdot mol^{-1}$. We prefer the 2nd law result $\Delta_fH° = 410.7\ kcal \cdot mol^{-1}$ since the else negative ($-63.3\ kcal \cdot mol^{-1}$) heat of dimerization is more consistent with the dimerization energies for the alkali metal fluorides.[2] The uncertainty in $\Delta_fH°$ is estimated as ±5.0 $kcal \cdot mol^{-1}$, however, we also include an alternate uncertainty (±9 $kcal \cdot mol^{-1}$) to cover the possibility that $M_gF_2(g)$ is linear.[2]

### Heat Capacity and Entropy

The dimer is assumed to have a bridge–bond structure of $D_{2h}$ symmetry similar to that suggested by Thompson and Carlson[3] for the dimers of several transition metal dichlorides. The two outer Mg–F bond lengths are assumed to be the same as that for $MgF_2$.[2] The four ring Mg–F' bond lengths are assumed to be 10% longer. The four atoms which lie in the ring form a square. The F'–MgF' bond angle is estimated as 135°. The individual moments of inertia are: $I_A = 9.0458 \times 10^{-38}$, $I_B = 7.8340 \times 10^{-38}$ and $I_C = 1.2118 \times 10^{-38}\ g \cdot cm^2$.

This planar bridge–bond structure will have six Raman ($3A_g + 2B_{1g} + 2B_{2g}$) and six infrared ($2B_{1u} + 2B_{2u} + 2B_{3u}$) active fundamentals. The Raman spectra of $MgF_2$ isolated in an argon matrix has been recorded by Lesiecki and Nibler[4] They assigned two bands observed at 585 and 353 $cm^{-1}$ to $\nu_1$ and $\nu_2$, respectively, of $Mg_2F_4$. Lesiecki and Nibler,[4] using a standard high–low frequency separation method and a diagonal force field, calculated $\nu_4$ as 508 $cm^{-1}$. The other three Raman active frequencies ($\nu_3$, $\nu_5$, $\nu_6$) are estimated by analogy with those for $MgF_2$ and $Na_2F_2$.[2] Four of the six infrared active fundamentals have been osbserved and assigned by Lesiecki and Nibler.[4] These frequencies were recorded in an argon matrix. Results of three independent infrared studies[5-7] conducted with various matrices support these assignments. The other two infrared active fundamentals ($\nu_8$ and $\nu_{10}$) are estimated from the bending frequency ($\nu_2 = 215\ cm^{-1}$) for $MgF_2$.[2] Following the observations made by Thompson and Carlson,[3] all the estimated frequencies are taken to lie above the bending frequency of the monomer.

### References

[1] J. Berkowitz and J. R. Marquart, J. Chem. Phys. 37, 1853 (1962).
[2] JANAF Thermochemical Tables: $MgF_2(g)$, 6–30–75, $Li_2F_2(g)$ and $Na_2F_2(g)$, 12–31–68, $K_2F_2(g)$, 6–30–69.
[3] K R. Thompson and K. D. Carlson, J. Chem. Phys. 49, 4379 (1968).
[4] M. L. Lesiecki and J. W. Nibler, to be published.
[5] R. H. Hauge, J. L. Margrave, and A. S. Kana'an, J. Chem. Soc. Faraday Trans. II 71, 1082 (1975).
[6] A. Snelson, J. Phys. Chem. 70, 3208 (1966).
[7] D. E. Mann, G. V. Calder, K. S. Seshadri, D. White, and M. J. Linevsky, J. Chem. Phys 46, 1138 (1967).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | $J \cdot K^{-1} mol^{-1}$ | | | $kJ \cdot mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0 | 0. | INFINITE | −21.143 | −1711.866 | −1711.866 | INFINITE |
| 100 | 55.670 | 247.462 | 419.349 | −17.189 | −1715.010 | −1703.781 | 889.964 |
| 200 | 89.656 | 297.494 | 346.359 | −9.773 | −1717.466 | −1691.447 | 441.761 |
| 250 | 100.233 | 318.704 | 338.746 | −5.011 | −1718.051 | −1684.868 | 352.034 |
| 298.15 | 107.501 | 337.014 | 337.014 | 0. | −1718.369 | −1678.445 | 294.057 |
| 300 | 107.735 | 337.680 | 337.016 | 0.199 | −1718.378 | −1678.197 | 292.200 |
| 350 | 113.108 | 354.713 | 338.349 | 5.727 | −1718.551 | −1671.485 | 249.455 |
| 400 | 117.026 | 370.086 | 341.372 | 11.486 | −1718.640 | −1664.754 | 217.395 |
| 450 | 119.941 | 384.046 | 345.350 | 17.413 | −1718.687 | −1658.015 | 192.457 |
| 500 | 122.154 | 396.803 | 349.866 | 23.468 | −1718.722 | −1651.272 | 172.507 |
| 600 | 125.214 | 419.367 | 359.619 | 35.849 | −1718.823 | −1637.774 | 142.581 |
| 700 | 127.164 | 438.825 | 369.576 | 48.474 | −1719.045 | −1624.251 | 121.203 |
| 800 | 128 475 | 455.897 | 379.321 | 61.260 | −1719.454 | −1610.683 | 105.167 |
| 900 | 129.395 | 471.085 | 388.689 | 74.157 | −1720.103 | −1597.051 | 92.690 |
| 1000 | 130.065 | 484.755 | 397.624 | 87.131 | −1738.221 | −1581.906 | 82.630 |
| 1100 | 130.567 | 497.176 | 406.118 | 100.164 | −1739.490 | −1566.213 | 74.373 |
| 1200 | 130.952 | 508.554 | 414.187 | 113.241 | −1740.767 | −1550.404 | 67 487 |
| 1300 | 131.254 | 519.048 | 421.855 | 126.352 | −1742.056 | −1534.489 | 61.657 |
| 1400 | 131.495 | 528.784 | 429.149 | 139.489 | −1998.180 | −1512.139 | 56.419 |
| 1500 | 131.690 | 537.863 | 436.097 | 152.649 | −1996.798 | −1477.470 | 51.450 |
| 1600 | 131.850 | 546.368 | 442.726 | 165.826 | −1995.436 | −1442.893 | 47.106 |
| 1700 | 131.984 | 554.365 | 449.060 | 179.018 | −1994.092 | −1408.400 | 43.275 |
| 1800 | 132.096 | 561.912 | 455.122 | 192.222 | −1992.765 | −1373.986 | 39.872 |
| 1900 | 132.191 | 569.057 | 460.932 | 205.437 | −1991.451 | −1339.645 | 36.829 |
| 2000 | 132.272 | 575.840 | 466.510 | 218.660 | −1990.148 | −1305.373 | 34.093 |
| 2100 | 132.342 | 582.295 | 471.871 | 231.891 | −1988.849 | −1271.167 | 31.619 |
| 2200 | 132.403 | 588.453 | 477.031 | 245.128 | −1987.549 | −1237.022 | 29.371 |
| 2300 | 132.456 | 594.340 | 482.004 | 258.371 | −1986.243 | −1202.936 | 27.320 |
| 2400 | 132.502 | 599.978 | 486.803 | 271.619 | −1984.923 | −1168.907 | 25.441 |
| 2500 | 132.544 | 605.388 | 491.439 | 284.871 | −1983.583 | −1134.934 | 23.713 |
| 2600 | 132.580 | 610.587 | 495.923 | 298.128 | −1982.218 | −1101.015 | 22.120 |
| 2700 | 132.613 | 615.591 | 500.263 | 311.387 | −1980.824 | −1067.149 | 20.645 |
| 2800 | 132.642 | 620.415 | 504.468 | 324.650 | −1979.394 | −1033.335 | 19.277 |
| 2900 | 132.668 | 625.070 | 508.547 | 337.916 | −1977.926 | −999.573 | 18.004 |
| 3000 | 132.692 | 629.568 | 512.507 | 351.184 | −1976.417 | −965.863 | 16.817 |
| 3100 | 132.713 | 633.919 | 516.353 | 364.454 | −1974.866 | −932.203 | 15.708 |
| 3200 | 132.733 | 638.133 | 520.093 | 377.726 | −1973.271 | −898.594 | 14.668 |
| 3300 | 132.751 | 642.218 | 523.733 | 391.000 | −1971.633 | −865.035 | 13.692 |
| 3400 | 132.767 | 646.181 | 527.276 | 404.276 | −1969.952 | −831.527 | 12.775 |
| 3500 | 132.782 | 650.030 | 530.728 | 417.554 | −1968.231 | −798.069 | 11.911 |
| 3600 | 132.795 | 653.770 | 534.095 | 430.833 | −1966.473 | −764.661 | 11.095 |
| 3700 | 132.808 | 657.409 | 537.378 | 444.113 | −1964.679 | −731.302 | 10.324 |
| 3800 | 132.819 | 660.951 | 540.584 | 457.394 | −1962.855 | −697.992 | 9.595 |
| 3900 | 132.830 | 664.401 | 543.715 | 470.677 | −1961.004 | −664.730 | 8.903 |
| 4000 | 132.840 | 667.764 | 546.774 | 483.960 | −1959.132 | −631.516 | 8 247 |
| 4100 | 132.849 | 671.044 | 549.765 | 497.245 | −1957.242 | −598.349 | 7.623 |
| 4200 | 132.857 | 674.246 | 552.691 | 510.530 | −1955.342 | −565.228 | 7.030 |
| 4300 | 132.865 | 677.372 | 555.554 | 523.816 | −1953.436 | −532.153 | 6.464 |
| 4400 | 132.873 | 680.427 | 558.358 | 537.103 | −1951.529 | −499.122 | 5.925 |
| 4500 | 132.880 | 683.413 | 561.104 | 550.391 | −1949.628 | −466.133 | 5.411 |
| 4600 | 132.886 | 686.333 | 563.795 | 563.679 | −1947.738 | −433.188 | 4.919 |
| 4700 | 132.892 | 689.191 | 566.432 | 576.968 | −1945.865 | −400.283 | 4 449 |
| 4800 | 132.898 | 691.989 | 569.019 | 590.257 | −1944.015 | −367.418 | 3.998 |
| 4900 | 132.903 | 694.730 | 571.557 | 603.547 | −1942.194 | −334.591 | 3.567 |
| 5000 | 132.908 | 697.415 | 574.047 | 616.838 | −1940.406 | −301.801 | 3.153 |
| 5100 | 132.913 | 700.047 | 576.492 | 630.129 | −1938.657 | −269.047 | 2.756 |
| 5200 | 132.918 | 702.628 | 578.893 | 643.421 | −1936.952 | −236.325 | 2.374 |
| 5300 | 132.922 | 705.160 | 581.251 | 656.713 | −1935.296 | −203.637 | 2.007 |
| 5400 | 132.926 | 707.644 | 583.569 | 670.005 | −1933.694 | −170.980 | 1.654 |
| 5500 | 132.930 | 710.083 | 585.847 | 683.298 | −1932.150 | −138.352 | 1.314 |
| 5600 | 132.933 | 712.478 | 588.087 | 696.591 | −1930.669 | −105.750 | 0.986 |
| 5700 | 132.937 | 714.831 | 590.290 | 709.884 | −1929.256 | −73.176 | 0.671 |
| 5800 | 132.940 | 717.143 | 592.457 | 723.178 | −1927.914 | −40.625 | 0.366 |
| 5900 | 132.943 | 719.416 | 594.590 | 736.472 | −1926.647 | −8.095 | 0.072 |
| 6000 | 132.946 | 721.650 | 596.689 | 749.767 | −1925.459 | 24.412 | −0.213 |

PREVIOUS. December 1975 (1 atm) CURRENT December 1975 (1 bar)

## Molybdenum Fluoride ($MoF_4$) IDEAL GAS $M_r = 171.933612$ Molybdenum Fluoride ($MoF_4$) $F_4Mo_1(g)$

$\Delta_fH°(0\ K) = -944.351 \pm 16.7\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = [328.940 \pm 8.4]\ J\ K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = -947.676 \pm 16.7\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

| $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|
| 0 | [3] |
| [15000] | [11] |
| [20000] | [9] |

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|
| [700](1) | [750](3) |
| [160](2) | [180](2) |

Point Group: [$T_d$] $\sigma = [12]$
Bond Distance: Mo–F = [1.82] Å
Bond Angle: F–Mo–F = [109.47]°
Product of the Moments of Inertia. $I_AI_BI_C = [2.163977 \times 10^{-113}]\ g^3{\cdot}cm^6$

### Enthalpy of Formation

We adopt the weighted average value derived by Brewer[1] from several divergent equilibria measurements. Weaver *et al.*[2] reported a partial pressure of $4.6 \times 10^{-6}$ atm $MoF_4(g)$ in equilibrium with Mo and $MoF_3$ solids at 973 K. Hildenbrand[3] has measured several gaseous equilibria for reactions involving $MoF_4(g)$ [1143–2146 K]; and Alikhanyan[4] has measured partial pressures for the reaction $MoF_5(g) + MoF_3(g) = 2\ MoF_4(g)$ [911 and 964 K]. Our 3rd law analyses of the equilibrium reactions, using auxiliary data from Brewer[1] for the $MoF_x$ compounds other than $MoF_4(g)$ and other auxiliary data from the JANAF Thermochemical Tables,[5] leads to $\Delta_fH°(MoF_4,\ g,\ 298.15\ K)$ values ranging from −216.0 to −226.6 kcal·mol$^{-1}$. The value of $\Delta_fH°(0\ K)$ combined with JANAF data[5] for Mo(g) and F(g) gives $\Delta_aH°(0\ K) = 456.357$ kcal mol$^{-1}$ and an average Mo–F bond energy of $\Delta_aH°(0\ K)/4 = 114.1 \pm 2$ kcal·mol$^{-1}$.

### Heat Capacity and Entropy

We use the vibrational frequencies and degeneracies estimated by Hildenbrand[3] and adopted by Brewer.[1] These are in reasonable agreement with the estimates of Tumanov and Galkin.[6] The structure is assumed to be tetrahedral and a Mo–F distance of 1.82 Å from $MoF_6(g)$ is used. The electronic contributions are those estimated by Brewer[1] based on crystal field theory. The principal moments of inertia are: $I_A = I_B = I_C = 27.8666 \times 10^{39}\ g{\cdot}cm^2$.

This table is based on the critical analysis of data existing in 1978 by Brewer.[1]

### References

[1] L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, personal communication, September 1978, of preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Eneergy Agency, Vienna, Austria.

[2] C. F. Weaver, H. A. Friedman, J. D. Redman, R. A. Strehlow, J. W. Gooch, Jr., and J. S. Gill, Oak Ridge National Laboratory Reports ONRL–4191, **142–146** (1967); ORNL–4254, **129–136** (1968), ORNL–4396, **157–162** (1969); ORNL–4400, **33–39** (1970); ORNL–4449, **113–121** (1970); ORNL–4586, **17** (1970); ORNL–4801, **21** (1972).

[3] D. L. Hildenbrand, J. Chem. Phys. 65, 614 (1976).

[4] A. S. Alikhanyan, V. S. Pervov, I. P. Malkervoa, V. D. Butskii, and V. I. Gorgoraki, Russ. J Inorg. Chem. 23, 817 (1978).

[5] JANAF Thermochemical Tables: S(g), 9–30–77; SF(g), 6–30–76; Mo(cr) and Mo(g), 3–31–78; F(g) 9–30–65.

[6] Yu. N. Tumanov and N. P. Galkin, Russ. J. Phys. Chem. 43, 464 (1969).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0 | INFINITE | −18.909 | −944.351 | −944.351 | INFINITE |
| 100 | 58.912 | 250.806 | 397.136 | −14.633 | −946.380 | −936.684 | 489.273 |
| 200 | 74.611 | 297.057 | 336.418 | −7.872 | −947.319 | −926.574 | 241.996 |
| 250 | 80.449 | 314.348 | 330.317 | −3.992 | −947.562 | −921.357 | 192.507 |
| 298.15 | 85.232 | 328.940 | 328.940 | 0. | −947.676 | −916.298 | 160.532 |
| 300 | 85.398 | 329.468 | 328.942 | 0.158 | −947.678 | −916.103 | 159.508 |
| 350 | 89.417 | 342.945 | 329.997 | 4.532 | −947.696 | −910.838 | 135.935 |
| 400 | 92.611 | 355.102 | 332.388 | 9.086 | −947.645 | −905.575 | 118.256 |
| 450 | 95.137 | 366.162 | 335.535 | 13.782 | −947.547 | −900.322 | 104.507 |
| 500 | 97.141 | 376.293 | 339.111 | 18.591 | −947.420 | −895.081 | 93.508 |
| 600 | 100.035 | 394.278 | 346.845 | 28.460 | −947.114 | −884.641 | 77.015 |
| 700 | 101.955 | 409.853 | 354.759 | 38.565 | −946.784 | −874.255 | 65.238 |
| 800 | 103.279 | 423.558 | 362.520 | 48.831 | −946.459 | −863.916 | 56.408 |
| 900 | 104.225 | 435.780 | 369.993 | 59.209 | −946.156 | −853.617 | 49.543 |
| 1000 | 104.921 | 446.799 | 377.132 | 69.668 | −945.889 | −843.350 | 44.052 |
| 1100 | 105.447 | 456.825 | 383.928 | 80.187 | −945.672 | −833.107 | 39.561 |
| 1200 | 105.854 | 466.018 | 390.391 | 90.753 | −945.517 | −822.881 | 35.819 |
| 1300 | 106.174 | 474.504 | 396.539 | 101.355 | −945.434 | −812.665 | 32.653 |
| 1400 | 106.432 | 482.383 | 402.393 | 111.986 | −945.435 | −802.453 | 29.940 |
| 1500 | 106.643 | 489.733 | 407.973 | 122.640 | −945.527 | −792.237 | 27.588 |
| 1600 | 106.819 | 496.621 | 413.301 | 133.313 | −945.718 | −782.012 | 25.530 |
| 1700 | 106.969 | 503.102 | 418.394 | 144.003 | −946.015 | −771.772 | 23.714 |
| 1800 | 107.102 | 509.220 | 423.272 | 154.707 | −946.422 | −761.511 | 22.098 |
| 1900 | 107.224 | 515.014 | 427.949 | 165.423 | −946.944 | −751.225 | 20.653 |
| 2000 | 107.340 | 520.517 | 432.441 | 176.151 | −947.584 | −740.907 | 19.351 |
| 2100 | 107.456 | 525.757 | 436.761 | 186.891 | −948.345 | −730.556 | 18.172 |
| 2200 | 107.575 | 530.758 | 440.921 | 197.642 | −949.228 | −720.165 | 17.099 |
| 2300 | 107.703 | 535.543 | 444.931 | 208.406 | −950.235 | −709.730 | 16.118 |
| 2400 | 107.842 | 540.130 | 448.803 | 219.183 | −951.368 | −699.250 | 15.219 |
| 2500 | 107.995 | 544.535 | 452.545 | 229.975 | −952.629 | −688.719 | 14.390 |
| 2600 | 108.166 | 548.774 | 456.165 | 240.783 | −954.031 | −678.136 | 13.624 |
| 2700 | 108.356 | 552.860 | 459.671 | 251.609 | −955.605 | −667.495 | 12.913 |
| 2800 | 108.566 | 556.804 | 463.070 | 262.455 | −957.406 | −656.792 | 12.253 |
| 2900 | 108.798 | 560.618 | 466.368 | 273.323 | −995.389 | −645.971 | 11.635 |
| 3000 | 109.053 | 564.310 | 469.572 | 284.215 | −995.825 | −633.914 | 11.037 |
| 3100 | 109.330 | 567.891 | 472.686 | 295.134 | −996.181 | −621.845 | 10.478 |
| 3200 | 109.629 | 571.366 | 475.716 | 306.082 | −996.451 | −609.765 | 9.953 |
| 3300 | 109.951 | 574.745 | 478.666 | 317.061 | −996.629 | −597.678 | 9.460 |
| 3400 | 110.293 | 578.032 | 481.540 | 328.073 | −996.711 | −585.587 | 8.996 |
| 3500 | 110.654 | 581.234 | 484.343 | 339.120 | −996.693 | −573.495 | 8.559 |
| 3600 | 111.034 | 584.357 | 487.078 | 350.204 | −996.572 | −561.405 | 8.146 |
| 3700 | 111.429 | 587.404 | 489.748 | 361.327 | −996.344 | −549.320 | 7.755 |
| 3800 | 111.839 | 590.382 | 492.358 | 372.491 | −996.007 | −537.243 | 7.385 |
| 3900 | 112.261 | 593.292 | 494.909 | 383.696 | −995.561 | −525.175 | 7.034 |
| 4000 | 112.693 | 596.140 | 497.404 | 394.943 | −995.003 | −513.121 | 6.701 |
| 4100 | 113.133 | 598.928 | 499.846 | 406.235 | −994.334 | −501.082 | 6.384 |
| 4200 | 113.578 | 601.659 | 502.238 | 417.570 | −993.553 | −489.060 | 6.082 |
| 4300 | 114.026 | 604.337 | 504.581 | 428.950 | −992.662 | −477.059 | 5.795 |
| 4400 | 114.474 | 606.964 | 506.878 | 440.375 | −991.660 | −465.080 | 5.521 |
| 4500 | 114.921 | 609.541 | 509.131 | 451.845 | −990.549 | −453.124 | 5.260 |
| 4600 | 115.365 | 612.072 | 511.342 | 463.359 | −989.330 | −441.195 | 5.010 |
| 4700 | 115.803 | 614.558 | 513.511 | 474.918 | −988.006 | −429.293 | 4.771 |
| 4800 | 116.233 | 617.000 | 515.642 | 486.520 | −986.578 | −417.420 | 4.542 |
| 4900 | 116.654 | 619.401 | 517.735 | 498.164 | −985.048 | −405.578 | 4.324 |
| 5000 | 117.064 | 621.762 | 519.792 | 509.850 | −1574.805 | −388.038 | 4.054 |
| 5100 | 117.461 | 624.084 | 521.814 | 521.576 | −1574.760 | −364.303 | 3.731 |
| 5200 | 117.845 | 626.369 | 523.803 | 533.342 | −1574.769 | −340.568 | 3.421 |
| 5300 | 118.213 | 628.617 | 525.760 | 545.145 | −1574.830 | −316.833 | 3.123 |
| 5400 | 118.565 | 630.830 | 527.685 | 556.984 | −1574.948 | −293.096 | 2.835 |
| 5500 | 118.900 | 633.009 | 529.580 | 568.857 | −1575.121 | −269.357 | 2.558 |
| 5600 | 119.217 | 635.154 | 531.446 | 580.763 | −1575.352 | −245.613 | 2.291 |
| 5700 | 119.516 | 637.267 | 533.284 | 592.700 | −1575.639 | −221.867 | 2.033 |
| 5800 | 119.796 | 639.348 | 535.095 | 604.666 | −1575.985 | −198.113 | 1.784 |
| 5900 | 120.057 | 641.398 | 536.879 | 616.659 | −1576.387 | −174.353 | 1.544 |
| 6000 | 120.299 | 643.418 | 538.638 | 628.677 | −1576.849 | −150.587 | 1.311 |

PREVIOUS: December 1978 (1 atm) CURRENT: December 1978 (1 bar)

## Molybdenum Fluoride Oxide ($MoF_4O$) IDEAL GAS $M_r$ = 187.933012 Molybdenum Fluoride Oxide ($MoF_4O$) $F_4Mo_1O_1(g)$

$\Delta_fH°(0\ K) = [-1248.030 \pm 126]\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = [330.617 \pm 8.4]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298\ 15\ K) = [-1255\ 200 \pm 126]\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies

| $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ |
|---|---|---|
| 1045 (1) | [600](1) | 720 (2) |
| [300](1) | [300](1) | 530 (2) |
| 680 (1) | [200](1) | [150](2) |

Ground State Quantum Weight: [1] $\sigma$ = [4]

Point Group. [$C_{4v}$]

Bond Distance: Mo–O = [1.64] Å, Mo–F = [1.82] Å

Bond Angles: O–Mo–F = [90]°; F–Mo–F = [90]°

Product of the Moments of Inertia: $I_AI_BI_C = [3.1468 \times 10^{-113}]\ g^3\ cm^6$

### Enthalpy of Formation

Zmbov *et al.*[1] investigated the stabilities of some molybdenum and tungsten oxyfluorides by means of mass spectrometry These studies led to enthalpies of formation for $MoO_2F_2(g)$, $WO_2F_2(g)$, and $WOF_4(g)$ which were used by the authors to develop a correlation among the enthalpies of formation of the oxides, oxyfluorides, and fluorides of Mo and W. $\Delta_fH°$(298.15 K) varies almost linearly with the number of oxygen atoms[1] for the series $WF_6$, $WOF_4$ and $WO_2F_2$. Assuming a similar variation for $MoF_6$, $MoOF_4$ and $MoO_2F_2$, we estimate $\Delta_fH°(MoOF_4, g) = -320\ kcal{\cdot}mol^{-1}$.

$\Delta_fH$ data[2] for $MoF_6(g)$, $MoO(g)$, $MoO_2(g)$, and $MoO_3(g)$ have been used to derive the following average bond dissociation energies:

$$\Delta H°(MoF, g)/6 = 107\ kcal{\cdot}mol^{-1}$$
$$\Delta H°(MoO_n, g)/n = 135\ kcal{\cdot}mol^{-1}$$

From these data we derive $\Delta_fH°(MoOF_4, g) = -271\ kcal{\cdot}mol^{-1}$.

The enthalpy of formation for $MoOF_4$ is tentatively selected as $-300 \pm 30\ kcal{\cdot}mol^{-1}$.

### Heat Capacity and Entropy

Blanchard[3] suggested that $MoOF_4(g)$ possessed $C_{4v}$ symmetry by reason of the similarity of its infrared spectra with that of $XeOF_4(g)$. X–ray diffraction studies of crystalline $MoOF_4$ by Edwards *et al.*[4,5] support this view. The structure of the molecule is assumed to be square–pyramidal. The bond lengths are from the crystallographic studies of $MoOF_4$ by Edwards *et al.*[4,5] Individual moments of inertia are $I_A = I_B = 27.437 \times 10^{-39}$, $I_C = 41.8010 \times 10^{-39}\ g{\cdot}cm^2$.

Blanchard[3] reported the following vibrational frequencies and assignments:

$$\nu_1 = 1045,\quad \nu_7 = 720,\quad \nu_3 = 680, \text{ and } \quad \nu_8 = 530\ cm^{-1}.$$

Similar frequencies have been reported by Edwards *et al.*[4] from their study of the infrared spectra of gaseous $MoOF_4$. The rest of the frequencies and assignments are estimated by comparison with data for $XeOF_4$.[6]

### References

[1] K F Zmbov, O. M. Uy and J. L. Margrave, J. Phys. Chem. 73, 3008 (1969).
[2] JANAF Thermochemical Tables.
[3] S. Blanchard, Commissariat a l'Energie Atomique Report CEA–R 3194, (1967).
[4] A. J. Edwards, G. R. Jones and B. R. Steventon, Chem. Commun. 462 (1967).
[5] A. J. Edwards and B. R. Steventon, J. Chem. Soc. 2503 (1968).
[6] G M. Begun, W. H. Fletcher and D. F. Smith, J. Chem Phys. 42, 2236 (1965).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0 | INFINITE | −19.407 | −1248.030 | −1248.030 | INFINITE |
| 100 | 53 979 | 250 195 | 403.835 | −15.364 | −1251 745 | −1233.323 | 644.222 |
| 200 | 78 838 | 295.560 | 338.941 | −8.676 | −1254.213 | −1213.820 | 317.017 |
| 250 | 88.874 | 314.265 | 332.167 | −4.476 | −1254.864 | −1203.639 | 251.487 |
| 298 15 | 96 740 | 330.617 | 330.617 | 0. | −1255.200 | −1193 739 | 209.138 |
| 300 | 97.009 | 331.216 | 330.618 | 0.179 | −1255.208 | −1193.358 | 207.782 |
| 350 | 103.440 | 346.673 | 331.824 | 5.197 | −1255.320 | −1183.038 | 176.559 |
| 400 | 108.488 | 360.828 | 334.578 | 10.500 | −1255.267 | −1172.714 | 153.141 |
| 450 | 112 460 | 373.845 | 338.228 | 16.028 | −1255.097 | −1162.404 | 134.928 |
| 500 | 115 608 | 385.863 | 342.398 | 21.732 | −1254.844 | −1152.117 | 120.361 |
| 600 | 120.165 | 407.373 | 351.478 | 33.537 | −1254.183 | −1131.631 | 98.517 |
| 700 | 123.201 | 426.139 | 360.832 | 45.715 | −1253.408 | −1111.267 | 82.924 |
| 800 | 125.304 | 442.736 | 370.053 | 58.147 | −1252.585 | −1091.017 | 71.236 |
| 900 | 126.812 | 457.587 | 378.968 | 70.756 | −1251 753 | −1070.871 | 62.152 |
| 1000 | 127.925 | 471.008 | 387.512 | 83.496 | −1250 937 | −1050.817 | 54.889 |
| 1100 | 128 769 | 483.242 | 395.667 | 96.333 | −1250.157 | −1030.843 | 48 951 |
| 1200 | 129.422 | 494.476 | 403.439 | 109.243 | −1249.431 | −1010 937 | 44.005 |
| 1300 | 129.937 | 504.856 | 410.846 | 122.212 | −1248.773 | −991.090 | 39.822 |
| 1400 | 130.350 | 514.501 | 417.910 | 135.227 | −1248.196 | −971.291 | 36.239 |
| 1500 | 130.686 | 523.506 | 424 653 | 148.280 | −1247 710 | −951.529 | 33.135 |
| 1600 | 130 964 | 531.949 | 431.098 | 161.363 | −1247.326 | −931.797 | 30 420 |
| 1700 | 131.195 | 539.896 | 437.266 | 174.471 | −1247.049 | −912.085 | 28.025 |
| 1800 | 131.389 | 547.401 | 443.178 | 187.600 | −1246.889 | −892.387 | 25.896 |
| 1900 | 131.555 | 554.509 | 448.852 | 200.748 | −1246.849 | −872.694 | 23.992 |
| 2000 | 131.696 | 561.261 | 454.305 | 213.911 | −1246.936 | −853.000 | 22.278 |
| 2100 | 131.819 | 567.689 | 459.553 | 227.087 | −1247.154 | −833.299 | 20.727 |
| 2200 | 131.925 | 573.824 | 464.609 | 240.274 | −1247.505 | −813.583 | 19.317 |
| 2300 | 132.018 | 579.690 | 469.485 | 253.471 | −1247.995 | −793.849 | 18.029 |
| 2400 | 132.100 | 585.311 | 474.195 | 266.677 | −1248.625 | −774.091 | 16.848 |
| 2500 | 132.172 | 590.705 | 478.748 | 279.891 | −1249.401 | −754.303 | 15.760 |
| 2600 | 132.236 | 595.890 | 483.155 | 293 111 | −1250.339 | −734.481 | 14.756 |
| 2700 | 132.293 | 600.882 | 487.423 | 306.338 | −1251.471 | −714 619 | 13.825 |
| 2800 | 132.345 | 605.694 | 491.562 | 319.570 | −1252.854 | −694 712 | 12.960 |
| 2900 | 132.391 | 610.339 | 495.578 | 332.806 | −1290.448 | −674 700 | 12.153 |
| 3000 | 132.433 | 614.828 | 499.479 | 346.048 | −1290.524 | −653.466 | 11.378 |
| 3100 | 132.470 | 619.171 | 503.270 | 359.293 | −1290.551 | −632.230 | 10.653 |
| 3200 | 132.505 | 623.377 | 506.958 | 372.542 | −1290.527 | −610.994 | 9 973 |
| 3300 | 132.536 | 627.455 | 510.548 | 385.794 | −1290.447 | −589 760 | 9.335 |
| 3400 | 132.564 | 631.412 | 514.045 | 399.049 | −1290.310 | −568.529 | 8.734 |
| 3500 | 132.590 | 635.255 | 517.453 | 412.306 | −1290.114 | −547.302 | 8.168 |
| 3600 | 132.614 | 638.991 | 520.778 | 425.567 | −1289.856 | −526.082 | 7.633 |
| 3700 | 132.637 | 642.624 | 524.022 | 438.829 | −1289.535 | −504.871 | 7 128 |
| 3800 | 132.657 | 646.162 | 527.190 | 452.094 | −1289.151 | −483.669 | 6.648 |
| 3900 | 132.676 | 649.608 | 530.285 | 465.361 | −1288.704 | −462.477 | 6.194 |
| 4000 | 132.693 | 652.967 | 533.310 | 478.629 | −1288.194 | −441.298 | 5.763 |
| 4100 | 132.709 | 656.244 | 536.269 | 491.899 | −1287.620 | −420.133 | 5.353 |
| 4200 | 132.724 | 659.442 | 539.163 | 505.171 | −1286.984 | −398.982 | 4.962 |
| 4300 | 132.738 | 662.565 | 541.997 | 518.444 | −1286.286 | −377.848 | 4.590 |
| 4400 | 132.752 | 665.617 | 544.772 | 531.719 | −1285.528 | −356.730 | 4.235 |
| 4500 | 132.764 | 668.601 | 547 491 | 544.994 | −1284.710 | −335.630 | 3.896 |
| 4600 | 132.775 | 671.519 | 550.155 | 558.271 | −1283.833 | −314.549 | 3.572 |
| 4700 | 132.786 | 674.374 | 552.768 | 571.549 | −1282.901 | −293.488 | 3.262 |
| 4800 | 132.796 | 677.170 | 555.331 | 584.828 | −1281.913 | −272.446 | 2.965 |
| 4900 | 132.805 | 679.908 | 557.845 | 598.109 | −1280.872 | −251.426 | 2.680 |
| 5000 | 132.814 | 682.591 | 560.313 | 611.390 | −1871.164 | −224.697 | 2.347 |
| 5100 | 132.823 | 685.222 | 562.737 | 624.671 | −1871.701 | −191.763 | 1.964 |
| 5200 | 132.831 | 687.801 | 565.117 | 637.954 | −1872.336 | −158.817 | 1.595 |
| 5300 | 132.838 | 690.331 | 567.456 | 651.237 | −1873.069 | −125.857 | 1.240 |
| 5400 | 132.845 | 692.814 | 569.755 | 664.522 | −1873.901 | −92.884 | 0.898 |
| 5500 | 132.852 | 695.252 | 572.014 | 677.807 | −1874.829 | −59.894 | 0.569 |
| 5600 | 132.858 | 697.646 | 574.236 | 691.092 | −1875.856 | −26.885 | 0.251 |
| 5700 | 132.864 | 699.997 | 576.422 | 704.378 | −1876.979 | 6.141 | −0.056 |
| 5800 | 132.870 | 702.308 | 578.573 | 717.665 | −1878.197 | 39.189 | −0.353 |
| 5900 | 132.875 | 704.579 | 580.689 | 730.952 | −1879.508 | 72.258 | −0.640 |
| 6000 | 132.880 | 706.813 | 582.773 | 744.240 | −1880 915 | 105.350 | −0.917 |

PREVIOUS June 1970 (1 atm) CURRENT June 1970 (1 bar)

Molybdenum Fluoride Oxide ($MoF_4O$) $F_4Mo_1O_1(g)$

## Tetrafluorohydrazine ($N_2F_4$) IDEAL GAS $M_r = 104.007012$ Tetrafluorohydrazine ($N_2F_4$) $F_4N_2(g)$

$\Delta_fH°(0\ K) = 2.430 \pm 10.5\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 301.191\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = -8.368 \pm 10.5\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|---|
| 1010 (1) | 549 (1) | 946 (1) |
| 998 (1) | 390 (1) | 737 (1) |
| 933 (1) | 122 (1) | 519 (1) |
| 591 (1) | 959 (1) | 467 (1) |

Ground State Quantum Weight: 1 $\sigma = 2$

Point Group: $C_2$

Bond Distances: N–N = [1.47 ] Å; N–F = [1.37] Å

Bond Angles: F–N–F = [108]°, N–N–F = [104]°; Dihedral Angle = [65]°

Product of the Moments of Inertia: $I_AI_BI_C = [1\ 1817 \times 10^{-113}]\ g^3 \cdot cm^6$

### Enthalpy of Formation

Armstrong *et al.*[1] studied the reaction $N_2F_4(g) + 16/3\ NH_3(g) = 4\ NH_4F(s) + 5/3\ N_2(g)$. From this reaction, they calculate the enthalpy of formation of $N_2F_4$ to be $-2.0 \pm 2.5$ kcal·mol$^{-1}$. The recalculated enthalpy of formation of $NH_4F(s)$ (refer to $NF_2$ table) differs from the value quoted in Circular 500 by 0.06 kcal·mol$^{-1}$. This correction would make the enthalpy of formation of tetrafluorohydrazine more negative by 0.24 kcal·mol$^{-1}$ In view of the large uncertainty in the enthalpy of formation, however, this correction was not applied.

### Heat Capacity and Entropy – $N_2F_4(g)$

The fundamental frequencies were taken from the vapor phase infrared work of Durig and Lord.[2] The principal moments of inertia were calculated from the rotational constants reported by Lide and Mann.[3] Lide and Mann calculated the bond angles for assumed values of the NN and NF distance.

The principal moments of inertia are: $I_A = 1.5051 \times 10^{-38}$, $I_B = 2.6315 \times 10^{-38}$, and $I_C = 2.9836 \times 10^{-38}\ g \cdot cm^2$.

### Heat Capacity and Entropy – $NF_2(g)$

Harmony *et al.*[4] investigated the infrared spectrum of $NF_2$. They were able to assign the band center at 1074 cm$^{-1}$ to the symmetric stretching mode $\nu_1$. The absorption in the 930–940 cm$^{-1}$ region was assigned to $\nu_3$.

Harmony and Myers[5] performed matrix isolation experiments on $NF_2$. They arrived at the assignment $\nu_1 = 1070$ cm$^{-1}$, $\nu_2 = 573$ cm$^{-1}$ and $\nu_3 = 931$ cm$^{-1}$. The stretching frequencies for similar molecules in an $N_2$ matrix are about 5 cm$^{-1}$ below the gas phase values. A comparison of the gas phase and matrix values of $\nu_1$ show excellent agreement.

Johnson and Colburn[6] report infrared studies on $NF_2$ but they draw no definite conclusions.

The gas phase value for $\nu_1$ and the matrix values of $\nu_2$ and $\nu_3$ were taken to represent the fundamental vibrational frequencies of $NF_2$.

Harmony *et al.*[4] estimated the N–F distance as 1.37 and used this with their data to calculate an F–N–F angle of 104 2° Using these data the moments of inertia are. $I_A = 7.3728 \times 10^{-39}$, $I_B = 1\ 2035 \times 10^{-39}$, and $I_C = 8.5763 \times 10^{-39}\ g \cdot cm^2$.

### References

[1] G. T. Armstrong, S. Marantz, and C. F. Coyle, U. S. Nat. Bur. Stand. Report 6584, (1959).
[2] J. R. Durig and R. C. Lord, Spectrochim. Acta 19, 1877 (1963).
[3] D. R. Lide, Jr., and D. E. Mann, J. Chem. Phys. 31, 1129 (1959).
[4] M. D. Harmony, R. J. Myers, L. J. Schoen, D. R. Lide, Jr., and D. E. Mann, J. Chem. Phys. 35, 1129 (1961).
[5] M. D. Harmony and R. J. Myers, J. Chem. Phys. 37, 636 (1962).
[6] F. A. Johnson and C. B. Colburn, Inorg. Chem. 1, 431 (1962).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −15.522 | 2.430 | 2.430 | INFINITE |
| 100 | 41 759 | 239.576 | 358.172 | −11.860 | −2.624 | 23.474 | −12.261 |
| 200 | 59.845 | 273.592 | 307.831 | −6.848 | −6.381 | 51.159 | −13.361 |
| 250 | 70.089 | 288.055 | 302.445 | −3.598 | −7.591 | 65.693 | −13.726 |
| 298.15 | 79.169 | 301.191 | 301.191 | 0. | −8.368 | 79.883 | −13.995 |
| 300 | 79.496 | 301.682 | 301.193 | 0.147 | −8.391 | 80 431 | −14.004 |
| 350 | 87.647 | 314.566 | 302.192 | 4.331 | −8.842 | 95.275 | −14.219 |
| 400 | 94.490 | 326.730 | 304.506 | 8.890 | −9 004 | 110.163 | −14.386 |
| 450 | 100 146 | 338.197 | 307.619 | 13.760 | −8.933 | 125.056 | −14.516 |
| 500 | 104.796 | 348.997 | 311.222 | 18.887 | −8.677 | 139.932 | −14.619 |
| 600 | 111.781 | 368.762 | 319.197 | 29.739 | −7.756 | 169.575 | −14.763 |
| 700 | 116.598 | 386.377 | 327.560 | 41.172 | −6.469 | 199.032 | −14.852 |
| 800 | 120.009 | 402 181 | 335.917 | 53.012 | −4.957 | 228.288 | −14 906 |
| 900 | 122.490 | 416.467 | 344.086 | 65.143 | −3.311 | 257.346 | −14.936 |
| 1000 | 124.341 | 429.473 | 351.984 | 77.489 | −1.585 | 286.216 | −14.950 |
| 1100 | 125.754 | 441.393 | 359.578 | 89.996 | 0.186 | 314.911 | −14 954 |
| 1200 | 126.854 | 452.384 | 366.860 | 102.629 | 1.978 | 343.443 | −14.950 |
| 1300 | 127.726 | 462.574 | 373.835 | 115.360 | 3.776 | 371.826 | −14.940 |
| 1400 | 128.427 | 472.066 | 380.517 | 128 169 | 5.570 | 400 070 | −14.927 |
| 1500 | 129.000 | 480.946 | 386.919 | 141.041 | 7.353 | 428 186 | −14.911 |
| 1600 | 129 473 | 489.287 | 393.059 | 153.965 | 9 121 | 456 184 | −14.893 |
| 1700 | 129.868 | 497.149 | 398.953 | 166.933 | 10.872 | 484.072 | −14 874 |
| 1800 | 130.202 | 504.582 | 404.617 | 179.937 | 12.607 | 511.857 | −14.854 |
| 1900 | 130.485 | 511 629 | 410.065 | 192.972 | 14.328 | 539.546 | −14.833 |
| 2000 | 130.728 | 518.328 | 415.312 | 206.033 | 16.039 | 567 145 | −14.812 |
| 2100 | 130.939 | 524.712 | 420.371 | 219.116 | 17 743 | 594.658 | −14.791 |
| 2200 | 131 121 | 530.807 | 425.253 | 232.219 | 19 448 | 622.090 | −14 770 |
| 2300 | 131.281 | 536.640 | 429.970 | 245.340 | 21.158 | 649.445 | −14 749 |
| 2400 | 131.422 | 542.230 | 434.532 | 258.475 | 22.881 | 676.725 | −14.729 |
| 2500 | 131.547 | 547.597 | 438.948 | 271.624 | 24.625 | 703.933 | −14.708 |
| 2600 | 131.657 | 552 759 | 443.227 | 284 784 | 26.394 | 731 070 | −14.687 |
| 2700 | 131.756 | 557.730 | 447.376 | 297.955 | 28 196 | 758.139 | −14 667 |
| 2800 | 131.845 | 562.523 | 451.403 | 311.135 | 30.037 | 785.141 | −14 647 |
| 2900 | 131.924 | 567.151 | 455.315 | 324.323 | 31.922 | 812.075 | −14 627 |
| 3000 | 131.996 | 571.625 | 459.118 | 337.519 | 33.856 | 838.944 | −14.607 |
| 3100 | 132.061 | 575.954 | 462.818 | 350.722 | 35.843 | 865 748 | −14.588 |
| 3200 | 132.120 | 580.148 | 466.419 | 363.931 | 37 888 | 892 487 | −14.568 |
| 3300 | 132.174 | 584.214 | 469.927 | 377.146 | 39 992 | 919.160 | −14.549 |
| 3400 | 132.224 | 588.161 | 473.347 | 390.366 | 42.159 | 945.769 | −14.530 |
| 3500 | 132.269 | 591.994 | 476.682 | 403.591 | 44.390 | 972.314 | −14.511 |
| 3600 | 132.310 | 595.721 | 479.938 | 416.820 | 46.688 | 998.794 | −14.492 |
| 3700 | 132.348 | 599.346 | 483.116 | 430.053 | 49.051 | 1025 209 | −14.473 |
| 3800 | 132.384 | 602.876 | 486.221 | 443.289 | 51 483 | 1051.559 | −14.455 |
| 3900 | 132 416 | 606.316 | 489.257 | 456.529 | 53 981 | 1077.845 | −14 436 |
| 4000 | 132.446 | 609 668 | 492.225 | 469.772 | 56.547 | 1104.065 | −14 418 |
| 4100 | 132.474 | 612.939 | 495.130 | 483 018 | 59.179 | 1130.220 | −14.399 |
| 4200 | 132.500 | 616 132 | 497.973 | 496.267 | 61.878 | 1156.311 | −14.381 |
| 4300 | 132.525 | 619.250 | 500.757 | 509.518 | 64 641 | 1182.336 | −14.363 |
| 4400 | 132.547 | 622.297 | 503.485 | 522.772 | 67.469 | 1208.296 | −14 344 |
| 4500 | 132.568 | 625.276 | 506.159 | 536.028 | 70.360 | 1234.192 | −14.326 |
| 4600 | 132.588 | 628.190 | 508.780 | 549.286 | 73.312 | 1260.022 | −14.308 |
| 4700 | 132 607 | 631.041 | 511.351 | 562.545 | 76.324 | 1285 788 | −14.290 |
| 4800 | 132.624 | 633.833 | 513.874 | 575.807 | 79.395 | 1311 489 | −14.272 |
| 4900 | 132.641 | 636.568 | 516.350 | 589.070 | 82.523 | 1337.126 | −14.254 |
| 5000 | 132.656 | 639.248 | 518.781 | 602.335 | 85.706 | 1362.697 | −14.236 |
| 5100 | 132.671 | 641.875 | 521.169 | 615.601 | 88.943 | 1388.205 | −14.218 |
| 5200 | 132.684 | 644.452 | 523.515 | 628.869 | 92.232 | 1413 649 | −14.200 |
| 5300 | 132.697 | 646.979 | 525.821 | 642.138 | 95.571 | 1439.029 | −14.182 |
| 5400 | 132.709 | 649.460 | 528.088 | 655.409 | 98.960 | 1464.346 | −14.165 |
| 5500 | 132.721 | 651.895 | 530.317 | 668.680 | 102.396 | 1489.599 | −14.147 |
| 5600 | 132.732 | 654.286 | 532.509 | 681.953 | 105 878 | 1514 790 | −14.129 |
| 5700 | 132.742 | 656.636 | 534.666 | 695.226 | 109.404 | 1539.917 | −14 112 |
| 5800 | 132.752 | 658.944 | 536.789 | 708.501 | 112.972 | 1564.982 | −14.094 |
| 5900 | 132.761 | 661.214 | 538.879 | 721 777 | 116.581 | 1589.987 | −14.077 |
| 6000 | 132.770 | 663.445 | 540.936 | 735.053 | 120.230 | 1614.929 | −14.059 |

PREVIOUS. March 1964 (1 atm) CURRENT: March 1964 (1 bar)

## Tungsten Fluoride Oxide ($WF_4O$) CRYSTAL $M_r = 275.843012$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -1406.908 \pm 62.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 5.021 \pm 4.2\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 175.728 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 379\ K$

### Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(WOF_4, cr, 298.15\ K) = -333.26\ kcal\ mol^{-1}$, is calculated from the enthalpy of formation of $WOF_4(g)$ less the enthalpy of sublimation, $\Delta_{sub} H°(298.15\ K) = 16.80\ kcal\ mol^{-1}$. This latter quantity is calculated by the 3rd law method from the vapor pressure equation determined by Cady and Hargreaves.[1] The 2nd law value is $\Delta_{sub} H°(298.15\ K) = 16.94\ kcal \cdot mol^{-1}$

### Heat Capacity and Entropy

The heat capacities are estimated from those of $WOCl_4(cr)$, $WO_3(cr)$, $WO_2(cr)$, $WCl_6(cr)$, and $WF_6(cr, l)$.[3]

The entropy, $S°(298.15\ K) = 42.0\ cal\ K^{-1} \cdot mol^{-1}$ is calculated from the vapor pressure equaiton of Cady and Hargreaves[1] using a 2nd law analysis.

This entropy is larger than the corresponding value for $WOCl_4(cr)$.[2] In both cases the entropies of the condensed phases are derived from gas phase values using 2nd law analysis of sublimation and vaporization data. The entropy of melting for $WOCl_4$ is an order of magnitude larger than that of $WOF_4$. This suggests some inconsistency in the data for $WOCl_4$ since all values for $WOF_4(cr, l, g)$ appear internally reasonable.

### Fusion Data

$T_{fus}$ is calculated as the temperature at which the Gibbs energy of reaction $WOF_4(cr) \rightarrow WOF_4(l)$ approaches zero. The difference between the enthalpies of formation for the crystal and liquid at the melting point is $\Delta_{fus} H°$.

Ruff *et al.*[3] reported the melting point as 383 K. Cady and Hargreaves[1] calculated the melting point as 378 K, and the heat of fusion as $2.26\ kcal \cdot mol^{-1}$ from vapor pressure equations for the crystal and liquid. This 2nd law value of $\Delta_{fus} H°$, when corrected for $\Delta C_p°$ of vaporization and sublimation, is in good agreement with the value adopted in this table.

### References

[1] G. H. Cady and G. B. Hargreaves, J. Chem. Soc. (London) **1961**, 1563.
[2] JANAF Thermochemical Tables: $WOCl_4(cr)$, 3-31-67, $WCl_6(cr)$, 12-31-66, $WF_6(cr)$, 3-31-67, $WO_2(cr)$, 9-30-66, $WO_3(cr)$, 9-30-66.
[3] O. Ruff, F. Eisner, and W. Heller, Z. Anorg. Chem. **52**, 256 (1907).

## Tungsten Fluoride Oxide ($WF_4O$) $F_4O_1W_1(cr)$

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| | $J \cdot K^{-1} mol^{-1}$ | | | $kJ \cdot mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 133.578 | 175.728 | 175.728 | 0. | −1406.908 | −1298.058 | 227.414 |
| 300 | 133.888 | 176.555 | 175.731 | 0.247 | −1406.848 | −1297.383 | 225.894 |
| 379.000 | 147.109 | 209.337 | 179.398 | 11.347 | --- CRYSTAL <--> LIQUID --- | | |
| 400 | 150.624 | 217.357 | 181.182 | 14.470 | −1403.013 | −1261.438 | 164.727 |
| 500 | 166.523 | 252.746 | 192.028 | 30.359 | −1397.900 | −1226.610 | 128.143 |
| 600 | 178.657 | 284.242 | 204.821 | 47.653 | −1391.690 | −1192.920 | 103.853 |
| 700 | 186.606 | 312.412 | 218.216 | 65.937 | −1384.737 | −1160.334 | 86.585 |
| 800 | 192.046 | 337.703 | 231.599 | 84.883 | −1377.323 | −1128.778 | 73.702 |
| 900 | 195.811 | 360.557 | 244.679 | 104.290 | −1369.616 | −1098.170 | 63.736 |
| 1000 | 197.903 | 381.310 | 257.321 | 123.990 | −1361.761 | −1068.430 | 55.809 |

PREVIOUS March 1967    CURRENT December 1971

## Tungsten Fluoride Oxide (WF$_4$O) LIQUID $M_r = 275.843012$ Tungsten Fluoride Oxide (WF$_4$O) F$_4$O$_1$W$_1$(l)

$S°(298.15\ K) = 178.915 \pm 4.2\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -1405.255 \pm 62.8\ kJ\cdot mol^{-1}$

$T_{fus} = 379\ K$ $\Delta_{fus}H° = 5.021 \pm 4.2\ kJ\cdot mol^{-1}$

### Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(WOF_4, l, 298.15\ K) = -335.84\ kcal\cdot mol^{-1}$ is calculated from that of the gas less the enthalpy eat of vaporization, $\Delta_{vap}H°(298\ 15\ K) = 16.38\ kcal\cdot mol^{-1}$. This latter value is calculated by the 3rd law method from the vapor pressure equation determined by Cady and Hargreaves.[1] The 2nd law value is $\Delta_{vap}H°(298.15\ K) = 16.50\ kcal\cdot mol^{-1}$.

### Heat Capacity and Entropy

The heat capacity is assumed to be constant at 7.25 cal $K^{-1}$ g-atom$^{-1}$ as suggested by Kubaschewski and Evans.[2] The entropy, $S°(298.15\ K) = 42.8\ cal\ K^{-1}\cdot mol^{-1}$ is calculated by a 2nd law analysis of the vapor pressure equation given by Cady and Hargreaves[1] for the system $WOF_4(l) \rightarrow WOF_4(g)$.

### Fusion Data

Refer to the crystal table for details.

### Vaporization Data

$T_{vap}$ is calculated as the temperature at which the fugacity is one atmosphere for the process $WOF_4(l) \rightarrow WOF_4(g)$ The difference between the enthalpies of formation for the liquid and gas at $T_{vap}$ is $\Delta_{vap}H°$.

Ruff *et al.*[3] reported the boiling point of $WOF_4(l)$ as 459 K. Cady and Hargreaves[1] calculated the boiling point as 459 K, and the enthalpy eat of vaporization as 14.23 kcal·mol$^{-1}$ from the vapor pressure equation for the liquid. This 2nd law value of $\Delta_{vap}H°$, when corrected for $\Delta C_p°$ of vaporization, is in good agreement with the value adopted in the tabulation.

### References

[1] G. H. Cady and G B. Hargreaves, J. Chem. Soc. (London) **1961**, 1563.
[2] O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, (1958).
[3] O. Ruff, F. Eisner, and W. Zeller, Z. Anorg. Chem. 52, 256 (1907).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log K$_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 182.004 | 178.915 | 178.915 | 0. | −1405.255 | −1297.355 | 227.291 |
| 300 | 182.004 | 180.041 | 178.918 | 0.337 | −1405.106 | −1296.686 | 225 773 |
| 379.000 | 182.004 | 222.585 | 183 759 | 14.715 | --- CRYSTAL <--> LIQUID --- | | |
| 400 | 182.004 | 232.400 | 186.057 | 18.537 | −1397.294 | −1261.736 | 164 766 |
| 500 | 182.004 | 273.013 | 199.538 | 36.738 | −1389.868 | −1228.713 | 128.363 |
| 600 | 182.004 | 306.196 | 214.633 | 54.938 | −1382.752 | −1197.155 | 104.222 |
| 700 | 182.004 | 334.252 | 229.769 | 73.138 | −1375.883 | −1166.768 | 87.065 |
| 800 | 182.004 | 358.555 | 244.382 | 91.339 | −1369.215 | −1137.351 | 74.261 |
| 900 | 182.004 | 379.992 | 258.282 | 109.539 | −1362.715 | −1108.760 | 64.351 |
| 1000 | 182.004 | 399.168 | 271.429 | 127.740 | −1356.359 | −1080.885 | 56.460 |

PREVIOUS: March 1967 CURRENT: December 1971

## Tungsten Fluoride Oxide ($WF_4O$) CRYSTAL-LIQUID

0 to 379 K crystal
above 379 K liquid

Refer to the individual tables for details.

## $M_r = 275.843012$ Tungsten Fluoride Oxide ($WF_4O$) $F_4O_1W_1(cr,l)$

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 133.578 | 175 728 | 175.728 | 0. | −1406.908 | −1298.058 | 227.414 |
| 300 | 133.888 | 176.555 | 175.731 | 0.247 | −1406.848 | −1297.383 | 225.894 |
| 379.000 | 147 109 | 209.337 | 179.398 | 11.347 | CRYSTAL <−−> LIQUID | | |
| 379.000 | 182.004 | 222.585 | 179.398 | 16.368 | TRANSITION | | |
| 400 | 182.004 | 232 400 | 181.926 | 20.190 | −1397.294 | −1261.736 | 164.766 |
| 500 | 182.004 | 273.013 | 196.233 | 38.390 | −1389.868 | −1228 713 | 128.363 |
| 600 | 182.004 | 306.196 | 211.879 | 56.590 | −1382.752 | −1197.155 | 104.222 |
| 700 | 182.004 | 334.252 | 227.408 | 74.791 | −1375.883 | −1166.768 | 87.065 |
| 800 | 182.004 | 358.555 | 242.316 | 92.991 | −1369.215 | −1137.351 | 74.261 |
| 900 | 182 004 | 379.992 | 256.446 | 111.192 | −1362.715 | −1108.760 | 64.351 |
| 1000 | 182.004 | 399.168 | 269.776 | 129.392 | −1356.359 | −1080.885 | 56.460 |

PREVIOUS: CURRENT· December 1971

$\Delta_f H°(0\ K) = -1328.914 \pm 62.8\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = [335.705 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -1336.621 \pm 62.8\ kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ | $\nu$, cm-1 |
|---|---|---|
| 1055 (1) | 620 (1) | 700 (2) |
| [300](1) | [300](1) | 560 (2) |
| 735 (1) | [200](1) | [150](2) |

Ground State Quantum Weight: [1] $\sigma$ = [4]
Point Group. [$C_{4v}$]
Bond Distances: W–O = [1.64]Å; W–F = [1.82] Å
Bond Angles: O–W–F = [90]°; F–W–F = [90]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.1909 \times 10^{-113}]\ g^3 \cdot cm^6$

## Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(WOF_4, g, 298.15\ K) = -319.46\ kcal \cdot mol^{-1}$, is calculated from the enthalpy of reaction data of Zmbov *et al.*[1] This data came from a mass spectrometric study of the equilibrium in the reaction:

$$2\ TaF_5(g) + WO_3(cr) = 2\ TaOF_3(g) + WOF_4(g).$$

## Heat Capacity and Entropy

The infrared spectra of $WOF_4$ and $MoOF_4$ in the vapor state are very similar[2, 3, 4] and have been interpreted on the basis of a monomeric unit with $C_{4v}$ symmetry[5] by comparison with the spectrum of $XeOF_4$.[6] Thus, as with $XeOF_4$ and $MoOF_4$, gaseous $WOF_4$ is assumed to be $C_{4v}$ symmetry with a square–pyamidal structure.

Blanchard[5] and Reynes[10] reported the following vibrational assignments and frequencies, the Q frequency being adopted in this tabulation:

$$\nu_1 = 1064(R),\ 1055(Q),\ 1047(P);\quad \nu_7 = 705(R),\ 700(Q),\ 690(P);\quad \nu_3 = 745(R),\ 735(Q),\ 720(P);\quad \nu_8 = 560\ cm^{-1}$$

Similar frequencies, as well as additional frequencies, have been reported by Ward and Stafford,[4] Edwards *et al.*,[3] and Edwards and Jones.[2] The remaining frequencies and assignments are estimated with regard to the preceding references, the data for $X_3OF_4$,[6] and results for $MoOF_4$.[7] There exists some controversy as the crystallographic structure of $WOF_4$. Beattie *et al.*[8] suggest fluorine–bridged tetramers as in $MoOF_4$[9] rather than an oxygen–bridged structure as suggested by Edwards and Jones.[2] This leads to significantly different bond lengths for W–F and W–O. Due to the similarities in the melt, solid, and vapor phase infrared spectra of $MoOF_4$ and $WOF_4$, one would suspect similar structures.[4] 8 The assumption is made that the structures are similar and thus the bond lengths are taken to be the same as those of $MoOF_4$. Further support for the bond length assumption is the similarity of bond lengths in $MoO_3$ and $WO_3$ and in $MoF_6$ and $WF_6$.[7]

## References

[1] K. F. Zmbov, O. M. Uy, and J. L. Margrave, J. Phys. Chem. **73**, 3008 (1969).
[2] A. J. Edwards and G. R. Jones, J. Chem. Soc. (London) **A1968**, 2074 (1968).
[3] A. J. Edwards, G. R. Jones, and B. R. Stevenson, Chem. Comm. 462 (1967).
[4] B. G. Ward and F. E. Stafford, J. Inorg. Chem. **7**, 2569 (1968).
[5] S. Blanchard, Commissariat a l'Energie Atomique Rep. CEA–R 3194 (1967); CA 67 48663d.
[6] G. M. Begun, W. A. Fletcher, and D. F. Smith, J. Chem. Phys. **42**, 2236 (1965).
[7] JANAF Thermochemical Tables. $MoOF_4(g)$, 6–30–70, $MoO_3(g)$, 6–30–68; $WO_3(g)$, 9–30–66; $MoF_6(g)$, 6–30–70; $WF_6(g)$, 3–31–67.
[8] I. R. Beattie, R. M. S. Livingston, D. J Reynolds, and G. A. Ozin, J. Chem. Soc. (London) **A1970**, 1210 (1970).
[9] A. J. Edwards and B. R. Stevenson, J. Chem. Soc. (London) **A1968**, 2503 (1968).
[10] J. Reynes, Commissariat a l'Energie Atomique, Bibliographic CEA–BIB–143 (1969).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
|---|---|---|---|---|---|---|---|
|  | J·K⁻¹mol⁻¹ |  |  | kJ·mol⁻¹ |  |  |  |
| 0 | 0. | 0. | INFINITE | −19.257 | −1328.914 | −1328 914 | INFINITE |
| 100 | 53.821 | 255.014 | 407.184 | −15.217 | −1332.792 | −1314.592 | 686.673 |
| 200 | 77.962 | 300.014 | 342.945 | −8.586 | −1335 482 | −1295.221 | 338.277 |
| 250 | 87.938 | 318.515 | 336.240 | −4.431 | −1336.218 | −1285.063 | 268.499 |
| 298.15 | 95.853 | 334.705 | 334.705 | 0. | −1336.621 | −1275.170 | 223.404 |
| 300 | 96.125 | 335.298 | 334.706 | 0.178 | −1336.631 | −1274.788 | 221.960 |
| 350 | 102.646 | 350.626 | 335.902 | 5.153 | −1336.795 | −1264.465 | 188.711 |
| 400 | 107.789 | 364.681 | 338.633 | 10.419 | −1336.777 | −1254.132 | 163.773 |
| 450 | 111.850 | 377.621 | 342.256 | 15.914 | −1336.627 | −1243.809 | 144.378 |
| 500 | 115.076 | 389.579 | 346.398 | 21.590 | −1336.381 | −1233.508 | 128.864 |
| 600 | 119.756 | 411 003 | 355.423 | 33.348 | −1335.707 | −1212.994 | 105 601 |
| 700 | 122.882 | 429.714 | 364.728 | 45 490 | −1334.897 | −1192.605 | 88.993 |
| 800 | 125.049 | 446.272 | 373.906 | 57.893 | −1334.026 | −1172.336 | 76.546 |
| 900 | 126.604 | 461.096 | 382.785 | 70 480 | −1333.140 | −1152.178 | 66.871 |
| 1000 | 127.753 | 474.497 | 391.297 | 83.200 | −1332.264 | −1132.119 | 59.136 |
| 1100 | 128.624 | 486.716 | 399.424 | 96.021 | −1331.416 | −1112.145 | 52.811 |
| 1200 | 129.299 | 497.938 | 407.172 | 108.919 | −1330.609 | −1092.247 | 47.544 |
| 1300 | 129.831 | 508.309 | 414.558 | 121.876 | −1329.852 | −1072.415 | 43.090 |
| 1400 | 130.258 | 517.947 | 421.603 | 134.882 | −1329.151 | −1052.639 | 39.274 |
| 1500 | 130.606 | 526.946 | 428.329 | 147.925 | −1328.511 | −1032.911 | 35.969 |
| 1600 | 130.892 | 535.385 | 434 759 | 161.001 | −1327 937 | −1013.223 | 33 078 |
| 1700 | 131.131 | 543.327 | 440.914 | 174 102 | −1327.429 | −993.569 | 30.529 |
| 1800 | 131.333 | 550.828 | 446.814 | 187.226 | −1326 988 | −973 944 | 28.263 |
| 1900 | 131.504 | 557.934 | 452.477 | 200.368 | −1326.611 | −954.341 | 26.237 |
| 2000 | 131.650 | 564.683 | 457.920 | 213.526 | −1326.298 | −934 756 | 24.413 |
| 2100 | 131.777 | 571.109 | 463.158 | 226.697 | −1326.043 | −915.186 | 22.764 |
| 2200 | 131 887 | 577.242 | 468.206 | 239.880 | −1325.842 | −895.626 | 21.265 |
| 2300 | 131 983 | 583.107 | 473.075 | 253.074 | −1325 689 | −876.074 | 19.896 |
| 2400 | 132.067 | 588.726 | 477 777 | 266.277 | −1325.578 | −856.528 | 18 642 |
| 2500 | 132 142 | 594 119 | 482.324 | 279 487 | −1325.502 | −836.986 | 17 488 |
| 2600 | 132.209 | 599.303 | 486.724 | 292 705 | −1325 453 | −817 446 | 16 423 |
| 2700 | 132.268 | 604.293 | 490.986 | 305.929 | −1325.450 | −797 908 | 15 436 |
| 2800 | 132.321 | 609.105 | 495.120 | 319 158 | −1325.523 | −778.368 | 14.521 |
| 2900 | 132.369 | 613.749 | 499.131 | 332.393 | −1325.705 | −758.824 | 13.668 |
| 3000 | 132.412 | 618.237 | 503.026 | 345.632 | −1326.018 | −739.272 | 12.872 |
| 3100 | 132.451 | 622.579 | 506.813 | 358.875 | −1326.502 | −719.706 | 12.127 |
| 3200 | 132.486 | 626.785 | 510.497 | 372.122 | −1327 184 | −700.122 | 11 428 |
| 3300 | 132.519 | 630.863 | 514.083 | 385.372 | −1328 087 | −680.513 | 10 772 |
| 3400 | 132.548 | 634 819 | 517.576 | 398.625 | −1329.241 | −660 872 | 10 153 |
| 3500 | 132.575 | 638.662 | 520.981 | 411 882 | −1330.711 | −641 194 | 9.569 |
| 3600 | 132.600 | 642.397 | 524.302 | 425.140 | −1332.590 | −621.468 | 9.017 |
| 3700 | 132.623 | 646.030 | 527.543 | 438.401 | −1369.743 | −601.492 | 8.492 |
| 3800 | 132.644 | 649.567 | 530.708 | 451.665 | −1369.152 | −580.737 | 7.983 |
| 3900 | 132.663 | 653 013 | 533.800 | 464.930 | −1368 497 | −559.997 | 7.500 |
| 4000 | 132.681 | 656.372 | 536.823 | 478.197 | −1367 778 | −539.275 | 7.042 |
| 4100 | 132.698 | 659.648 | 539.779 | 491.466 | −1366.997 | −518.572 | 6 607 |
| 4200 | 132.714 | 662.846 | 542.671 | 504 737 | −1366.152 | −497.889 | 6.192 |
| 4300 | 132.728 | 665.969 | 545.502 | 518.009 | −1365.246 | −477.227 | 5 797 |
| 4400 | 132.742 | 669.021 | 548.275 | 531.283 | −1364.280 | −456.586 | 5.420 |
| 4500 | 132.754 | 672.004 | 550.991 | 544.558 | −1363.253 | −435.968 | 5.061 |
| 4600 | 132.766 | 674 922 | 553.654 | 557 834 | −1362.169 | −415.374 | 4.717 |
| 4700 | 132.777 | 677.777 | 556.265 | 571.111 | −1361.028 | −394.804 | 4.388 |
| 4800 | 132.788 | 680.573 | 558.825 | 584.389 | −1359.832 | −374.258 | 4.073 |
| 4900 | 132.798 | 683.311 | 561.338 | 597.668 | −1358.582 | −353.738 | 3 771 |
| 5000 | 132.807 | 685.994 | 563.804 | 610.949 | −1357.281 | −333.244 | 3.481 |
| 5100 | 132.815 | 688 624 | 566.226 | 624.230 | −1355 930 | −312.777 | 3.203 |
| 5200 | 132.824 | 691.203 | 568.605 | 637.512 | −1354.531 | −292.336 | 2.937 |
| 5300 | 132.831 | 693.733 | 570.942 | 650.794 | −1353.086 | −271.923 | 2.680 |
| 5400 | 132.839 | 696.216 | 573.239 | 664.078 | −1351.597 | −251.538 | 2.433 |
| 5500 | 132.846 | 698.654 | 575 497 | 677.362 | −1350.065 | −231.181 | 2.196 |
| 5600 | 132.852 | 701.048 | 577.718 | 690.647 | −1348 493 | −210.851 | 1.967 |
| 5700 | 132.858 | 703.399 | 579.902 | 703.932 | −1346.883 | −190.551 | 1.746 |
| 5800 | 132.864 | 705.710 | 582.051 | 717.219 | −1345.236 | −170.278 | 1.534 |
| 5900 | 132.870 | 707.981 | 584.167 | 730.505 | −1343.554 | −150.035 | 1.328 |
| 6000 | 132.875 | 710.214 | 586.249 | 743.793 | −1341.841 | −129.820 | 1.130 |

PREVIOUS· December 1971 (1 atm) CURRENT· December 1971 (1 bar)

## Lead Fluoride ($PbF_4$) IDEAL GAS $M_r$ = 283.193612 Lead Fluoride ($PbF_4$) $F_4Pb_1(g)$

$S°(298.15 K) = [333.602 \pm 12 6] J K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0 K) = -1128 678 \pm 20 9 kJ \cdot mol^{-1}$
$\Delta_f H°(298.15 K) = -1133 446 \pm 20.9 kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, $cm^{-1}$ |
|---|
| [564](1) |
| [158](2) |
| [570](3) |
| [180](3) |

Ground State Quantum Weight: [1] $\sigma$ = [12]
Point Group: [$T_d$]
Bond Distance. Pb–F = [2.08] Å
Bond Angle: F–Pb–F = [109° 28']
Product of the Moments of Inertia. $I_A I_B I_C = [4 821770 \times 10^{-113}] g^3 \cdot cm^6$

### Enthalpy of Formation

A 3rd law analysis of the partial pressure data at 988 K reported by Zmbov *et al.*[1] for the equilibrium 2 $PbF_2(g) = PbF_4(g) + Pb(g)$ gives $\Delta_r H°(298 15 K) = -16.15 kcal \cdot mol^{-1}$. There are inconsistencies in the published results but the partial pressure data are correctly given.[2] The 2nd law enthalpy of reaction derived by Zmbov *et al.*[1] from a graphical plot of six ion current quotient values vs reciprocal temperature (approximately 1020 to 1110 K), when corrected to 298.15 K, is in agreement with the 3rd law value of $-16.15 kcal \cdot mol^{-1}$. Combining this enthalpy of reaction with $\Delta_f H°(PbF_2, g, 298.15 K) = -104.0 \pm 1 kcal \cdot mol^{-1}$ [3] and $\Delta_f H°(Pb, g, 298.15 K) = 46.75 \pm 0.13 kcal \cdot mol^{-1}$ [3] gives the adopted $\Delta_f H°(PbF_4, g, 298.15 K) = -270.9 \pm 5 kcal \cdot mol^{-1}$ The adopted enthalpy of formation leads to a dissociation energy $\Delta_a H° = 16.96$ eV for the process $PbF_4(g) = Pb(g) + 4 F(g)$. This is consistent with $\Delta_a H° = 8 10$ eV for $PbF_2(g)$[3] and $D_0^\circ = 3.64$ eV for PbF(g).[3]

### Heat Capacity and Entropy

The molecular constants and vibrational frequencies are those calculated by Aleksandrovskaya *et al* [4] Later works[5 6 7] mistakenly cite this work as observed data. A band at 663 $cm^{-1}$ was recently observed in an infrared study by Hauge *et al.*[8] and was assigned to matrix isolated $PbF_4$. Calculation with infrared active $\nu_3 = 663 cm^{-1}$ decreases $S°(298 15 K)$ by 0.45 cal $K^{-1} mol^{-1}$. Only the calculated frequencies are used for the present table pending more complete observation.

### References

[1] K. Zmbov, J. W Hastie, and J. L. Margrave, Trans. Faraday Soc 64, 861 (1968).
[2] J. W. Hastie, U. S. Nat. Bur. Stand., personal communication, (December 26, 1973).
[3] JANAF Thermochemical Tables: Pb(g), 3–31–62; $PbF_2(g)$, 12–31–73; PbF(g), 12–31–73; F(g), 9–30–65.
[4] A. M. Aleksandrovskaya, I. V. Rigina, and I. N. Godnev, Optics and Spectrosc. 7, 495 (1959).
[5] G. Nagarajan, Bull Soc. Chim Belges 71, 119 (1962).
[6] M. Radhakrishnan, Indian J. Pure Appl. Phys. 1, 402 (1963).
[7] S. P. Singh, Labdev, Part A 7, 185 (1969).
[8] R. H. Hauge, J. W. Hastie, and J. L. Margrave, J. Mol. Spectrosc 45, 420 (1973).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0 | 0. | INFINITE | −19.761 | −1128.678 | −1128.678 | INFINITE |
| 100 | 59.551 | 251.440 | 406.137 | −15.470 | −1131 968 | −1119.354 | 584 691 |
| 200 | 79.572 | 299.488 | 341.603 | −8.423 | −1133.303 | −1106.086 | 288.880 |
| 250 | 86.207 | 317.993 | 335.075 | −4.270 | −1133.461 | −1099.258 | 229.677 |
| 298.15 | 90.935 | 333.602 | 333.602 | 0. | −1133.446 | −1092.670 | 191 431 |
| 300 | 91.090 | 334 165 | 333 604 | 0.168 | −1133.443 | −1092 417 | 190.207 |
| 350 | 94.654 | 348.489 | 334.727 | 4.817 | −1133.326 | −1085.588 | 162.015 |
| 400 | 97.277 | 361.308 | 337.263 | 9.618 | −1133.160 | −1078 779 | 140.874 |
| 450 | 99.239 | 372.884 | 340.588 | 14.533 | −1132.976 | −1071 992 | 124.434 |
| 500 | 100.733 | 383.421 | 344.352 | 19.534 | −1132.789 | −1065.226 | 111.283 |
| 600 | 102 801 | 401.984 | 352.453 | 29 719 | −1132.441 | −1051 747 | 91.563 |
| 700 | 104 120 | 417.937 | 360.695 | 40.070 | −1137 015 | −1037.524 | 77.421 |
| 800 | 105 007 | 431.902 | 368.741 | 50.529 | −1136 792 | −1023.326 | 66.816 |
| 900 | 105.630 | 444.308 | 376.461 | 61.063 | −1136.552 | −1009.157 | 58.570 |
| 1000 | 106.083 | 455.462 | 383.813 | 71.649 | −1136.300 | −995 015 | 51.974 |
| 1100 | 106.422 | 465.590 | 390.794 | 82.275 | −1136.038 | −980.900 | 46.579 |
| 1200 | 106.683 | 474.861 | 397.419 | 92.931 | −1135.768 | −966.808 | 42.084 |
| 1300 | 106.887 | 483.409 | 403.709 | 103.610 | −1135.498 | −952.739 | 38.282 |
| 1400 | 107.050 | 491.336 | 409.688 | 114.307 | −1135.245 | −938.690 | 35.023 |
| 1500 | 107 182 | 498.727 | 415.381 | 125.019 | −1135.019 | −924.659 | 32.199 |
| 1600 | 107.290 | 505.648 | 420.808 | 135.743 | −1134.825 | −910.641 | 29 729 |
| 1700 | 107.380 | 512.155 | 425.992 | 146.476 | −1134.668 | −896.634 | 27.550 |
| 1800 | 107.456 | 518.295 | 430.951 | 157.218 | −1134.547 | −882.636 | 25 613 |
| 1900 | 107.520 | 524.106 | 435.702 | 167.967 | −1134.462 | −868 644 | 23.881 |
| 2000 | 107.575 | 529.623 | 440.262 | 178.722 | −1134.409 | −854.655 | 22.321 |
| 2100 | 107.622 | 534 872 | 444.643 | 189.482 | −1311.605 | −833.553 | 20 733 |
| 2200 | 107 663 | 539.880 | 448.859 | 200.246 | −1311.212 | −810.798 | 19 251 |
| 2300 | 107.699 | 544.667 | 452.921 | 211.014 | −1310.902 | −788.059 | 17.897 |
| 2400 | 107 731 | 549.251 | 456.840 | 221.786 | −1310.669 | −765.332 | 16 657 |
| 2500 | 107.758 | 553.649 | 460.625 | 232.560 | −1310.506 | −742 613 | 15.516 |
| 2600 | 107 783 | 557.876 | 464.285 | 243.338 | −1310.407 | −719.899 | 14.463 |
| 2700 | 107.805 | 561.944 | 467 827 | 254 117 | −1310.362 | −697 189 | 13 488 |
| 2800 | 107.825 | 565.865 | 471.259 | 264.898 | −1310.362 | −674.479 | 12.583 |
| 2900 | 107.843 | 569.649 | 474.587 | 275 682 | −1310.396 | −651 768 | 11.740 |
| 3000 | 107.859 | 573.306 | 477.817 | 286.467 | −1310.454 | −629 056 | 10.953 |
| 3100 | 107.873 | 576.843 | 480.954 | 297.254 | −1310.525 | −606.342 | 10.217 |
| 3200 | 107.886 | 580.268 | 484.005 | 308.042 | −1310.601 | −583 625 | 9.527 |
| 3300 | 107.898 | 583.588 | 486.972 | 318.831 | −1310.669 | −560 906 | 8.878 |
| 3400 | 107 909 | 586.809 | 489.862 | 329.621 | −1310.721 | −538.185 | 8.268 |
| 3500 | 107.919 | 589.937 | 492.676 | 340.413 | −1310 749 | −515 463 | 7.693 |
| 3600 | 107.928 | 592.977 | 495.420 | 351.205 | −1310 743 | −492.740 | 7.149 |
| 3700 | 107.937 | 595.935 | 498.097 | 361.998 | −1310 697 | −470 018 | 6.635 |
| 3800 | 107.945 | 598.813 | 500.710 | 372.792 | −1310.604 | −447.299 | 6.149 |
| 3900 | 107.952 | 601.617 | 503.262 | 383.587 | −1310 458 | −424.581 | 5.687 |
| 4000 | 107 958 | 604.350 | 505.755 | 394.383 | −1310.253 | −401.869 | 5.248 |
| 4100 | 107.965 | 607.016 | 508.192 | 405.179 | −1309.986 | −379 163 | 4.831 |
| 4200 | 107.970 | 609.618 | 510.576 | 415 976 | −1309.652 | −356.463 | 4.433 |
| 4300 | 107.976 | 612.159 | 512.909 | 426.773 | −1309.249 | −333 774 | 4.055 |
| 4400 | 107.981 | 614.641 | 515.193 | 437.571 | −1308 774 | −311 093 | 3.693 |
| 4500 | 107.985 | 617.068 | 517.430 | 448.369 | −1308.226 | −288 424 | 3.348 |
| 4600 | 107.990 | 619.441 | 519.622 | 459.168 | −1307.603 | −265.769 | 3.018 |
| 4700 | 107.994 | 621.764 | 521.771 | 469.967 | −1306.905 | −243 128 | 2.702 |
| 4800 | 107.998 | 624.037 | 523.878 | 480.767 | −1306.131 | −220.502 | 2.400 |
| 4900 | 108 001 | 626.264 | 525.945 | 491.567 | −1305.281 | −197.894 | 2.110 |
| 5000 | 108.005 | 628.446 | 527.973 | 502.367 | −1304.357 | −175.303 | 1.831 |
| 5100 | 108.008 | 630.585 | 529.964 | 513 167 | −1303.357 | −152.732 | 1.564 |
| 5200 | 108.011 | 632.682 | 531.919 | 523 968 | −1302.285 | −130 181 | 1.308 |
| 5300 | 108.014 | 634.740 | 533.840 | 534.770 | −1301.141 | −107.651 | 1.061 |
| 5400 | 108.017 | 636.759 | 535.727 | 545.571 | −1299.926 | −85 144 | 0.824 |
| 5500 | 108.019 | 638 741 | 537.582 | 556.373 | −1298.642 | −62.660 | 0.595 |
| 5600 | 108.022 | 640.687 | 539.406 | 567.175 | −1297.291 | −40 199 | 0.375 |
| 5700 | 108.024 | 642.599 | 541.200 | 577.977 | −1295.875 | −17.764 | 0.163 |
| 5800 | 108 026 | 644.478 | 542.964 | 588 780 | −1294.397 | 4.646 | −0.042 |
| 5900 | 108.028 | 646.325 | 544.700 | 599.582 | −1292.856 | 27.031 | −0.239 |
| 6000 | 108.030 | 648.140 | 546.409 | 610.385 | −1291.258 | 49.387 | −0 430 |

PREVIOUS December 1973 (1 atm) CURRENT December 1973 (1 bar)

$S°(298.15\ K) = 299.644 \pm 0.4\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -756.882 \pm 20.9\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -763.162 \pm 20.9\ kJ{\cdot}mol^{-1}$

| Vibrational Frequencies and Degeneracies | | |
|---|---|---|
| $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ |
| 891.5(1) | 228.0(1) | 532.5(1) |
| 558.4(1) | 475.0(1) | 867.0(1) |
| 353.0(1) | 728.0(1) | 233.0(1) |

Ground State Quantum Weight: 1; Point Group: $C_{2v}$ $\sigma = 2$
Bond Distances: S–F* = 1.545 ± 0.003 S–F** = 1.646 ± 0.003 Å
Bond Angles: F*–S–F* = 101.55 ± 0.5°; F*–S–F** = 87.81 ± 0.5°
F**–S–F** = 173.07 ± 0.5° (*–equatorial **–axial)
Product of Moments of Inertia: $I_AI_BI_C = 6.723859 \times 10^{-114}\ g^3{\cdot}cm^6$

## Enthalpy of Formation

Data on $\Delta_fH°$ published prior to 1970 have been reviewed by O'Hare *et al.*[1] We reanalyze this earlier work together with more recent studies. Unless otherwise indicated, all auxiliary data are taken from JANAF tables.[2] We also include, for those reactions involving the formation of HF, $\Delta_fH°$ values which have been derived in previous analyses.[11, 12, 13]

| Source | Method | Reaction | $\Delta_rH°(T/K)$ kcal·mol$^{-1}$ | $\Delta_fH°(SF_4, g, 298.15\ K)$, From (Ref.) | kcal·mol$^{-1}$ This Work |
|---|---|---|---|---|---|
| 3 | Calorimetric | $SF_4(g) + 2\ H_2(g) = 4\ HF(l) + S(cr)$ | 104.8(298)[b] ± 4.0 | 185.2[11, 12]<br>188.5[13] | 184.7[a]<br>± 6.0 |
| 4 | Calorimetric | $SF_4(g) + 3\ H_2O(l) = 4\ HF(aq) + H_2SO_3(aq)$ | [c] | 179.0[11] | 180.8 |
| 5-8 | Appearance Potentials[d] | $SF_6(g) = SF_4(g) + 2\ F(g)$ | 145.0 ± 4.6(0) | 181.6 ± 5.0 | |
| 8 | Appearance Potentials[e] | $NSF_3(g) + F(g) = SF_4(g) + N(g)$ | 17.5(0) | 161.8 | |
| 9 | Appearance Potentials[f] | $SF_6(g) = SF_4(g) + 2\ F(g)$ | 116.2(0) | 210.4 | |

[a] Auxiliary $\Delta_fH°(298.15\ K)$ data in kcal·mol$^{-1}$· $NSF_3(g)$, −85.2 ± 0.5;[1] HF(l), −72.37.[2, 10]
[b] Results reduced with HF PVT and calorimetric data from.[10]
[c] Hydrolysis data unavailable; $\Delta_rH°$ value from[11] adjusted for changes in $\Delta_fH°$ of HF(aq).
[d] Ion Processes: $SF_6(g) + e^- = SF_4^+(g) + 2\ F(g) + 2\ e^-$ $SF_4(g) + e^- = SF_4^+(g) + 2\ e^-$
[e] Ion Processes: $SF_4(g) + e^- = SF_3^+(g) + F(g) + 2\ e^-$ $NSF_3(g) + e^- = SF_3^+(g) + N(g) + 2\ e^-$
[f] Ion Processes: $SF_5(g) + e^- = SF_4(g) + F\ (g)$ $SF_5(g) + e^- = SF_5\ (g)$ $SF_6(g) + e^- = SF_5\ (g) + F(g)$

All of these studies are relatively imprecise, suggesting the need for an unequivocal redetermination of $\Delta_fH°$. Both calorimetric results[3, 4] are based on measurements made with impure samples (−98% $SF_4$) and suffer from the additional uncertainties introduced by the formation of HF. The ionization processes involve unknown kinetic and excitation energies, as evidenced by the widely scattered results. The first three $\Delta_fH°$ values listed above are reasonably consistent; thus, we are led to adopt their mean value of $\Delta_fH°(SF_4, g, 298.15\ K) = -182.4$ kcal·mol$^{-1}$. The estimated uncertainty is ± 5.0 kcal·mol$^{-1}$. Our $\Delta_fH°$ value corresponds to a enthalpy of atomization and average bond dissociation energy of 320.1 and 80.0 kcal·mol$^{-1}$, respectively.

## Heat Capacity and Entropy

Detailed structural data determined by electron diffraction[14] and microwave spectroscopy[15] show good agreement. We arbitrarily adopt the microwave data which indicate a trigonal bipyramid structure with two inequivalent sets of fluorine atoms. The inequivalence of the fluorines is also supported by nuclear resonance[16, 17] and x-ray photoelectron spectroscopic[18, 19] studies. The principal moments of inertia are: $I_A = 12.5525 \times 10^{-39}$, $I_B = 20.5464 \times 10^{-39}$ and $I_C = 26.0707 \times 10^{-39}\ g{\cdot}cm^2$.

Various spectroscopic methods have been used to study the vibrational spectrum of $SF_4$. These studies include crystal,[20] liquid[21] and gas[22] phase Raman and gas[21-23] phase and argon matrix isolation[24] infrared spectra. The measured frequencies show good agreement but various interpretations of the observed spectra have been presented. We choose to adopt the results of the latest interpretation by Levin.[20] It should be noted that the vibrational assignments are immaterial for the purpose of evaluating the thermal functions since none of the fundamentals are degenerate. MO calculations[25] predict a singlet ground state with no excited states lying at energies which would be significant in the statistical calculations.

Our thermal functions essentially extend and update those reported by O'Hare[11] but are in disagreement with other literature data.[26, 27] The functions reported by Radhakrishnan[26] are based on an incorrect structure and older vibrational frequencies.[21] The set of frequencies used by Wilkins[27] are very similar to ours but his moments of inertia appear unrealistic. We conclude that his thermal functions[27] are erroneous.

## References

[1] P. A. O'Hare, W. N. Hubbard, O. Glemser, and J. Wegener, J. Chem. Thermodyn. 2, 71 (1970).
[2] JANAF Thermochemical Tables: HF(g), 12–31–68, F(g), 9–30–65; $SF_6$(g), 6–30–76; F (g), 12–31–71, N(g), 3–31–61.

Continued on page 1216

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −15.782 | −756.882 | −756.882 | INFINITE |
| 100 | 42.613 | 235.853 | 357.961 | −12.211 | −759.814 | −748.073 | 390.754 |
| 200 | 62.633 | 271.650 | 306.302 | −6.931 | −762.034 | −735.376 | 192.060 |
| 250 | 71.003 | 286.554 | 300.887 | −3.583 | −762.711 | −728.628 | 152.238 |
| 298.15 | 77.598 | 299.644 | 299.644 | 0. | −763.162 | −722.020 | 126.495 |
| 300 | 77.824 | 300.125 | 299.646 | 0.144 | −763.176 | −721.764 | 125.670 |
| 350 | 83.238 | 312.545 | 300.614 | 4.176 | −763.488 | −714.836 | 106.683 |
| 400 | 87.497 | 323.949 | 302.828 | 8.448 | −765.907 | −707.783 | 92.427 |
| 450 | 90.849 | 334.456 | 305.766 | 12.910 | −766.704 | −700.478 | 81.309 |
| 500 | 93.504 | 344.171 | 309.127 | 17.522 | −767.493 | −693.074 | 72.405 |
| 600 | 97.341 | 361.583 | 316.453 | 27.078 | −768.469 | −678.089 | 59.033 |
| 700 | 99.891 | 376.792 | 324.010 | 36.947 | −769.049 | −662.976 | 49.472 |
| 800 | 101.653 | 390.252 | 331.465 | 47.030 | −769.397 | −647.797 | 42.297 |
| 900 | 102.914 | 402.302 | 338.678 | 57.261 | −822.730 | −631.503 | 36.651 |
| 1000 | 103.844 | 413 196 | 345.594 | 67.602 | −821.626 | −610.315 | 31.880 |
| 1100 | 104.547 | 423.128 | 352.198 | 78.023 | −820.516 | −589.237 | 27.981 |
| 1200 | 105.091 | 432.249 | 358.494 | 88.506 | −819.412 | −568.260 | 24.736 |
| 1300 | 105.519 | 440.678 | 364.496 | 99.037 | −818.322 | −547.376 | 21.994 |
| 1400 | 105.863 | 448.511 | 370.220 | 109.607 | −817.251 | −526.574 | 19.647 |
| 1500 | 106.143 | 455.824 | 375.686 | 120.207 | −816.205 | −505.848 | 17.615 |
| 1600 | 106.373 | 462.682 | 380.911 | 130.834 | −815.184 | −485 191 | 15.840 |
| 1700 | 106.565 | 469.137 | 385.913 | 141.481 | −814.191 | −464.597 | 14.275 |
| 1800 | 106.726 | 475.233 | 390.708 | 152.146 | −813.222 | −444.060 | 12.886 |
| 1900 | 106.864 | 481.007 | 395.310 | 162.825 | −812.275 | −423.578 | 11.645 |
| 2000 | 106.981 | 486.491 | 399.733 | 173.518 | −811.347 | −403 144 | 10.529 |
| 2100 | 107.083 | 491.714 | 403.989 | 184.221 | −810.430 | −382.757 | 9.521 |
| 2200 | 107.171 | 496.697 | 408.091 | 194.934 | −809.519 | −362.412 | 8.605 |
| 2300 | 107.248 | 501.463 | 412.048 | 205.655 | −808.606 | −342.109 | 7.770 |
| 2400 | 107.316 | 506.029 | 415.869 | 216.383 | −807.685 | −321.847 | 7.005 |
| 2500 | 107.376 | 510.411 | 419.564 | 227.118 | −806.748 | −301.623 | 6.302 |
| 2600 | 107.429 | 514.623 | 423.139 | 237.858 | −805.788 | −281.437 | 5.654 |
| 2700 | 107.477 | 518.679 | 426.603 | 248.603 | −804.798 | −261.288 | 5.055 |
| 2800 | 107.519 | 522.588 | 429.962 | 259.353 | −803.771 | −241.177 | 4.499 |
| 2900 | 107.557 | 526.362 | 433.221 | 270.107 | −802.702 | −221.103 | 3.982 |
| 3000 | 107.592 | 530.009 | 436.387 | 280.865 | −801.586 | −201.067 | 3.501 |
| 3100 | 107.623 | 533.537 | 439.464 | 291.625 | −800.417 | −181.069 | 3.051 |
| 3200 | 107.652 | 536.954 | 442.458 | 302.389 | −799.193 | −161.109 | 2.630 |
| 3300 | 107.677 | 540.267 | 445.372 | 313.156 | −797.910 | −141.188 | 2.235 |
| 3400 | 107.701 | 543.482 | 448.210 | 323.925 | −796.566 | −121.308 | 1.864 |
| 3500 | 107.723 | 546.605 | 450.977 | 334.696 | −795.159 | −101.467 | 1.514 |
| 3600 | 107.743 | 549.640 | 453.676 | 345.469 | −793.687 | −81.668 | 1.185 |
| 3700 | 107 761 | 552.592 | 456.310 | 356.244 | −792.150 | −61.911 | 0.874 |
| 3800 | 107.778 | 555.466 | 458.881 | 367.021 | −790.547 | −42.196 | 0.580 |
| 3900 | 107.793 | 558.266 | 461.394 | 377.800 | −788.878 | −22.524 | 0.302 |
| 4000 | 107.808 | 560.995 | 463.850 | 388.580 | −787.144 | −2.896 | 0.038 |
| 4100 | 107.821 | 563.657 | 466.252 | 399.361 | −785.346 | 16.688 | −0.213 |
| 4200 | 107.834 | 566.256 | 468.602 | 410.144 | −783.484 | 36.228 | −0.451 |
| 4300 | 107.845 | 568.793 | 470.903 | 420.928 | −781.559 | 55.721 | −0.677 |
| 4400 | 107.856 | 571.273 | 473.156 | 431.713 | −779.573 | 75.170 | −0.892 |
| 4500 | 107.866 | 573.696 | 475.363 | 442.499 | −777.527 | 94.574 | −1.098 |
| 4600 | 107.876 | 576.067 | 477.527 | 453.286 | −775.423 | 113.930 | −1.294 |
| 4700 | 107.885 | 578.387 | 479.648 | 464.074 | −773.262 | 133.241 | −1.481 |
| 4800 | 107.893 | 580.659 | 481.729 | 474.863 | −771.046 | 152.505 | −1.660 |
| 4900 | 107.901 | 582.884 | 483.771 | 485.653 | −768.777 | 171.722 | −1.831 |
| 5000 | 107.908 | 585.064 | 485.775 | 496.443 | −766.457 | 190.893 | −1.994 |
| 5100 | 107.915 | 587.201 | 487.743 | 507.235 | −764.086 | 210.016 | −2.151 |
| 5200 | 107.922 | 589.296 | 489.676 | 518.026 | −761.668 | 229.093 | −2.301 |
| 5300 | 107.928 | 591.352 | 491.575 | 528.819 | −759.204 | 248.123 | −2.445 |
| 5400 | 107.934 | 593.369 | 493.441 | 539.612 | −756.695 | 267.105 | −2.584 |
| 5500 | 107.939 | 595.350 | 495.276 | 550.406 | −754.143 | 286.041 | −2.717 |
| 5600 | 107.945 | 597.295 | 497.081 | 561.200 | −751.549 | 304.930 | −2.844 |
| 5700 | 107.949 | 599.205 | 498.856 | 571.995 | −748.916 | 323.772 | −2.967 |
| 5800 | 107.954 | 601.083 | 500.602 | 582.790 | −746.245 | 342.568 | −3.085 |
| 5900 | 107.959 | 602 928 | 502.321 | 593.585 | −743.537 | 361.318 | −3.199 |
| 6000 | 107.963 | 604.743 | 504.013 | 604.382 | −740.794 | 380.021 | −3.308 |

PREVIOUS: June 1976 (1 atm) CURRENT June 1976 (1 bar)

## Sulfur Fluoride, Ion ($SF_4^+$) IDEAL GAS $M_r = 108.053063$ Sulfur Fluoride, Ion ($SF_4^+$) $F_4S_1^+(g)$

$S^\circ(298.15\ K) = [311.7 \pm 8]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H^\circ(0\ K) = 415.4 \pm 50\ kJ{\cdot}mol^{-1}$

$\Delta_f H^\circ(298.15\ K) = 416.0 \pm 50\ kJ{\cdot}mol^{-1}$

| Electronic Levels and Quantum Weights | |
|---|---|
| $\epsilon_i$, $cm^{-1}$ | $g_i$ |
| 0 | [2] |
| 26213 | [2] |

| Vibrational Frequencies and Degeneracies | | |
|---|---|---|
| $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ |
| [850](1) | [200](1) | [500](1) |
| [500](1) | [450](1) | [800](1) |
| [300](1) | [700](1) | [200](1) |

Point Group: $[C_{2v}]$ $\sigma = [2]$

Bond Distance: S–F* = [1.62] Å; S–F** = [1.73] Å

Bond Angles: F*–S–F* = [109]°; F*–S–F** = [88.3]°; F**–S–F** = [174]°

(* – equatorial ** – axial)

Product of Moments of Inertia: $I_A I_B I_C = [9.391199 \times 10^{-114}]\ g^3{\cdot}cm^6$

### Enthalpy of Formation

The electron–impact AP of $SF_4^*$ from $SF_4$ has been reported as 12.28 ± 0.03 eV,[1] 12.08 ± 0 1 eV,[2] and 12.1 ± 0.5 eV [2] Using the mean value (12.15 eV) of these three measured AP as $\Delta_r H^\circ(0\ K)$ for the direct ionization process $SF_4(g) + e^- \rightarrow SF_4^+ + 2\ e^-$, we obtain the adopted value $\Delta_f H^\circ(SF_4^+, g, 0\ K) = 99.3\ kcal{\cdot}mol^{-1}$, by combining $\Delta_r H^\circ(0\ K)$ with $\Delta_f H^\circ(SF_4, g, 0\ K) = -180.9 \pm 5\ 0\ kcal{\cdot}mol^{-1}$.[3] We estimate that the adiabatic AP (or IP) could be as much as 0.3 eV lower than the measured vertical values,[1,2] suggesting uncertainties in $\Delta_r H^\circ(0\ K)$ and $\Delta_f H^\circ(0\ K)$ of ±7.0 $kcal{\cdot}mol^{-1}$ and ±12.0 $kcal{\cdot}mol^{-1}$, respectively. Our predictions are based on the fact that photoelectron studies[4] on the species $ClF_3$ show that the first adiabatic ionization potential is 0.23 eV lower than the vertical value and 0.35 eV lower than the results obtained by the electron–impact method. The similarity in the structures of $SF_4$ and $ClF_3$ has been noted,[5] and we predict that the geometry changes produced by ionization should also be very similar for the two fluorides.

Additional information is available which tends to provide some support for our adopted value of $IP(SF_4) = 12.15 \pm 0.3$ eV. Fehsenfeld[6] has observed a charge–transfer reaction between $SF_4^+$ and NO which sets the lower limit of IP at 9 25 eV. Binding energies[7] for $SF_4$ and $SF_4^+$, computed by CNDO/2 calculations and rescaled according to energy partitioning concepts, have been combined to give IP values of 11.1 eV and 10.6 eV. Three independent measurements[2,8,9] of the fragment–ion AP for $SF_4^+$ from $SF_6$ are in agreement with the result AP = 18.61 eV. We combine this $AP(SF_4^+/SF_6)$ with our adopted IP value and obtain $\Delta_r H^\circ(0\ K) = 149.0\ kcal{\cdot}mol^{-1}$ for the process $SF_6(g) = SF_4(g) + 2F(g)$. This leads to a $\Delta_f H^\circ$ of $-176.2\ kcal{\cdot}mol^{-1}$ for $SF_4$ which compares favorably with JANAF data.[3]

$\Delta_f H^\circ$ is calculated to be 99.4 $kcal{\cdot}mol^{-1}$ at 298.15 K. Also, we find that the primary bond dissociation energy $D_0^\circ(SF_3^+-F)$ is 12.9 $kcal{\cdot}mol^{-1}$ which when compared with $D_0^\circ$ values[3] for $SF_4$ (80.0 $kcal{\cdot}mol^{-1}$) and $SF_4^-$ (46.6 $kcal{\cdot}mol^{-1}$) indicates that the trend is $D_0^\circ(SF_4) >> D_0^\circ(SF_4^-) >> D_0^\circ(SF_4^+)$. The observed instability of the radical cation towards dissociation to $SF_3^+$ and F is consistent with ion abundances[9,10] obtained for $SF_4^+$ and $SF_3^+$ in the mass spectra of $SF_5Cl$ and $SF_6$. Values of the ratio $I(SF_3^+)/I(SF_4^+)$ lie in the range 3.1–7.0. (See the $SF_3^+(g)$ table for a discussion on its stability.) The enthalpy of atomization and mean bond dissociation energy are 278.8 $kcal{\cdot}mol^{-1}$ and 69.7 $kcal{\cdot}mol^{-1}$, respectively.

### Heat Capacity and Entropy

Delwiche[8] has reported an ionization efficiency curve for $SF_4^+$ which was obtained from retarded potential difference (RPD) measurements on $SF_6$. This curve shows the existence of two excited states, lying 26213 $cm^{-1}$ and 45167 $cm^{-1}$ above the ground state. The level at 45167 $cm^{-1}$ is not included here since it has a negligible effect on the thermal functions. We assume that the one unpaired electron forms two doublet states which are non–degenerate.

The ESR spectrum[11] of $SF_4^+$, recorded during the radiolysis of $SF_6$ with 2.8 MeV electrons, suggests that the four fluorine nuclei are equivalent. However, the assignment of this spectrum to $SF_4^+$ has been questioned by Morton and Preston[12] who presented evidence which indicates that the radical responsible is more likely be be $SF_5$. Their re–assignment[12] is substantiated by the results of SCF MO calculations[13] on $SF_5$. By analogy with the isoelectronic radical $PF_4$,[14,15] we predict that the $SF_4^+$ structure is trigonal bipyramid with the unpaired electron occupying one of the equatorial positions. We use bond angles from $PF_4$[14] and assume that the loss of an electron from $SF_4$ increases both the equatorial and axial bond lengths by 5%. Our view that the bonding in $SF_4^+$ is weaker than that in $SF_4$ follows the predictions[14] made for $PF_4$ and is further confirmed by the fact that the mean bond dissociation energy in $SF_4$ (80 0 $kcal{\cdot}mol^{-1}$) is roughly 10 $kcal{\cdot}mol^{-1}$ greater than in $SF_4^+$ (69.7 $kcal{\cdot}mol^{-1}$). The individual moments of inertia are: $I_A = 14.2509 \times 10^{-39}$, $I_B = 22.1083 \times 10^{-39}$, and $I_C = 29.8073 \times 10^{-39}\ g{\cdot}cm^2$.

We estimate vibrational frequencies from those for $SF_4$[3] by considering the effect of the structural changes brought about by ionization. On going from $SF_4$ to $SF_4^+$, we expect a decrease in all frequencies to reflect the weaker bonding in the cation.

### References

[1] O. Glemser, A. Muller, D. Bohler, and B. Krebs, Z. anorg. allgem. Chem. 357, 184 (1968).
[2] D. L. Hildenbrand, J. Phys. Chem. 77, 897 (1973).

Continued from page 1216

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p^\circ$ = 0.1 MPa

| | $J{\cdot}K^{-1}mol^{-1}$ | | | $kJ{\cdot}mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −16.505 | 415.404 | | |
| 100 | 45.321 | 244.482 | 372.760 | −12.828 | | | |
| 200 | 65.909 | 282.444 | 318.604 | −7.232 | | | |
| 250 | 74.087 | 298.061 | 312.961 | −3.725 | | | |
| 298.15 | 80.395 | 311.671 | 311.671 | 0. | 416.044 | 447.346 | −78.373 |
| 300 | 80.609 | 312.169 | 311.672 | 0.149 | 416.074 | 447.540 | −77.924 |
| 350 | 85.696 | 324.993 | 312.674 | 4.312 | 416.932 | 452.718 | −67.564 |
| 400 | 89.643 | 336.705 | 314.956 | 8.700 | 415.668 | 457.854 | −59.790 |
| 450 | 92.718 | 347.449 | 317.978 | 13.262 | 416.010 | 463.099 | −53.755 |
| 500 | 95.133 | 357.347 | 321.427 | 17.960 | 416.348 | 468.315 | −48.925 |
| 600 | 98.591 | 375.021 | 328.922 | 27.659 | 417.593 | 478.601 | −41.666 |
| 700 | 100.869 | 390.401 | 336.630 | 37.640 | 419.202 | 488.645 | −36.463 |
| 800 | 102.435 | 403.979 | 344.217 | 47.809 | 421.021 | 498.443 | −32.545 |
| 900 | 103.550 | 416.112 | 351.543 | 58.112 | 369.836 | 509.086 | −29.547 |
| 1000 | 104.370 | 427.066 | 358.557 | 68.510 | 373.077 | 524.384 | −27.391 |
| 1100 | 104 989 | 437.044 | 365.245 | 78.979 | 376.314 | 539.358 | −25.612 |
| 1200 | 105.467 | 446.201 | 371.615 | 89.503 | 379.537 | 554.038 | −24.117 |
| 1300 | 105.843 | 454.658 | 377.682 | 100.069 | 382.741 | 568.450 | −22.841 |
| 1400 | 106.144 | 462.513 | 383.464 | 110.669 | 385.920 | 582.616 | −21.738 |
| 1500 | 106.389 | 469.845 | 388.981 | 121.296 | 389.071 | 596.555 | −20.774 |
| 1600 | 106.591 | 476.718 | 394.252 | 131.945 | 392.193 | 610.286 | −19.924 |
| 1700 | 106 758 | 483.185 | 399.295 | 142.613 | 395.286 | 623.822 | −19.168 |
| 1800 | 106.900 | 489.291 | 404.127 | 153.296 | 398.352 | 637.177 | −18.490 |
| 1900 | 107.020 | 495.075 | 408.763 | 163.992 | 401.394 | 650.361 | −17.880 |
| 2000 | 107.123 | 500.567 | 413.217 | 174.699 | 404.416 | 663.387 | −17.326 |
| 2100 | 107.211 | 505.795 | 417.502 | 185.416 | 407.425 | 676.261 | −16.821 |
| 2200 | 107.288 | 510.785 | 421.630 | 196.141 | 410.427 | 688.992 | −16.359 |
| 2300 | 107.356 | 515.555 | 425.610 | 206.874 | 413.429 | 701.588 | −15.934 |
| 2400 | 107 415 | 520.126 | 429.454 | 217.612 | 416.439 | 714.052 | −15.541 |
| 2500 | 107.468 | 524.512 | 433.169 | 228.356 | 419.464 | 726.390 | −15.177 |
| 2600 | 107.514 | 528.727 | 436.764 | 239.105 | 422.511 | 738.607 | −14.839 |
| 2700 | 107.556 | 532.786 | 440.246 | 249.859 | 425.589 | 750.706 | −14.523 |
| 2800 | 107.594 | 536.698 | 443.621 | 260.617 | 428.702 | 762.691 | −14.228 |
| 2900 | 107.629 | 540 474 | 446.896 | 271.378 | 431.857 | 774.563 | −13.951 |
| 3000 | 107.660 | 544.124 | 450.076 | 282.142 | 435.059 | 786.326 | −13.691 |
| 3100 | 107.689 | 547 654 | 453.167 | 292.910 | 438.312 | 797.982 | −13.446 |
| 3200 | 107.716 | 551.074 | 456.174 | 303.680 | 441.621 | 809.531 | −13.214 |
| 3300 | 107.742 | 554.389 | 459.100 | 314.453 | 444.989 | 820.977 | −12.995 |
| 3400 | 107.766 | 557.606 | 461.950 | 325.228 | 448.419 | 832.319 | −12.787 |
| 3500 | 107.790 | 560.730 | 464.728 | 336.006 | 451.911 | 843.559 | −12.589 |
| 3600 | 107.813 | 563.767 | 467.437 | 346.786 | 455.469 | 854.700 | −12.401 |
| 3700 | 107.835 | 566.721 | 470.081 | 357.569 | 459.092 | 865.739 | −12.222 |
| 3800 | 107.858 | 569.597 | 472.662 | 368.353 | 462.781 | 876.680 | −12.051 |
| 3900 | 107.880 | 572.399 | 475.183 | 379.140 | 466.536 | 887.524 | −11.887 |
| 4000 | 107.903 | 575.131 | 477.648 | 389.929 | 470.358 | 898.270 | −11.730 |
| 4100 | 107.927 | 577.795 | 480.058 | 400.721 | 474.245 | 908.919 | −11.580 |
| 4200 | 107.951 | 580.396 | 482.417 | 411.515 | 478.197 | 919.474 | −11.435 |
| 4300 | 107.976 | 582.937 | 484.725 | 422.311 | 482.213 | 929.933 | −11.296 |
| 4400 | 108.002 | 585.419 | 486.985 | 433.110 | 486.291 | 940.298 | −11.163 |
| 4500 | 108.029 | 587.847 | 489.200 | 443.911 | 490.431 | 950.570 | −11.034 |
| 4600 | 108.057 | 590.221 | 491.370 | 454.716 | 494.631 | 960.749 | −10.910 |
| 4700 | 108.086 | 592.546 | 493.498 | 465.523 | 498.889 | 970.836 | −10.790 |
| 4800 | 108.117 | 594.821 | 495.585 | 476.333 | 503.205 | 980.832 | −10.674 |
| 4900 | 108.148 | 597.051 | 497.633 | 487.146 | 507.576 | 990.738 | −10.561 |
| 5000 | 108.182 | 599.236 | 499.644 | 497.963 | 512.001 | 1000.553 | −10.453 |
| 5100 | 108.216 | 601.379 | 501.618 | 508.783 | 516.479 | 1010.280 | −10.347 |
| 5200 | 108.252 | 603.481 | 503.556 | 519.606 | 521.007 | 1019.919 | −10.245 |
| 5300 | 108.290 | 605.543 | 505.461 | 530.433 | 525.585 | 1029.469 | −10.146 |
| 5400 | 108.329 | 607.567 | 507.333 | 541.264 | 530.210 | 1038.933 | −10.050 |
| 5500 | 108.369 | 609.556 | 509.174 | 552.099 | 534.882 | 1048.311 | −9.956 |
| 5600 | 108.410 | 611.509 | 510.984 | 562.938 | 539.599 | 1057.604 | −9.865 |
| 5700 | 108.453 | 613 428 | 512.764 | 573.781 | 544.359 | 1066.811 | −9.776 |
| 5800 | 108.497 | 615.314 | 514.516 | 584.628 | 549.161 | 1075.935 | −9.690 |
| 5900 | 108.542 | 617.169 | 516.241 | 595.480 | 554.004 | 1084.976 | −9.606 |
| 6000 | 108.589 | 618.994 | 517.938 | 606.337 | 558.887 | 1093.934 | −9 524 |

PREVIOUS. December 1976 (1 atm) CURRENT. December 1976 (1 bar)

# Sulfur Fluoride, Ion ($SF_4^-$) IDEAL GAS

$M_r = 108.054161$ **Sulfur Fluoride, Ion ($SF_4^-$)** $F_4S_1^-(g)$

$\Delta_f H^\circ(0\ K) = -877.685 \pm 33.5\ kJ \cdot mol^{-1}$
$S^\circ(298.15\ K) = [312.962 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H^\circ(298.15\ K) = -887.464 \pm 33.5\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

| State | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|
| $[^2A_1]$ | 0 | [2] |
| $[^2B_1]$ | [15000] | [2] |

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|---|
| [500](1) | [375](1) | [150](2) |
| [430](1) | [325](1) | |
| [300](1) | [595](2) | |

Point Group: $[D_{4h}]$ $\sigma = [8]$
Bond Distance: S–F = [1.63 ± 0.1] Å
Bond Angle: F–S–F = [90]°
Product of the Moments of Inertia: $I_A I_B I_C = [9\ 4210 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p^\circ$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log K$_f$ |
| 0 | 0. | 0. | INFINITE | −18.480 | −877.685 | | |
| 100 | 50.869 | 236.570 | 382.190 | −14.562 | | | |
| 200 | 75.553 | 279.949 | 320.747 | −8.160 | | | |
| 250 | 83.644 | 297.728 | 314.402 | −4.168 | | | |
| 298.15 | 89.187 | 312.962 | 312.962 | 0. | −887.464 | −844.038 | 147.872 |
| 300 | 89.365 | 313.514 | 312.964 | 0.165 | −887.495 | −843.769 | 146.913 |
| 350 | 93.431 | 327.613 | 314.068 | 4.741 | −888.303 | −836.416 | 124.828 |
| 400 | 96.371 | 340.291 | 316.567 | 9.490 | −891.285 | −828.863 | 108.238 |
| 450 | 98.542 | 351.773 | 319.851 | 14.365 | −892.708 | −820.984 | 95.297 |
| 500 | 100.180 | 362.244 | 323.574 | 19.335 | −894.178 | −812.933 | 84.927 |
| 600 | 102.430 | 380.725 | 331.601 | 29.475 | −896.648 | −796.445 | 69.337 |
| 700 | 103.854 | 396.629 | 339 781 | 39.794 | −898.858 | −779.568 | 58.172 |
| 800 | 104.807 | 410.563 | 347.776 | 50.230 | −900.931 | −762.384 | 49.779 |
| 900 | 105.473 | 422.948 | 355.453 | 60.746 | −956.058 | −743.864 | 43.173 |
| 1000 | 105.957 | 434.087 | 362.769 | 71.318 | −956.800 | −720.248 | 37.622 |
| 1100 | 106.319 | 444.204 | 369.719 | 81.933 | −957.575 | −696.555 | 33.077 |
| 1200 | 106.596 | 453.467 | 376.318 | 92.579 | −958.386 | −672.790 | 29.286 |
| 1300 | 106.814 | 462.009 | 382.585 | 103.250 | −959.235 | −648.956 | 26.075 |
| 1400 | 106.987 | 469.931 | 388.545 | 113.941 | −960.123 | −625.056 | 23.321 |
| 1500 | 107.128 | 477.317 | 394.219 | 124.647 | −961.050 | −601.090 | 20.932 |
| 1600 | 107.244 | 484.235 | 399.631 | 135.366 | −962.015 | −577.062 | 18.839 |
| 1700 | 107.342 | 490.740 | 404.801 | 146.095 | −963.018 | −552.972 | 16.991 |
| 1800 | 107.425 | 496.877 | 409.748 | 156.833 | −964.054 | −528.821 | 15.346 |
| 1900 | 107 499 | 502.688 | 414.488 | 167.580 | −965.119 | −504.613 | 13.873 |
| 2000 | 107.564 | 508.203 | 419.037 | 178.333 | −966.208 | −480.348 | 12.545 |
| 2100 | 107.625 | 513 453 | 423.409 | 189.092 | −967.314 | −456.028 | 11.343 |
| 2200 | 107.682 | 518.461 | 427.616 | 199.858 | −968.429 | −431.655 | 10.249 |
| 2300 | 107.738 | 523.249 | 431.671 | 210.629 | −969.545 | −407.231 | 9.248 |
| 2400 | 107.793 | 527.835 | 435.583 | 221.405 | −970.654 | −382.758 | 8.331 |
| 2500 | 107.849 | 532.237 | 439.362 | 232.187 | −971.749 | −358.240 | 7.485 |
| 2600 | 107.907 | 536 468 | 443.016 | 242.975 | −972.820 | −333.679 | 6.704 |
| 2700 | 107.968 | 540.541 | 446.553 | 253.769 | −973.860 | −309.076 | 5.979 |
| 2800 | 108.031 | 544.469 | 449.980 | 264.569 | −974.861 | −284.436 | 5.306 |
| 2900 | 108.098 | 548.261 | 453.304 | 275.375 | −975.818 | −259.761 | 4.679 |
| 3000 | 108.168 | 551.927 | 456.531 | 286.189 | −976.725 | −235.054 | 4.093 |
| 3100 | 108.241 | 555.475 | 459.666 | 297 009 | −977.576 | −210.318 | 3.544 |
| 3200 | 108.319 | 558 913 | 462.714 | 307.837 | −978.366 | −185.555 | 3.029 |
| 3300 | 108.399 | 562.247 | 465.680 | 318.673 | −979.092 | −160.768 | 2.545 |
| 3400 | 108.483 | 565.484 | 468.568 | 329.517 | −979.751 | −135.960 | 2.089 |
| 3500 | 108.570 | 568.630 | 471.382 | 340.370 | −980.341 | −111.134 | 1.659 |
| 3600 | 108.660 | 571.690 | 474.126 | 351.231 | −980.860 | −86.292 | 1.252 |
| 3700 | 108.752 | 574.668 | 476.803 | 362.102 | −981.306 | −61.436 | 0.867 |
| 3800 | 108.846 | 577.570 | 479.417 | 372.981 | −981.679 | −36.570 | 0.503 |
| 3900 | 108.942 | 580.398 | 481.970 | 383.871 | −981.978 | −11.694 | 0.157 |
| 4000 | 109.039 | 583.158 | 484.465 | 394.770 | −982.203 | 13.188 | −0.172 |
| 4100 | 109.138 | 585.852 | 486.905 | 405.679 | −982.356 | 38.074 | −0.485 |
| 4200 | 109.236 | 588.483 | 489.293 | 416.597 | −982.437 | 62.964 | −0.783 |
| 4300 | 109.336 | 591.054 | 491.630 | 427.526 | −982.446 | 87.854 | −1.067 |
| 4400 | 109.435 | 593.569 | 493.918 | 438.465 | −982.385 | 112.745 | −1.338 |
| 4500 | 109.534 | 596.029 | 496.160 | 449.413 | −982.255 | 137.633 | −1.598 |
| 4600 | 109.632 | 598.438 | 498.357 | 460.371 | −982.059 | 162.517 | −1.845 |
| 4700 | 109.730 | 600.797 | 500.512 | 471.339 | −981.796 | 187.397 | −2.083 |
| 4800 | 109.826 | 603 108 | 502.625 | 482.317 | −981.470 | 212.270 | −2.310 |
| 4900 | 109.921 | 605.373 | 504.699 | 493.305 | −981.082 | 237.135 | −2.528 |
| 5000 | 110.014 | 607.595 | 506.735 | 504.301 | −980.634 | 261.992 | −2.737 |
| 5100 | 110.105 | 609.774 | 508.734 | 515.307 | −980.128 | 286.840 | −2.938 |
| 5200 | 110.194 | 611.913 | 510 698 | 526.322 | −979.565 | 311.678 | −3.131 |
| 5300 | 110.281 | 614.013 | 512.627 | 537.346 | −978.948 | 336.503 | −3.316 |
| 5400 | 110.366 | 616.075 | 514.524 | 548.378 | −978.278 | 361.317 | −3.495 |
| 5500 | 110.448 | 618.101 | 516.389 | 559.419 | −977.558 | 386.117 | −3.667 |
| 5600 | 110.528 | 620.092 | 518.223 | 570.468 | −976.788 | 410.905 | −3.833 |
| 5700 | 110.605 | 622.049 | 520.027 | 581.524 | −975.972 | 435.677 | −3.993 |
| 5800 | 110.679 | 623.973 | 521.803 | 592.589 | −975.110 | 460.435 | −4.147 |
| 5900 | 110.751 | 625.866 | 523.551 | 603.660 | −974.205 | 485.179 | −4.295 |
| 6000 | 110.820 | 627 728 | 525.271 | 614 739 | −973.257 | 509.906 | −4.439 |

PREVIOUS: December 1976 (1 atm) CURRENT December 1976 (1 bar)

## Enthalpy of Formation

We adopt $\Delta_f H^\circ(SF_4^-, g, 0\ K) = -209.8 \pm 8.0$ kcal mol$^{-1}$ and EA($SF_4$) = 1.25 ± 0.56 eV. The value of $\Delta_f H^\circ(0\ K)$ is obtained from the electron–impact appearance potential for $SF_4^-$ from $SF_6$, reported by Harland and Thynne[1] as AP = 5.0 ± 0.1 eV. This value has been verified in an independent study.[9] We assume that the negative ion is formed by the process $SF_6(g) + e^- = SF_4^-(g) + 2\ F(g)$ with no excess energies. We estimate the error in the electron–impact experiments to be ±0.3 eV (7.0 kcal mol$^{-1}$) which when combined with the uncertainties in the auxiliary data[2] gives an overall uncertainty in $\Delta_f H^\circ(0\ K)$ of ±8.0 kcal mol$^{-1}$ Our adopted value of EA = 1.25 eV is supported by EA = 1.5 eV[3] and EA = 1.26 eV[10] which were predicted by theoretical calculations.

In the same paper, Harland and Thynne[1] also reported the AP($SF_4^-/SF_5Cl$) as 4.1 ± 0 1 eV. This leads to $\Delta_f H^\circ(SF_4^-, g, 0\ K) = -199.9 \pm 5.0$ kcal mol$^{-1}$ and EA($SF_4$) = 0.82 ± 0.4 eV. They[1] also reported appearance potentials for $SF_3^-$ and $SF_5^-$ from $SF_5Cl$ which give EA values that are several tenths of an electron volt below JANAF data.[2] Thus, we are led to conclude that dissociative ionization of $SF_5Cl$ probably involves excess energies and that the derived electron affinities are lower limit values.

Our adopted results give $\Delta_f H^\circ(298.15\ K) = -212.1$ kcal mol$^{-1}$ and a fluoride–ion affinity (IA) of IA($SF_3$) = 30.5 kcal·mol$^{-1}$. Also, we find that the primary bond dissociation energy $D_0^\circ(SF_3^- – F)$ is 46.6 kcal·mol$^{-1}$ which when compared with $D_0^\circ$ values[2] for $SF_4$ (80.0 kcal·mol$^{-1}$) and $SF_4^+$ (12.9 kcal·mol$^{-1}$) indicates that the trend is $D_0^\circ(SF_4) >> D_0^\circ(SF_4^-) >> D_0^\circ(SF_4^+)$. These thermochemical predictions of the $SF_4^-$ stability are consistent with an autodetachment lifetime of 16.3 μsec, as measured by Harland and Thynne[4] using time–of–flight techniques. The enthalpy of atomization ($\Delta_a H^\circ$) for the products $S(g) + F^-(g) + 3\ F(g)$ and mean bond dissociation energy are 270.5 kcal·mol$^{-1}$ and 67.7 kcal·mol$^{-1}$, respectively.

## Heat Capacity and Entropy

We assume a square–planar configuration ($D_{4h}$ symmetry) similar to that found for the isoelectronic radical $ClF_4$.[5-7] We estimate the bond length to be slightly greater (0.03Å) than the mean (1.60Å) of the equatorial and axial S–F bonds in $SF_4$.[2] An upper limit of 1.70Å can be established from results of MO calculations on $ClF_4$.[7] The individual moments of inertia are: $I_A = 3\ 3526 \times 10^{-38}$ and $I_B = I_C = 1.6763 \times 10^{-38}\ g \cdot cm^2$.

The square–planar structure follows the vibrational representation $A_1 + A_2 + 2B_1 + B_2 + 2E$. We estimate the seven fundamentals by comparison with the observed frequencies for the approximately square–planar $SF_4$ part of $SF_5^-$.[2] Comparison of the experimentally measured frequencies for the related species $ClF_5$[2] and $ClF_4^-$ [8] suggests that this procedure should give reliable estimates.

The electronic states and levels are based on those for $ClF_4$ which were predicted by Ungemach and Schaefer[7] from MO calculations. An independent MO study of $ClF_4$ by Gregory[6] indicates that the upper level is an $^2A_2$ state. This, however, would not alter our functions since both configurations have the same degeneracy.

## References

[1] P. Harland and J. C. J. Thynne, J. Phys. Chem. 73, 4031 (1969).
[2] JANAF Thermochemical Tables. $SF_4(g)$ and $SF_6(g)$, 6–30–76; $SF_3^-(g)$, $SF_5^-(g)$ and $SF_4^+(g)$, 12–31–76; $ClF_5(g)$, 6–30–66, F(g), 9–30–65.
[3] A. L. Companion, Theoret. Chim. Acta (Berl.) 25, 268 (1972).
[4] P. W. Harland and J. C. J. Thynne, J. Phys. Chem. 75, 3517 (1971).

Continued on page 1216

## Tetrafluorosilane ($SiF_4$) IDEAL GAS $M_r$ = 104.079112 Tetrafluorosilane ($SiF_4$) $F_4Si_1(g)$

$S°(298.15 K) = 282.760 \pm 0.42$ J·K⁻¹·mol⁻¹

$\Delta_f H°(0\ K) = -1609.428 \pm 0.84$ kJ·mol⁻¹

$\Delta_f H°(298\ 15\ K) = -1614.940 \pm 0.84$ kJ·mol⁻¹

Vibrational Frequencies and Degeneracies

| $\nu$, cm⁻¹ | $\nu$, cm⁻¹ |
|---|---|
| 800.8(1) | 1029.6(3) |
| 264.2(2) | 388.7(3) |

Ground State Quantum Weight: [1] $\sigma = 12$

Point Group: $T_d$

Bond Distance: Si–F = 1.552 ± 0.002 Å

Bond Angle: F–Si–F = 109° 28'

Product of the Moments of Inertia: $I_A I_B I_C = 8.321027 \times 10^{-114}\ g^3 \cdot cm^6$

### Enthalpy of Formation

The adopted $\Delta_f H°(SiF_4, g, 298.15\ K) = -385.98 \pm 0.20$ kcal·mol⁻¹ is the result of measurement of the direct combination of the elements in a bomb calorimeter by Wise *et al.*[1] and is the value recommended by CODATA.[2] Bousquet *et al.*[3] determined $\Delta_f H°(298.15\ K) = -385 \pm 4$ kcal·mol⁻¹, also by fluorine combustion calorimetry, which is less precise but is in agreement with the adopted value. An average result, $\Delta_f H°(298.15\ K) = -372.4 \pm 0.4$ kcal·mol⁻¹ by Vorob'ev *et al.*[4] from the reaction of $SiF_4(g)$ and Na(cr) and from two rather involved enthalpy of solution schemes, is not used.

Using JANAF auxiliary values,[5] $\Delta_a H°(0\ K) = 564.76 \pm 3$ kcal mol⁻¹ is calculated for the process $SiF_4(g) = Si(g) + 4\ F(g)$.

### Heat Capacity and Entropy

The four fundamental vibrational frequencies are adopted from the vapor–phase Raman spectral investigation of Clark and Rippon.[6] Jones *et al.*[7] photographed the Raman spectrum of the liquid and assigned values of 800, 268, 1010, and 390 cm⁻¹ to the four fundamental vibrational frequencies. Yost *et al.*[8] determined only $\nu_1$ at 800 cm⁻¹ Shimanouchi[9] references four articles including that of Jones *et al.*[7] and has selected 800, 268, 1032, and 389 cm⁻¹. All of these assignments are in good agreement.

The interatomic distances from electron diffraction studies were found to be 1.555 ± 0.002 and 2.534 ± 0.003 Å for Si–F and F...F, respectively, by Beagley *et al.*[10] and 1.552 ± 0.002 and 2.534 ± 0.003 Å by Hagen and Hedberg.[11] The value of Si–F = 1.552 ± 0.002 Å is adopted because it is in agreement with the F...F distance and the tetrahedral bond angle The three principal moments of inertia are: $I_A = I_B = I_C = 20.2640 \times 10^{-39}\ g \cdot cm^2$.

Our calculation of $S°(298\ 15\ K) = 67.55 \pm 0.10$ cal K⁻¹ mol⁻¹ agrees with the value recommended by CODATA.[2]

### References

[1] S. S. Wise, J. L. Margrave, H. M. Feder, and W. N Hubbard, J. Phys. Chem 67, 815 (1963).
[2] ICSU–CODATA Task Group on Key Values for Thermodynamics, CODATA Bulletin No. 17, (1976).
[3] J. Bousquet, J. Carre, P. Claudy, J. Etienne, P. Provencal, J. Thourey, and P Barberi, J. Chem. Phys Physicochim. Biol. 69, 1065 (1972).
[4] A. F. Vorob'ev, V. P. Kolesov, and S. M. Skuratov, Zh. Neorgan. Khim. 5, 1402 (1960).
[5] JANAF Thermochemical Tables: F(g), 9–30–65; Si(g), 3–31–67.
[6] R J. H Clark and D. M. Rippon, J. Mol. Spectrosc. 44, 479 (1972).
[7] E. A. Jones, J S. Kirby–Smith, P. J H Woltz, and A. H. Nielsen, J. Chem. Phys. 19, 242 (1951).
[8] D. M. Yost, E. N. Lassettre, and S. T. Gross, J Chem. Phys. 4, 325 (1936).
[9] T. Shimanouchi, NSRDS–NBS 39, (1972).
[10] B. Beagley, D. P. Brown, and J. M. Freeman, J. Mol. Struct. 18, 337 (1973).
[11] K. Hagen and K Hedberg, J. Chem. Phys. 59, 1549 (1973).

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0 | 0. | INFINITE | −15.356 | −1609.428 | −1609.428 | INFINITE |
| 100 | 41.815 | 220.670 | 339.001 | −11.833 | −1611.986 | −1599.596 | 835.543 |
| 200 | 60 878 | 255.943 | 289.111 | −6.634 | −1613.823 | −1586.418 | 414.330 |
| 250 | 67.873 | 270.301 | 283.941 | −3.410 | −1614.454 | −1579.491 | 330.017 |
| 298.15 | 73.621 | 282.760 | 282.760 | 0. | −1614.940 | −1572.711 | 275.532 |
| 300 | 73.825 | 283.216 | 282.761 | 0.136 | −1614 957 | −1572.449 | 273.788 |
| 350 | 78.887 | 294.987 | 283.679 | 3.958 | −1615.348 | −1565.332 | 233.613 |
| 400 | 83 143 | 305.807 | 285.778 | 8.012 | −1615.642 | −1558.165 | 203.476 |
| 450 | 86.687 | 315.811 | 288.566 | 12.260 | −1615.851 | −1550 967 | 180.032 |
| 500 | 89.626 | 325.102 | 291 761 | 16.670 | −1615.992 | −1543.750 | 161 274 |
| 600 | 94.090 | 341.862 | 298 746 | 25.870 | −1616.116 | −1529.287 | 133.136 |
| 700 | 97.207 | 356.614 | 305.980 | 35.444 | −1616.093 | −1514.816 | 113 037 |
| 800 | 99.433 | 369.747 | 313.145 | 45.282 | −1615.983 | −1500.354 | 97.963 |
| 900 | 101.063 | 381.558 | 320.102 | 55.311 | −1615.824 | −1485.910 | 86.240 |
| 1000 | 102.285 | 392.272 | 326.791 | 65 481 | −1615.645 | −1471.484 | 76.862 |
| 1100 | 103.221 | 402.067 | 333 196 | 75.758 | −1615.463 | −1457.077 | 69.191 |
| 1200 | 103 952 | 411.081 | 339.316 | 86.118 | −1615.294 | −1442.686 | 62.798 |
| 1300 | 104.532 | 419.425 | 345.161 | 96.543 | −1615.147 | −1428.308 | 57.390 |
| 1400 | 105.000 | 427 190 | 350 746 | 107 021 | −1615.034 | −1413.941 | 52.755 |
| 1500 | 105.383 | 434.447 | 356.087 | 117.541 | −1614.959 | −1399.580 | 48.738 |
| 1600 | 105.699 | 441.259 | 361.199 | 128 095 | −1614.928 | −1385.222 | 45.223 |
| 1700 | 105.963 | 447.675 | 366.099 | 138.679 | −1665.120 | −1370 418 | 42.108 |
| 1800 | 106.186 | 453.738 | 370 801 | 149.286 | −1664.952 | −1353.088 | 39.266 |
| 1900 | 106.376 | 459.485 | 375.319 | 159.915 | −1664.787 | −1335.767 | 36.723 |
| 2000 | 106.540 | 464.945 | 379.665 | 170.561 | −1664.622 | −1318.454 | 34 434 |
| 2100 | 106.681 | 470.147 | 383.851 | 181.222 | −1664.455 | −1301.150 | 32.364 |
| 2200 | 106.803 | 475.113 | 387.887 | 191.896 | −1664.279 | −1283.854 | 30 483 |
| 2300 | 106.911 | 479.863 | 391 783 | 202.582 | −1664.090 | −1266.565 | 28.765 |
| 2400 | 107.005 | 484.415 | 395.549 | 213.278 | −1663.880 | −1249.286 | 27.190 |
| 2500 | 107.089 | 488 785 | 399.191 | 223.983 | −1663 644 | −1232.016 | 25.742 |
| 2600 | 107.163 | 492.986 | 402.719 | 234.696 | −1663.375 | −1214.756 | 24.405 |
| 2700 | 107.229 | 497.032 | 406.137 | 245 415 | −1663.068 | −1197.508 | 23.167 |
| 2800 | 107.289 | 500.933 | 409.454 | 256 141 | −1662.717 | −1180.271 | 22.018 |
| 2900 | 107.342 | 504.698 | 412 673 | 266.873 | −1662.316 | −1163.047 | 20.949 |
| 3000 | 107.391 | 508.338 | 415.802 | 277.610 | −1661.862 | −1145.839 | 19.951 |
| 3100 | 107.435 | 511.860 | 418.844 | 288.351 | −1661.349 | −1128.647 | 19.018 |
| 3200 | 107.474 | 515.272 | 421.804 | 299.096 | −1660.775 | −1111.472 | 18.143 |
| 3300 | 107.511 | 518.580 | 424.687 | 309.846 | −1660.137 | −1094.316 | 17.322 |
| 3400 | 107.544 | 521.790 | 427.496 | 320.598 | −1659.432 | −1077 180 | 16.549 |
| 3500 | 107.574 | 524.908 | 430.235 | 331.354 | −1658.660 | −1060.066 | 15.821 |
| 3600 | 107.602 | 527.938 | 432.907 | 342.113 | −2041.969 | −1032.514 | 14.981 |
| 3700 | 107 628 | 530.887 | 435.515 | 352.875 | −2040.643 | −1004.492 | 14.181 |
| 3800 | 107.652 | 533.758 | 438.063 | 363.639 | −2039.247 | −976.507 | 13 423 |
| 3900 | 107.674 | 536.554 | 440.553 | 374.405 | −2037.783 | −948.558 | 12.705 |
| 4000 | 107 694 | 539.280 | 442.987 | 385.173 | −2036.248 | −920.649 | 12.022 |
| 4100 | 107 713 | 541 940 | 445.368 | 395.944 | −2034.645 | −892.779 | 11.374 |
| 4200 | 107 730 | 544.536 | 447.699 | 406 716 | −2032.973 | −864.948 | 10.757 |
| 4300 | 107 747 | 547.071 | 449.980 | 417 490 | −2031.234 | −837.159 | 10.169 |
| 4400 | 107 762 | 549.548 | 452.215 | 428.265 | −2029.427 | −809.410 | 9.609 |
| 4500 | 107.776 | 551.970 | 454.405 | 439.042 | −2027.554 | −781.703 | 9.074 |
| 4600 | 107 789 | 554.339 | 456.552 | 449.820 | −2025 617 | −754.039 | 8.562 |
| 4700 | 107.802 | 556.657 | 458.657 | 460 600 | −2023.617 | −726.417 | 8.073 |
| 4800 | 107.814 | 558.927 | 460.723 | 471.381 | −2021.554 | −698.839 | 7.605 |
| 4900 | 107.825 | 561.150 | 462.750 | 482.162 | −2019.432 | −671.305 | 7.156 |
| 5000 | 107.835 | 563.329 | 464.739 | 492.945 | −2017.250 | −643.814 | 6.726 |
| 5100 | 107.845 | 565.464 | 466.694 | 503 729 | −2015.012 | −616.367 | 6.313 |
| 5200 | 107 854 | 567.558 | 468.613 | 514.514 | −2012.718 | −588.965 | 5.916 |
| 5300 | 107.863 | 569.613 | 470.500 | 525.300 | −2010.371 | −561.607 | 5.535 |
| 5400 | 107.871 | 571 629 | 472.354 | 536.087 | −2007.971 | −534.295 | 5.168 |
| 5500 | 107.879 | 573.608 | 474.177 | 546.874 | −2005.521 | −507 027 | 4.815 |
| 5600 | 107.886 | 575.552 | 475.970 | 557.663 | −2003.022 | −479.804 | 4.475 |
| 5700 | 107.893 | 577.462 | 477.734 | 568.452 | −2000.477 | −452.627 | 4.148 |
| 5800 | 107.900 | 579.338 | 479.469 | 579.241 | −1997.886 | −425.494 | 3.832 |
| 5900 | 107.906 | 581.183 | 481.178 | 590.031 | −1995.253 | −398.406 | 3.527 |
| 6000 | 107.912 | 582.997 | 482.860 | 600.822 | −1992.577 | −371.364 | 3.233 |

PREVIOUS: June 1976 (1 atm)    CURRENT: June 1976 (1 bar)

Tetrafluorosilane ($SiF_4$) $F_4Si_1(g)$

## Titanium Fluoride ($TiF_4$) CRYSTAL $M_r$ = 123.873612 Titanium Fluoride ($TiF_4$) $F_4Ti_1(cr)$

$\Delta_f H°(0\ K) = -1647.108 \pm 3.8\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 133.955\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -1649\ 333 \pm 3.8\ kJ \cdot mol^{-1}$

$T_{fus} = 558.6\ K$

### Enthalpy of Formation

The enthalpy of formation of $TiF_4(cr)$ was measured using a fluorine bomb calorimeter by Greenberg *et al.*[1] Gross *et al.*[2] reported a value of $-393.4\ kcal \cdot mol^{-1}$ for $\Delta_f H°(298.15\ K)$. The latter measurements were not corrected for impurities in the titanium sample, thus the value reported by Greenberg *et al.*[1] is adopted.

### Heat Capacity and Entropy

The heat capacity of $TiF_4(cr)$ has been measured over the temperature range 6 to 304 K by Euler and Westrum.[3] They obtained the value of $S°(298.15\ K)$ based on $S°(10\ K) = 0.11\ cal\ K^{-1} \cdot mol^{-1}$. Heat capacities above 300 K are estimated from those of $ZrF_4(cr)$.[4]

### Sublimation Data

The sublimation point is calculated as the temperature at which the fugacity is one atmosphere for the process $TiF_4(cr) = TiF_4(g)$. The enthalpy of sublimation is obtained from the data of Hall *et al.*[5]

### References

[1] E. Greenberg, J. L. Settle, and W. N. Hubbard, J. Phys. Chem. 6, 1345 (1962).
[2] P. Gross, C. Hayman, and D. L. Levi, XVIIth Interim. Cong. Pure Appl. Chem. Abstr. , 90 (1959).
[3] R. D. Euler and E. F. Westrum, Jr., J. Phys. Chem. 5, 132 (1961).
[4] R. A. McDonald, G. C. Sinke, and D. R. Stull, J. Chem. Eng. Data , 83 (1962).
[5] E. H. Hall, J. M. Blocher, Jr., and I. E. Campbell, J. Electrochem. Soc. 05, 275 (1958).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | $J \cdot K^{-1} mol^{-1}$ | | | $kJ \cdot mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −20.255 | −1647 108 | −1647 108 | INFINITE |
| 100 | 54.518 | 41.970 | 219.476 | −17.751 | −1650.978 | −1620.275 | 846.345 |
| 200 | 92.383 | 92.772 | 143.789 | −10.204 | −1651.206 | −1589.254 | 415.071 |
| 298.15 | 114.265 | 133.955 | 133.955 | 0. | −1649.333 | −1559.177 | 273.161 |
| 300 | 114 600 | 134.663 | 133.957 | 0.212 | −1649.284 | −1558.618 | 271.380 |
| 400 | 126.650 | 169.380 | 138.609 | 12.309 | −1646.239 | −1528.835 | 199.645 |
| 500 | 134.557 | 198.535 | 147.757 | 25.389 | −1642.630 | −1499.893 | 156.693 |
| 600 | 140.080 | 223.578 | 158.357 | 39.133 | −1638.659 | −1471.714 | 128.124 |
| 700 | 144 139 | 245.489 | 169.272 | 53.352 | −1634.431 | −1444.221 | 107.769 |
| 800 | 147.235 | 264.946 | 180.038 | 67.926 | −1630.000 | −1417.348 | 92.543 |
| 900 | 149.662 | 282.432 | 190.460 | 82.775 | −1625.451 | −1391 039 | 80.734 |
| 1000 | 151.670 | 298.307 | 200.463 | 97.844 | −1620.883 | −1365.239 | 71.313 |
| 1100 | 153.302 | 312.842 | 210.028 | 113.095 | −1616.386 | −1339.893 | 63.626 |
| 1200 | 154 641 | 326.239 | 219.161 | 128.494 | −1615.974 | −1314.832 | 57.233 |
| 1300 | 155.812 | 338.665 | 227.882 | 144.018 | −1610.969 | −1289.939 | 51.830 |
| 1400 | 156.816 | 350.249 | 236.213 | 159.650 | −1605 977 | −1265.432 | 47.214 |
| 1500 | 157.695 | 361.099 | 244 181 | 175.377 | −1601.022 | −1241.281 | 43.225 |

PREVIOUS June 1964 CURRENT. September 1967

Titanium Fluoride ($TiF_4$) $F_4Ti_1(cr)$

**Titanium Fluoride (TiF₄)** **IDEAL GAS** $M_r = 123.873612$ **Titanium Fluoride (TiF₄)** $F_4Ti_1(g)$

$S°(298\ 15\ K) = [314\ 928 \pm 2.1]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -1547.811 \pm 4.2\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -1551.427 \pm 4.2\ kJ{\cdot}mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|
| [701](1) | [750](3) |
| [168](2) | [178](3) |

Ground State Quantum Weight: [1] $\sigma = [12]$
Point Group: [$T_d$]
Bond Distance Ti-F = [1.80]Å
Bond Angle. F-Ti-F = [109°28′]
Product of the Moments of Inertia: $I_AI_BI_C = [2\ 025160 \times 10^{-113}]\ g^3{\cdot}cm^6$

## Enthalpy of Formation

The enthalpy of formation of $TiF_4(g)$ is calculated from that of the crystal and the enthalpy of sublimation, $\Delta_{sub}H°(298.15\ K)$, obtained from vapor pressure measurements. Hall *et al* [1] have reported extensive vapor pressure data for the reaction $TiF_4(cr) = TiF_4(g)$. 2nd and 3rd law analyses of their data yielded the following results.

| Method | Data Points | T/K | $\Delta_rH°(298.15\ K)$, kcal·mol$^{-1}$ 2nd law | 3rd law | Drift cal K$^{-1}$ mol$^{-1}$ | $\Delta_rH°(298\ 15\ K)$* kcal mol$^{-1}$ |
|---|---|---|---|---|---|---|
| 1. Spoon Gauge | 25** | 441-552 | 23.5 ± 0 1 | 23.37 | −0.3 ± 0.1 | −370.8 |
| 2. Ruff-Fischer | 6 | 435-498 | 23.0 ± 0.4 | 23.40 | +0 9 ± 0.9 | −370.8 |
| 3. Transpiration | 3 | 426-512 | 25.8 ± 2.0 | 23.72 | −4.5 ± 4.3 | −370.5 |
| 4. Rodebush | 6 | 473-537 | 23.7 ± 0.6 | 23.39 | −0.5 ± 1.2 | −370.8 |
| 5. 1, 2, and 4 | 36*** | 435-552 | 23.4 ± 0.1 | 23.37 | −0.1 ± 0.1 | −370.8 |

* Calculation based on 3rd law $\Delta_rH°$.
** Four points rejected due to failure of a statistical test.
*** Eight points rejected due to failure of a statistical test.

## Heat Capacity and Entropy

The interatomic distance is obtained from a correlation of the measured values for $TiCl_4(g)$, $TiBr_4(g)$, $TiCl_6^{-2}$ and $TiF_6^{-2}$ The principal moments of inertia are $I_A = I_B = I_C = 27.2575 \times 10^{-39}\ g{\cdot}cm^2$.

The vibrational frequencies are estimated by a valence force field treatment of estimated force constants The force constants are estimated from a correlation with the constants of $CF_4$, $SiF_4$, $CCl_4$, $SiCl_4$, $CBr_4$, $SiBr_4$, $TiCl_4$, and $TiBr_4$. The resulting frequencies are adjusted so that calculations of $\Delta_{sub}H°(298.15\ K)$ by both 2nd and 3rd law methods are in agreement.

## References

[1] E. H. Hall, J. M. Blocher, Jr., and I. E. Campbell, J. Electrochem. Soc. 105, 275 (1958).

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

|  | J·K$^{-1}$mol$^{-1}$ |  |  | kJ·mol$^{-1}$ |  |  |  |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −18.863 | −1547.811 | −1547.811 | INFINITE |
| 100 | 58.633 | 236.952 | 383.035 | −14 608 | −1549.930 | −1538.725 | 803.748 |
| 200 | 74.506 | 283 076 | 322.400 | −7.865 | −1550.962 | −1527.071 | 398.830 |
| 250 | 80.375 | 300.348 | 316.305 | −3.989 | −1551.255 | −1521.061 | 317.808 |
| 298 15 | 85 177 | 314.928 | 314.928 | 0. | −1551.427 | −1515.229 | 265.462 |
| 300 | 85.344 | 315.455 | 314.930 | 0 158 | −1551.432 | −1515.004 | 263.786 |
| 350 | 89.374 | 328.925 | 315.984 | 4.529 | −1551.525 | −1508.925 | 225.195 |
| 400 | 92.577 | 341 077 | 318.374 | 9.081 | −1551.561 | −1502.836 | 196.250 |
| 450 | 95 109 | 352.133 | 321.520 | 13 776 | −1551.558 | −1496.745 | 173.738 |
| 500 | 97.118 | 362.262 | 325.095 | 18.584 | −1551.530 | −1490.656 | 155.728 |
| 600 | 100 018 | 380.244 | 332.826 | 28 451 | −1551.435 | −1478.490 | 128 714 |
| 700 | 101 942 | 395.816 | 340.737 | 38.555 | −1551.322 | −1466.341 | 109 420 |
| 800 | 103.269 | 409.520 | 348.496 | 48.819 | −1551.202 | −1454.209 | 94 950 |
| 900 | 104.217 | 421 741 | 355.968 | 59.196 | −1551 124 | −1442.090 | 83.697 |
| 1000 | 104.915 | 432.759 | 363.105 | 69.655 | −1551 167 | −1429.975 | 74.694 |
| 1100 | 105 442 | 442.785 | 369.900 | 80.174 | −1551 403 | −1417.846 | 67.328 |
| 1200 | 105.849 | 451 977 | 376.362 | 90.739 | −1555.824 | −1405.567 | 61.183 |
| 1300 | 106.170 | 460 463 | 382.509 | 101.340 | −1555 741 | −1393.049 | 55.973 |
| 1400 | 106.427 | 468.341 | 388.362 | 111.971 | −1555 751 | −1380.535 | 51.508 |
| 1500 | 106.636 | 475 691 | 393.941 | 122.624 | −1555.869 | −1368.016 | 47 639 |
| 1600 | 106.808 | 482.579 | 399.268 | 133.297 | −1556 108 | −1355.485 | 44.252 |
| 1700 | 106 952 | 489 058 | 404.361 | 143.985 | −1556 483 | −1342.935 | 41.263 |
| 1800 | 107 072 | 495.175 | 409.238 | 154.686 | −1557.005 | −1330.359 | 38 606 |
| 1900 | 107 175 | 500.967 | 413.915 | 165.399 | −1557.684 | −1317.751 | 36.227 |
| 2000 | 107 263 | 506.467 | 418.406 | 176.121 | −1573.217 | −1304.647 | 34 074 |
| 2100 | 107.338 | 511.702 | 422.725 | 186.851 | −1574 985 | −1291.176 | 32.116 |
| 2200 | 107 404 | 516.697 | 426.884 | 197.588 | −1576.750 | −1277.620 | 30.335 |
| 2300 | 107 462 | 521.472 | 430.894 | 208.332 | −1578.507 | −1263.983 | 28.706 |
| 2400 | 107.512 | 526.047 | 434.764 | 219.080 | −1580.249 | −1250.271 | 27.211 |
| 2500 | 107.557 | 530.437 | 438.503 | 229.834 | −1581 968 | −1236.486 | 25.835 |
| 2600 | 107.597 | 534.656 | 442.121 | 240.592 | −1583 658 | −1222.634 | 24.563 |
| 2700 | 107 632 | 538.718 | 445 624 | 251.353 | −1585.314 | −1208.716 | 23 384 |
| 2800 | 107.664 | 542.632 | 449 019 | 262 118 | −1586.928 | −1194.739 | 22.288 |
| 2900 | 107 692 | 546 411 | 452.313 | 272.886 | −1588.495 | −1180.704 | 21.267 |
| 3000 | 107 718 | 550 062 | 455.510 | 283 656 | −1590 011 | −1166.617 | 20.313 |
| 3100 | 107.741 | 553.595 | 458 618 | 294.429 | −1591.470 | −1152.479 | 19.419 |
| 3200 | 107.763 | 557.016 | 461.639 | 305.204 | −1592.871 | −1138.296 | 18.581 |
| 3300 | 107.782 | 560.332 | 464.580 | 315.982 | −1594.209 | −1124.069 | 17.793 |
| 3400 | 107.800 | 563.550 | 467.444 | 326.761 | −1595.482 | −1109.804 | 17.050 |
| 3500 | 107.816 | 566.675 | 470.235 | 337.542 | −1596.689 | −1095.501 | 16.349 |
| 3600 | 107.830 | 569 713 | 472.956 | 348.324 | −1597.827 | −1081.165 | 15.687 |
| 3700 | 107.844 | 572.667 | 475 611 | 359 108 | −2007.995 | −1059.010 | 14.951 |
| 3800 | 107.857 | 575.543 | 478.203 | 369.893 | −2007.761 | −1033.365 | 14.205 |
| 3900 | 107.868 | 578.345 | 480.735 | 380.679 | −2007.512 | −1007.726 | 13.497 |
| 4000 | 107.879 | 581.076 | 483.210 | 391 466 | −2007.248 | −982.094 | 12.825 |
| 4100 | 107.889 | 583 740 | 485.629 | 402.255 | −2006.968 | −956.469 | 12.186 |
| 4200 | 107.898 | 586.340 | 487.996 | 413.044 | −2006.670 | −930.850 | 11.577 |
| 4300 | 107.907 | 588.879 | 490.313 | 423.834 | −2006.354 | −905.240 | 10.996 |
| 4400 | 107.915 | 591.360 | 492.582 | 434.625 | −2006.020 | −879.636 | 10.443 |
| 4500 | 107 923 | 593.785 | 494.804 | 445 417 | −2005.666 | −854.040 | 9.913 |
| 4600 | 107.930 | 596.157 | 496.981 | 456.210 | −2005.292 | −828.452 | 9.407 |
| 4700 | 107.936 | 598 479 | 499.116 | 467.003 | −2004.897 | −802.873 | 8.923 |
| 4800 | 107.943 | 600.751 | 501.210 | 477.797 | −2004.482 | −777.302 | 8.459 |
| 4900 | 107 948 | 602.977 | 503.264 | 488.592 | −2004.044 | −751.741 | 8.014 |
| 5000 | 107.954 | 605 158 | 505.280 | 499.387 | −2003.585 | −726.188 | 7.586 |
| 5100 | 107.959 | 607.296 | 507.260 | 510.183 | −2003.103 | −700.645 | 7.176 |
| 5200 | 107 964 | 609.392 | 509.204 | 520.979 | −2002.598 | −675.111 | 6.782 |
| 5300 | 107 969 | 611.449 | 511 114 | 531.775 | −2002.070 | −649.587 | 6.402 |
| 5400 | 107.973 | 613 467 | 512.990 | 542.572 | −2001.517 | −624.074 | 6.037 |
| 5500 | 107.977 | 615.448 | 514.835 | 553.370 | −2000.941 | −598.572 | 5.685 |
| 5600 | 107 981 | 617.394 | 516.649 | 564.168 | −2000.340 | −573.079 | 5.345 |
| 5700 | 107.985 | 619.305 | 518.434 | 574.966 | −1999.715 | −547.598 | 5.018 |
| 5800 | 107 988 | 621 183 | 520.189 | 585.765 | −1999.064 | −522.128 | 4.702 |
| 5900 | 107 991 | 623 029 | 521.917 | 596.564 | −1998.388 | −496.669 | 4 397 |
| 6000 | 107.995 | 624.844 | 523.617 | 607.363 | −1997.687 | −471.223 | 4.102 |

PREVIOUS: September 1967 (1 atm)    CURRENT September 1967 (1 bar)

**Titanium Fluoride (TiF₄)** $F_4Ti_1(g)$

## Zirconium Fluoride ($ZrF_4$) CRYSTAL $M_r = 167.213612$ Zirconium Fluoride ($ZrF_4$) $F_4Zr_1(cr)$

$S°(298.15\ K) = 104.700 \pm 0.21\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{trs}\ (\alpha \rightarrow \beta) = 723\ K$
$T_{fus} = 1205 \pm 2\ K$

$\Delta_f H°(0\ K) = -1905.601 \pm 0.11\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -1911.251 \pm 0.11\ kJ{\cdot}mol^{-1}$
$\Delta_{trs} H° = $ Unknown
$\Delta_{fus} H° = 64.224 \pm 0.42\ kJ{\cdot}mol^{-1}$

### Enthalpy of Formation

The enthalpy of formation of zirconium tetrafluoride was measured by direct combination of the elements in a bomb calorimeter by Greenberg *et al.*[1] The reported value, $\Delta_f H°(ZrF_4,\ cr,\ 298.15\ K) = -456.80 \pm 0.25\ kcal{\cdot}mol^{-1}$, is adopted.

### Heat Capacity and Entropy

The low temperature heat capacities in the temperature range 5 to 307 K were determined by adiabatic calorimetry by Westrum.[2] Using these low temperature $C_p°$ data the value of $S°(298.15\ K)$ is derived as $25.024 \pm 0.05\ cal\ K^{-1}{\cdot}mol^{-1}$ based on $S°(10\ K) = 0.0074\ cal\ K^{-1}{\cdot}mol^{-1}$.

McDonald *et al.*[3] measured the high temperature enthalpies of $ZrF_4(cr)$ at temperatures 283.9–1225.8 K in a copper block drop calorimeter. Smith *et al.*[4] used a Bunsen ice calorimeter for the enthalpy measurements in the temperature range 273–1150 K. These two sets of enthalpy data are not in good agreement. It is possible that the discrepancies are due to the difference in crystal structure of the samples used (see "Transition Data" for more information). In order to join smoothly with the low temperature heat capacities at 298.15 K, the high temperature heat capacities derived from the enthalpy data of McDonald *et al.*[3] are adopted. The $C_p°$ values above 1200 K are obtained by smooth extrapolation.

Fontana and Winand[8] also measured the enthalpy of $ZrF_4$ in the range 773–1350 K Their reported average heat capacity in this range and their reported enthalpies are considerably lower than those adopted.

### Transition Data

Gaudreau[5] presented evidence that $ZrF_4$ has three crystal structures (α, β, and ) and one amorphous form. Chretien and Gaudreau[6] found that $ZrF_4(cr)$ has an α (tetragonal) and β (monoclinic) form with a transition temperature of $T_{trs} = 723$ K. The crystal data compilation of Donnay and Ondik[7] tabulated two monoclinic structures for $ZrF_4$; one of which was specified as the β form while no mention was made of a tetragonal form.

The $ZrF_4$ sample employed by McDonald *et al.*[3] for enthalpy measurement was prepared by dissolving hafnium-free zirconium metal in 48% aqueous HF, and the resulting solution was evaporated to dryness. The crystalline product was heated slowly to 773 K in a platinum boat in a slow current of anhydrous HF. X-ray diffraction showed only crysalline $ZrF_4$. Wet analysis indicated 54.6% Zr (theory 54.55) and 44.9% F (theory 45.45). Due to the above facts we are uncertain whether the sample prepared is a mixture of α and β forms of a pure $ZrF_4$(β). Smith *et al.*[4] obtained their $ZrF_4$ sample from the Oak Ridge National Laboratories, Oak Ridge, Tenn. Since the method of preparation of the compound is unavailable from the report, we do not know what kind of sample they used for measurement.

Because of the above unresolved situation, we emphasize that this $ZrF_4(cr)$ table is not strictly a α, β-combined phase table. However, the differences in the calculated functions are probably not significant.

### Fusion Data

$T_{fus}$ and $\Delta_{fus}H°$ are taken from McDonald *et al*[3]. The values were obtained under conditions greater than one atmosphere. Fontana and Winand[8] reported a heat of melting of $11.81 \pm 2.40\ kcal{\cdot}mol^{-1}$ (under pressure).

### Sublimation Data

The sublimation temperature ($T_{sub} = 1179$) is calculated as the temperature at which the fugacity is one atmosphere for the process $ZrF_4(cr) = ZrF_4(g)$. Since the sublimation temperature is lower than the melting point, the $ZrF_4$ sublimes before it melts.

### References

[1] E. Greenberg, J. L. Settle, H. M. Feder and W. N. Hubbard, J. Phys. Chem. 65, 1168 (1961).
[2] E. F. Westrum, Jr., J. Chem. Eng. Data 10, 140 (1965).
[3] R. A. McDonald, G. C. Sinke and D. R. Stull, J. Chem. Eng. Data 7, 83 (1962).
[4] D. F Smith, W C. Miller and A. R. Taylor, Jr., U S. Bur. Mines RI 5964, (1962).
[5] B. Gaudreau, Rev Chim. Minerale 2, 1 (1965); CA 63 17245d.
[6] A. Chretien and B. Gaudreau, Compt. Rend. 246, 2266 (1958), Compt. Rend. 248, 2878 (1959).
[7] J. D. H. Donnay and H. M. Ondik, "Crystal Data, Determinative Tables," 3rd ed., Vol. 2, Nat. Bur. Stand. and Joint Committee on Powder Diffraction Standards, (1973).
[8] A. Fontana and R. Winand J. Nucl. Mat. 3, 295 (1972).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | $J{\cdot}K^{-1}mol^{-1}$ | | | $kJ{\cdot}mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0 | 0. | INFINITE | −17.497 | −1905.601 | −1905.601 | INFINITE |
| 100 | 42.091 | 22.932 | 182.385 | −15.945 | −1910.750 | −1877.563 | 980.738 |
| 200 | 84.559 | 66.906 | 113.663 | −9.351 | −1912.207 | −1843.517 | 481.477 |
| 298.15 | 103.596 | 104.700 | 104.700 | 0. | −1911.251 | −1809.955 | 317.097 |
| 300 | 103.805 | 105.342 | 104.702 | 0.192 | −1911.222 | −1809.327 | 315.032 |
| 400 | 113.470 | 136.661 | 108.907 | 11.101 | −1909.310 | −1775.635 | 231.874 |
| 500 | 119.704 | 162.685 | 117.134 | 22.776 | −1906.992 | −1742.478 | 182.035 |
| 600 | 123 972 | 184.911 | 126.623 | 34 973 | −1904.433 | −1709.812 | 148.852 |
| 700 | 126.984 | 204.264 | 136.362 | 47.531 | −1901.745 | −1677.587 | 125.183 |
| 800 | 129 411 | 221.379 | 145.940 | 60.351 | −1898.994 | −1645.751 | 107.457 |
| 900 | 131.838 | 236.761 | 155.191 | 73.413 | −1896.187 | −1614.264 | 93.689 |
| 1000 | 134.097 | 250.772 | 164.059 | 86.713 | −1893.323 | −1583.092 | 82.692 |
| 1100 | 136.231 | 263.652 | 172.535 | 100.228 | −1890.419 | −1552.210 | 73 708 |
| 1200 | 138.281 | 275.592 | 180.632 | 113.953 | −1891.188 | −1521.371 | 66.224 |
| 1300 | 140.373 | 286 743 | 188.370 | 127.885 | −1887.663 | −1490.695 | 59.897 |
| 1400 | 142.507 | 297.225 | 195.774 | 142.031 | −1884.009 | −1460.296 | 54.484 |

PREVIOUS. June 1969 CURRENT· June 1975

## Zirconium Fluoride ($ZrF_4$) IDEAL GAS $M_r$ = 167.213612 Zirconium Fluoride ($ZrF_4$) $F_4Zr_1(g)$

$S°$(298.15 K) = [319.516 ± 4.2] J·K$^{-1}$·mol$^{-1}$

$\Delta_f H°$(0 K) = −1669.395 ± 3.3 kJ·mol$^{-1}$
$\Delta_f H°$(298.15 K) = −1673.600 ± 3.3 kJ·mol$^{-1}$

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|
| [630](1) | 668(3) |
| [180](2) | 190(3) |

Ground State Quantum Weight: [1]
Point Group: $T_d$ $\sigma$ = 12
Bond Distance. Zr–F = 1 94 ± 0.02 Å
Bond Angle: F–Zr–F = 109° 28'
Products of the Moments of Inertia: $I_A I_B I_C$ = 3.174220 × 10$^{-113}$ g$^3$·cm$^6$

### Enthalpy of Formation

The vapor pressures of $ZrF_4$(cr) in the temperature range 617–1150 K were determined by many investigators using various methods Based on the reported vapor pressure data, the corresponding enthalpies of sublimation are evaluated by the 2nd and 3rd law methods. Using the 3rd law $\Delta_{sub}H$(298.15 K) and $\Delta_f H°$($ZrF_4$, cr, 298 15 K) = −456.8 kcal mol$^{-1}$, the enthalpies of formation at 298.15 K for $ZrF_4$(g) are evaluated. The results are presented in the table below. The values of $\Delta_f H°$($ZrF_4$, g, 298.15 K), listed in the last column of this table are in excellent agreement which indicate that the estimated missing vibrational frequencies $\nu_1$ and $\nu_2$ are reasonable The enthalpy of formation at 298.15 K for $ZrF_4$ (g) is adopted as −400.0 kcal·mol$^{-1}$.

| Source | Method | T/K | Points | $\Delta_{sub}H°$(298 15 K), kcal·mol$^{-1}$ 2nd law | 3rd law | Drift J K$^{-1}$·mol$^{-1}$ | $\Delta_f H°$(298.15 K) kcal mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 1 | unavailable | 950–1150 | eqn | 56.49 ± 0 12 | 56.83 | 0.3 | −399.97 |
| 2 | transpiration | 617–881 | 14 | 60.67 ± 0.09 | 57.13 | −3.4 ± 0.1 | −399.67 |
| 3 | transpiration | 900–1150 | 6 | 60.64 ± 0.13 | 57.24 | −3 3 ± 0.1 | −399.56 |
| 4 | quasistatic | 710–808 | 29 | 56.11 ± 0.62 | 56.65 | 0.5 ± 0.6 | −400.15 |
| 5 | torsion/effusion | 748–849 | 15 | 55 81 ± 1.44 | 57.05 | 1.5 ± 1.8 | −399.75 |
| 6 | torsion/effusion | 735–825 | 10 | 52.59 ± 0.39 | 57.09 | 5.7 ± 0.5 | −399.71 |
| 7 | Knudsen–effusion | 720–825 | 5 | 51.53 ± 0.05 | 54.79 | 4.1 ± 0.1 | −402.01 |
| 8 | mass spectrometry | 700–900 | 5 | 59.25 ± 2.34 | 57.30 | −2.4 ± 2.9 | −399.50 |
| 9 | "bell method" | 1000–1150 | eqn | 57.38 ± 0.12 | 56.89 | −0.5 | −399.91 |
| 10 | mass spectrometry | 769 | 1 | — | 57.58 | — | −399.22 |

### Heat Capacity and Entropy

The molecular structure of $ZrF_4$(g) has been studied by electron diffraction by Spiridonov.[11] The configuration was found to be a regular tetrahedron with interatomic distance Zr–F = 1.94 ± 0.02 Å and F–Zr–F bond angle = 109.47° which are adopted.

Employing the estimated interaction coefficients and interatomic distance Zr–F = 1.85 Å, Godnev *et al.*[12] calculated three vibrational frequencies for $ZrF_4$(g) as $\nu_2$ = 150–200, and $\nu_4$ = 180 ± 230 cm$^{-1}$ Bucher *et al.*[13] observed the infrared spectra of some group IV halides and assigned $\nu_3$ = 668 and $\nu_4$ = 190 ± 20 cm$^{-1}$ for $ZrF_4$ (g). The frequency $\nu_3$ has also been reported as 670 cm$^{-1}$.[14] In studying matrix isolated $ZrF_4$, Hauge *et al.*[15] found a strong infrared band at 668.0 cm$^{-1}$ in an argon matrix and 677.0 cm$^{-1}$ in a neon matrix, both of which were attributed to the $\nu_3$ stretch frequency. The values of $\nu_3$ and $\nu_4$ adopted here are those reported by Buchler *et al.*[13] The adopted $\nu_1$ is obtained by correlating the corresponding frequencies of the tetrafluorides of C, Pb, Si, Ti and Ge with their respective interatomic distances. $\nu_2$ is calculated from $\nu_1$, $\nu_3$ and $\nu_4$ usng the relationship[15] $\nu_3\nu_4/\nu_1\nu_2 = 2/3 + 4$ F/Zr where F and Zr are gram atomic weights of fluorine and zirconium, respectively. Vibrational frequencies (635, 178, 668, and 190 cm$^{-1}$) were suggested by Godnev *et al.*[12] who also critically examined the sublimation data in order to achieve internal consistency. These values are in good agreement with our adopted values. The three principal moments of inertia are $I_A = I_B = I_C$ = 31.6625 × 10$^{-39}$ g·cm$^2$.

### References

[1] S. Lauter, Dissertation Technische Hohschule Hannover, 1948 (Cited in reference 9).
[2] K. A. Sense, M. Snyder and R. B. Filbert, Jr., J Phys. Chem. 58, 995 (1954).
[3] K. A. Sense, C. A. Alexander, R. E. Bowman and R. B Filbert, Jr, J. Phys. Chem. 61, 337 (1957).
[4] S. Cantor, R. F. Newton, W. R. Grimes and F. F. Blankenship, J. Phys Chem. 62, 96 (1958).

Continued on page 1216

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| T/K | $C_p°$ (J·K$^{-1}$mol$^{-1}$) | $S°$ (J·K$^{-1}$mol$^{-1}$) | $-[G°-H°(T_r)]/T$ (J·K$^{-1}$mol$^{-1}$) | $H°-H°(T_r)$ (kJ·mol$^{-1}$) | $\Delta_f H°$ (kJ·mol$^{-1}$) | $\Delta_f G°$ (kJ·mol$^{-1}$) | log $K_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0. | 0. | INFINITE | −18.942 | −1669.395 | −1669.395 | INFINITE |
| 100 | 57.127 | 240.945 | 388.852 | −14.791 | −1671.944 | −1660.559 | 867.387 |
| 200 | 75.813 | 286.909 | 327.175 | −8.053 | −1673.258 | −1648.568 | 430.562 |
| 250 | 82.385 | 304.559 | 320.928 | −4.092 | −1673.517 | −1642.362 | 343.153 |
| 298.15 | 87.393 | 319.516 | 319.516 | 0. | −1673.600 | −1636.352 | 286.682 |
| 300 | 87.561 | 320.057 | 319.518 | 0.162 | −1673.601 | −1636.120 | 284.874 |
| 350 | 91.536 | 333.867 | 320.599 | 4 644 | −1673.567 | −1629.875 | 243.246 |
| 400 | 94.573 | 346.297 | 323.048 | 9.300 | −1673.461 | −1623.640 | 212.026 |
| 450 | 96.905 | 357.577 | 326.267 | 14.089 | −1673.310 | −1617.421 | 187 745 |
| 500 | 98 716 | 367.885 | 329.921 | 18.982 | −1673.135 | −1611.220 | 168.323 |
| 600 | 101.275 | 386.127 | 337 808 | 28.991 | −1672.764 | −1598.872 | 139.194 |
| 700 | 102.939 | 401.872 | 345.861 | 39.207 | −1672.417 | −1586.585 | 118.392 |
| 800 | 104.071 | 415.696 | 353.744 | 49.561 | −1672.132 | −1574.344 | 102.794 |
| 900 | 104.872 | 428.002 | 361.324 | 60.011 | −1671.939 | −1562.133 | 90.664 |
| 1000 | 105.459 | 439.084 | 368.555 | 70.529 | −1671.856 | −1549.938 | 80 960 |
| 1100 | 105.900 | 449 157 | 375.432 | 81.097 | −1671.899 | −1537.745 | 73.021 |
| 1200 | 106.239 | 458.386 | 381.965 | 91.705 | −1675.785 | −1525.320 | 66.395 |
| 1300 | 106.506 | 466.901 | 388.176 | 102.343 | −1675.554 | −1512.791 | 60.785 |
| 1400 | 106.719 | 474.802 | 394.084 | 113.005 | −1675.384 | −1500.278 | 55.976 |
| 1500 | 106.893 | 482.171 | 399.714 | 123.685 | −1675.288 | −1487 775 | 51.809 |
| 1600 | 107.035 | 489.074 | 405.086 | 134.382 | −1675.276 | −1475.275 | 48.163 |
| 1700 | 107.153 | 495.567 | 410.219 | 145.092 | −1675.357 | −1462.772 | 44.946 |
| 1800 | 107.253 | 501.695 | 415.132 | 155.812 | −1675.542 | −1450.262 | 42.086 |
| 1900 | 107.338 | 507.496 | 419.842 | 166.542 | −1675.837 | −1437.740 | 39.526 |
| 2000 | 107.410 | 513 003 | 424.364 | 177.279 | −1676.249 | −1425.198 | 37.222 |
| 2100 | 107 472 | 518.245 | 428.710 | 188 023 | −1676.782 | −1412.633 | 35 137 |
| 2200 | 107.526 | 523.246 | 432.895 | 198.773 | −1698.764 | −1399.294 | 33.223 |
| 2300 | 107.574 | 528.027 | 436.928 | 209.528 | −1699.970 | −1385.654 | 31.469 |
| 2400 | 107 615 | 532.606 | 440.820 | 220.288 | −1701.161 | −1371.963 | 29 860 |
| 2500 | 107.652 | 537.000 | 444.580 | 231.051 | −1702.330 | −1358.222 | 28.379 |
| 2600 | 107.685 | 541.223 | 448.216 | 241.818 | −1703.472 | −1344.435 | 27.010 |
| 2700 | 107 714 | 545.288 | 451.736 | 252.588 | −1704.579 | −1330.605 | 25 742 |
| 2800 | 107.740 | 549.205 | 455.148 | 263.361 | −1705.645 | −1316.735 | 24.564 |
| 2900 | 107.763 | 552.987 | 458.457 | 274 136 | −1706.666 | −1302.827 | 23.466 |
| 3000 | 107.785 | 556.640 | 461.669 | 284.914 | −1707.635 | −1288.885 | 22.441 |
| 3100 | 107 804 | 560.175 | 464.790 | 295.693 | −1708.548 | −1274.911 | 21.482 |
| 3200 | 107.821 | 563.598 | 467.825 | 306.474 | −1709.403 | −1260.909 | 20.582 |
| 3300 | 107.837 | 566.916 | 470.777 | 317.257 | −1710.196 | −1246.881 | 19 736 |
| 3400 | 107.851 | 570 135 | 473.652 | 328.042 | −1710.924 | −1232.830 | 18.940 |
| 3500 | 107.865 | 573.262 | 476.454 | 338.827 | −1711.586 | −1218 759 | 18.189 |
| 3600 | 107 877 | 576.301 | 479.186 | 349.614 | −1712.180 | −1204.669 | 17 479 |
| 3700 | 107.888 | 579.257 | 481.850 | 360.403 | −1712.705 | −1190.564 | 16.808 |
| 3800 | 107.898 | 582.134 | 484.452 | 371.192 | −1713.161 | −1176.447 | 16.171 |
| 3900 | 107 908 | 584.937 | 486.992 | 381.982 | −1713.547 | −1162.317 | 15.567 |
| 4000 | 107 917 | 587.669 | 489.475 | 392.774 | −1713.864 | −1148.179 | 14.994 |
| 4100 | 107.925 | 590.334 | 491.903 | 403.566 | −1714.113 | −1134 034 | 14.448 |
| 4200 | 107.932 | 592.934 | 494.278 | 414.359 | −1714.293 | −1119.883 | 13.928 |
| 4300 | 107.940 | 595.474 | 496.602 | 425.152 | −1714.407 | −1105.729 | 13.432 |
| 4400 | 107.946 | 597.956 | 498.877 | 435.946 | −1714.454 | −1091.573 | 12.959 |
| 4500 | 107.952 | 600.382 | 501.106 | 446.741 | −1714.436 | −1077.416 | 12.506 |
| 4600 | 107.958 | 602 754 | 503.290 | 457.537 | −1714.355 | −1063.261 | 12.074 |
| 4700 | 107.964 | 605.076 | 505.431 | 468.333 | −1714.211 | −1049.108 | 11.660 |
| 4800 | 107.969 | 607.349 | 507.531 | 479.130 | −2274.943 | −1023.342 | 11.136 |
| 4900 | 107 974 | 609.576 | 509.591 | 489.927 | −2274.331 | −997.273 | 10.631 |
| 5000 | 107.978 | 611.757 | 511.612 | 500 724 | −2273.679 | −971.218 | 10.146 |
| 5100 | 107.982 | 613.895 | 513.597 | 511.522 | −2272.986 | −945.175 | 9.681 |
| 5200 | 107.986 | 615.992 | 515.546 | 522.321 | −2272.252 | −919.146 | 9.233 |
| 5300 | 107.990 | 618.049 | 517.461 | 533.120 | −2271 479 | −893.132 | 8.802 |
| 5400 | 107.994 | 620 068 | 519.342 | 543.919 | −2270.665 | −867.134 | 8.388 |
| 5500 | 107.997 | 622.049 | 521.191 | 554.718 | −2269.812 | −841.151 | 7.989 |
| 5600 | 108.000 | 623 995 | 523.010 | 565.518 | −2268.920 | −815.182 | 7.604 |
| 5700 | 108.003 | 625.907 | 524.798 | 576.318 | −2267.988 | −789.232 | 7.232 |
| 5800 | 108.006 | 627.785 | 526.558 | 587.119 | −2267.018 | −763.297 | 6.874 |
| 5900 | 108.009 | 629.632 | 528.289 | 597.920 | −2266.009 | −737.379 | 6.528 |
| 6000 | 108.011 | 631.447 | 529.994 | 608.721 | −2264 961 | −711.479 | 6.194 |

PREVIOUS June 1975 (1 atm) CURRENT: June 1975 (1 bar)

## Hydrogen Fluoride ($H_5F_5$) IDEAL GAS $M_r = 100.031715$ Hydrogen Fluoride ($H_5F_5$) $F_5H_5(g)$

$S°(298.15\ K) = [408.442 \pm 20.9]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = [-1475.453 \pm 25.1]\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [-1489.713 \pm 25.1]\ kJ{\cdot}mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ |
|---|
| [202](5) |
| [53](4) |
| [962](5) |
| [552](5) |
| [3060](5) |

Ground State Quantum Weight: 1 $\sigma = [5]$
Point Group: $[C_5]$
Bond Distance: F–F = [2.5] Å
Product of the Moments of Inertia: $I_A I_B I_C = [1.059909 \times 10^{-112}]\ g^3{\cdot}cm^6$

| Enthalpy Reference Temperature = $T_r$ = 298.15 K | | | | | | | Standard State Pressure = $p°$ = 0.1 MPa |
|---|---|---|---|---|---|---|---|
| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −28.970 | −1475.453 | −1475.453 | INFINITE |
| 100 | 87.374 | 288.122 | 515.288 | −22.717 | −1483.965 | −1445.003 | 754.792 |
| 200 | 115.893 | 357.974 | 420.354 | −12.476 | −1487.781 | −1404.344 | 366.777 |
| 250 | 127.570 | 385.117 | 410.650 | −6.383 | −1488.935 | −1383.343 | 289.034 |
| 298.15 | 137.321 | 408.442 | 408.442 | 0. | −1489.713 | −1362.931 | 238.780 |
| 300 | 137.665 | 409.293 | 408.445 | 0.254 | −1489.737 | −1362.144 | 237.170 |
| 350 | 146.155 | 431.171 | 410.153 | 7.356 | −1490.230 | −1340.836 | 200.109 |
| 400 | 153.197 | 451.162 | 414.048 | 14.846 | −1490.459 | −1319.475 | 172.306 |
| 450 | 159.042 | 469.554 | 419.207 | 22.656 | −1490.467 | −1298.100 | 150.679 |
| 500 | 163.954 | 486.572 | 425.103 | 30.734 | −1490.291 | −1276.733 | 133.379 |
| 600 | 171.866 | 517.195 | 437.958 | 47.543 | −1489.489 | −1234.088 | 107.437 |
| 700 | 178.225 | 544.180 | 451.243 | 65.057 | −1488.199 | −1191.617 | 88.920 |
| 800 | 183.685 | 568.343 | 464.396 | 83.158 | −1486.503 | −1149.359 | 75.045 |
| 900 | 188.530 | 590.263 | 477.182 | 101.773 | −1484.459 | −1107.336 | 64.268 |
| 1000 | 192.872 | 610.356 | 489.509 | 120.847 | −1482.120 | −1065.556 | 55.659 |
| 1100 | 196.766 | 628.925 | 501.349 | 140.333 | −1479.531 | −1024.023 | 48.627 |
| 1200 | 200.244 | 646.198 | 512.709 | 160.187 | −1476.738 | −982.735 | 42.777 |
| 1300 | 203.341 | 662.350 | 523.605 | 180.369 | −1473.781 | −941.687 | 37.837 |
| 1400 | 206.091 | 677.522 | 534.063 | 200.843 | −1470.693 | −900.872 | 33.612 |
| 1500 | 208.529 | 691.826 | 544.108 | 221.577 | −1467.506 | −860.281 | 29.958 |
| 1600 | 210.691 | 705.354 | 553.767 | 242.540 | −1464.243 | −819.906 | 26.767 |
| 1700 | 212.608 | 718.186 | 563.065 | 263.707 | −1460.923 | −779.736 | 23.958 |
| 1800 | 214.311 | 730.388 | 572.024 | 285.054 | −1457.560 | −739.763 | 21.467 |
| 1900 | 215.826 | 742.016 | 580.667 | 306.563 | −1454.163 | −699.978 | 19.244 |
| 2000 | 217.176 | 753.122 | 589.015 | 328.214 | −1450.740 | −660.372 | 17.247 |
| 2100 | 218.383 | 763.747 | 597.084 | 349.993 | −1447.291 | −620.939 | 15.445 |
| 2200 | 219.464 | 773.932 | 604.893 | 371.886 | −1443.819 | −581.670 | 13.811 |
| 2300 | 220.435 | 783.709 | 612.456 | 393.882 | −1440.321 | −542.560 | 12.322 |
| 2400 | 221.309 | 793.110 | 619.789 | 415.970 | −1436.795 | −503.602 | 10.961 |
| 2500 | 222.097 | 802.160 | 626.904 | 438.141 | −1433.236 | −464.792 | 9.711 |
| 2600 | 222.811 | 810.885 | 633.813 | 460.387 | −1429.640 | −426.125 | 8.561 |
| 2700 | 223.459 | 819.307 | 640.528 | 482.701 | −1426.002 | −387.598 | 7.499 |
| 2800 | 224.048 | 827.444 | 647.059 | 505.077 | −1422.319 | −349.205 | 6.515 |
| 2900 | 224.585 | 835.316 | 653.416 | 527.509 | −1418.585 | −310.945 | 5.601 |
| 3000 | 225.076 | 842.938 | 659.607 | 549.992 | −1414.798 | −272.815 | 4.750 |
| 3100 | 225.525 | 850.325 | 665.641 | 572.523 | −1410.954 | −234.813 | 3.957 |
| 3200 | 225.938 | 857.492 | 671.525 | 595.096 | −1407.050 | −196.935 | 3.215 |
| 3300 | 226.317 | 864.451 | 677.266 | 617.709 | −1403.085 | −159.180 | 2.520 |
| 3400 | 226.666 | 871.212 | 682.871 | 640.359 | −1399.058 | −121.546 | 1.867 |
| 3500 | 226.989 | 877.787 | 688.347 | 663.042 | −1394.966 | −84.032 | 1.254 |
| 3600 | 227.287 | 884.186 | 693.698 | 685.756 | −1390.811 | −46.635 | 0.677 |
| 3700 | 227.564 | 890.417 | 698.931 | 708.498 | −1386.591 | −9.354 | 0.132 |
| 3800 | 227.820 | 896.489 | 704.051 | 731.268 | −1382.309 | 27.811 | −0.382 |
| 3900 | 228.059 | 902.410 | 709.061 | 754.062 | −1377.964 | 64.863 | −0.869 |
| 4000 | 228.281 | 908.187 | 713.967 | 776.879 | −1373.558 | 101.803 | −1.329 |
| 4100 | 228.488 | 913.827 | 718.773 | 799.717 | −1369.092 | 138.631 | −1.766 |
| 4200 | 228.682 | 919.335 | 723.483 | 822.576 | −1364.569 | 175.351 | −2.181 |
| 4300 | 228.863 | 924.718 | 728.101 | 845.453 | −1359.989 | 211.961 | −2.575 |
| 4400 | 229.032 | 929.981 | 732.630 | 868.348 | −1355.354 | 248.465 | −2.950 |
| 4500 | 229.191 | 935.130 | 737.073 | 891.259 | −1350.667 | 284.863 | −3.307 |
| 4600 | 229.340 | 940.169 | 741.433 | 914.186 | −1345.929 | 321.155 | −3.647 |
| 4700 | 229.481 | 945.103 | 745.714 | 937.127 | −1341.141 | 357.345 | −3.971 |
| 4800 | 229.613 | 949.936 | 749.919 | 960.082 | −1336.306 | 393.433 | −4.281 |
| 4900 | 229.737 | 954.671 | 754.049 | 983.050 | −1331.425 | 429.417 | −4.578 |
| 5000 | 229.854 | 959.314 | 758.108 | 1006.029 | −1326.499 | 465.304 | −4.861 |
| 5100 | 229.965 | 963.867 | 762.098 | 1029.020 | −1321.529 | 501.090 | −5.132 |
| 5200 | 230.070 | 968.333 | 766.021 | 1052.022 | −1316.517 | 536.780 | −5.392 |
| 5300 | 230.169 | 972.717 | 769.880 | 1075.034 | −1311.463 | 572.372 | −5.641 |
| 5400 | 230.263 | 977.020 | 773.676 | 1098.056 | −1306.369 | 607.868 | −5.880 |
| 5500 | 230.352 | 981.246 | 777.412 | 1121.086 | −1301.234 | 643.268 | −6.109 |
| 5600 | 230.436 | 985.397 | 781.089 | 1144.126 | −1296.059 | 678.578 | −6.330 |
| 5700 | 230.516 | 989.477 | 784.709 | 1167.173 | −1290.845 | 713.792 | −6.541 |
| 5800 | 230.593 | 993.486 | 788.274 | 1190.229 | −1285.591 | 748.915 | −6.745 |
| 5900 | 230.665 | 997.429 | 791.786 | 1213.292 | −1280.297 | 783.948 | −6.941 |
| 6000 | 230.734 | 1001.306 | 795.246 | 1236.362 | −1274.963 | 818.889 | −7.129 |

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

### Enthalpy of Formation

The enthalpy of 5 HF(g) → $H_5F_5$(g) was taken as the mean of the 3rd law values which were determined from the equilibrium data of two investigations. Briegleb and Strohmeier[1] measured the vapor density of associated HF between 20 and 60°C and between 50 and 650 torr. Franck and Meyer[2] measured $C_p°$ between −20 and 100°C and between 100 and 700 torr. Each investigation evaluated $K_p$ at n = 2, 3, 4, ... for the reactions n(HF) → $(HF)_n$ and reported 2nd law values of $\Delta_f H$ and $\Delta_f S$. At n = 5 their 2nd law values differed by 5.2 kcal·mol$^{-1}$, which was taken as an estimate of error, while the calculated 3rd law values differed by 3.1 kcal·mol$^{-1}$. Using $\Delta_f H°(298.15\ K) = -30.35$ kcal·mol$^{-1}$ and auxiliary JANAF data[3] gives the enthalpy of formation of $H_5F_5$(g).

### Heat Capacity and Entropy

The molecular structure of $H_5F_5$ was assumed as planar with the F atoms forming the vertices of a regular pentagon and with the H atoms also lying on the circumscribed circle. That rings are more stable than open chains was confirmed by Del Bene and Pople's[4] theoretical molecular-orbital studies on HF polymers. The length of side (F–F axis) was taken from Atoji and Lipscomb's[5] X-ray studies of solid HF (F–F = 2.49 Å) and agrees with the 2.52 Å which Janzen and Bartell[6] determined for HF gaseous polymers by electron diffraction. The low F-bending frequency (53 cm$^{-1}$) was taken from Boutin *et al.*)[7] The other vibrational frequencies were taken from Kittelberger and Hornig's[8] work on crystalline HF. Huong and Couzi[9] and Smith[10] have made spectral studies of the gas phase in the range from 350 to 4000 cm$^{-1}$.

The National Bureau of Standards prepared this table[11] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[11] we recalculate the table in terms of 1973 fundamental constants,[12] 1975 atomic weights,[13] and current JANAF reference states for the elements.

### References

[1] G. Briegleb and W. Strohmeier, Z. Elektrochem. 57, 668 (1953).
[2] E. U. Franck and F. Meyer, Z. Elektrochem 63, 571 (1959).
[3] JANAF Thermochemical Tables: HF(g), 6–30–77.
[4] J. E. Del Bene and J. A. Pople, J. Chem. Phys. 55, 2296 (1971).
[5] M. Atoji and W. N. Lipscomb, Acta Cryst. 7, 173 (1954).
[6] J. Janze and L. S. Bartell, J. Chem. Phys. 50, 3611 (1969).
[7] H. Boutin, G. J. Safford and V. Brajovic, J. Chem. Phys. 39, 3135 (1963).
[8] J. S. Kittelberger and D. F. Hornig, J. Chem. Phys. 46, 3099 (1967).
[9] P. V. Huong and M. Couzi, J. Chim. Phys. 66, 1309 (1969).
[10] D. F. Smith, J. Chem. Phys. 28, 1040 (1958); 48, 1429 (1968).
[11] S. Abramowitz et al., U. S. Nat. Bur. Stand. Report 10904, 239, (1972).
[12] CODATA Task Group on Fundamental Constants, CODATA Bulletin 11, (December 1973).
[13] IUPAC Commission on Atomic Weights, Pure Appl. Chem. 47, 75 (1976).

## Iodine Fluoride ($IF_5$) IDEAL GAS $M_r = 221.896515$ Iodine Fluoride ($IF_5$) $F_5I_1(g)$

$S°(298.15\ K) = 334.663 \pm 2\ 1\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -831.702 \pm 1.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -840.315 \pm 1.5\ kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ |
|---|---|---|
| 710(1) | 604(1) | 631(2) |
| 616(1) | [257](1) | 372(2) |
| 318(1) | 276(1) | 190(2) |

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: $C_{4v}$
Bond Distances: I–F(equatorial) = [1 86] Å; I–F(axial) = [1.75] Å
Bond Angle. F–I–F = [90]°
Product of the Moments of Inertia: $I_A I_B I_C = [4.104805 \times 10^{-113}]\ g^3 \cdot cm^6$

### Enthalpy of Formation

The adopted value is derived from calorimetric data of Settle *et al* [1] for the combustion of iodine in fluorine. Although the combustions gave various mixtures of $IF_5$ and $IF_7$, the proportions ranged up to almost pure pentafluoride. Reduction of the data gave $\Delta_f H° = -210.80 \pm 0.32\ kcal \cdot mol^{-1}$ for $IF_5(l)$ at 298.15 K. The result is essentially independent of the heptafluoride.

Comparison values of $-208.9 \pm [>1]$ and $-208.8 \pm [>1\ 7]\ kcal \cdot mol^{-1}$ may be obtained from calorimetric data of Woolf[2] for hydrolysis in water and in aqueous KOH. Uncertainties for these values include large contributions due to auxiliary data.[3] In particular, we estimate lower limits of $\pm 0.8\ kcal \cdot mol^{-1}$ for $\Delta_f H°$ of $HIO_3(1250\ H_2O)$ and $KIO_3(1250\ H_2O)$ by comparison with recent data.[4]

$\Delta_f H°$ for the ideal gas is derived from that of the liquid by use of $\Delta_{vap} H° = 9.96\ kcal \cdot mol^{-1}$ at 298.15 K. $\Delta_{vap} H°$ was derived by Osborne *et al.*[5] from measurements of vapor pressure and the second virial coefficient.

### Heat Capacity and Entropy

There is no published structural determination for gaseous $IF_5$, but spectral data are consistent with $C_{4v}$ symmetry and a configuration which is approximately a square pyramid. It is uncertain whether the iodine is located above, in, or below the base of the pyramid and whether or not the axial and equatorial I–F distances are equal. We adopt the structure used by Begun *et al.*[7] in correlation of infrared and Raman spectra of $BrF_5$, $IF_5$, $ClF_5$, and $XeOF_4$ by normal coordinate analysis. In this structure the axial bond length is shorter than the equatorial length and the values are close to those observed experimentally for $IF_7$. The iodine is presumed to be in the base of the pyramid. Simplified Huckel–molecular–orbital calculations[8] predict that $C_{4v}$ is the most stable symmetry, that the axial bond is shorter, and that the equatorial flourines are distorted toward the axial fluorine. It is not clear to what extent these predictions depend on the simplified HMO model used in the calculations. Begun *et al.*[7] note that the normal coordinate calculations are insensitive to changes in the bond angles. Principal moments are $I_A = 43.6575 \times 10^{-39}$, $I_B = I_C = 30.6631 \times 10^{-39}\ g \cdot cm^2$.

Vibrational frequencies are based on the assignments of Begun *et al.*[7] as modified by the vapor–phase Raman spectra observed by Selig.[6] Location of the band center of $\nu_9(\sim 200\ cm^{-1})$ is difficult, so we substitute the liquid value of 190 $cm^{-1}$. The Raman–active fundamental $\nu_5$ is not observed for $IF_5$ or any of the similar molecules, so its value is taken from the calculations.[7] Osborne *et al* [5] used calorimetric data at low temperatures to derive $S° = 57.96 \pm 0.06\ cal\ K^{-1} \cdot mol^{-1}$ for the liquid at 330 K. Combining this with $\Delta_{vap} S°$ based on their vapor pressure equation, the authors obtained $S° = 83.06 \pm 0.20\ cal\ K^{-1} \cdot mol^{-1}$ for the ideal gas at 330 K. The corresponding value from this table (82.50) is lower by 0.56 cal $K^{-1} \cdot mol^{-1}$. Part of this difference arises from uncertainties in $\nu_5$ and $\nu_9$ the product of the moments of inertia. We estimate this uncertainty at about 0.5 cal $K \cdot mol^{-1}$. Another source of minor uncertainty is the neglect of anharmonicity in the calculations.

### References

[1] L. Settle, J. H. E. Jeffes, P. A. G. O'Hare and W. N. Hubbard, presented at the 23rd Annual Calorimetry Conference, Midland, Michigan, (August 1968).
[2] A. Woolf, J. Chem. Soc. 231 (1951).
[3] $\Delta_f H°$ values $H_2O(l)$ and $KIO_3(1250\ H_2O)$ are derived from U S. Nat. Bur. Stand. Tech. Note 270–3, (1968), in combination with V. B. Parker, NSRDS–NBS 2, (1965).
[4] P. B. Howard and H. A. Skinner, J. Chem. Soc A1967, 269 (1967); C. Wu, M. M. Birky and L. G Hepler, J. Phys. Chem. 67, 1202 (1963).
[5] D W. Osborne, F. Schreiner, H. Selig, to be published.
[6] H Selig and H. Holzman, Isreal J. Chem. 7, 417 (1969).
[7] G. M. Begun, W. H Fletcher and D. F. Smith, J. Chem. Phys. 42, 2236 (1965).
[8] R. M. Gavin, J Chem. Educ. 46, 413 (1969).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | $J \cdot K^{-1} mol^{-1}$ | | | $kJ \cdot mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| | 0. | 0. | INFINITE | −20.049 | −831.702 | −831 702 | INFINITE |
| 100 | 52.519 | 250.536 | 412.327 | −16 179 | −836.625 | −816.036 | 426.254 |
| 200 | 83.943 | 297.260 | 343.540 | −9.256 | −839.491 | −794.121 | 207.403 |
| 250 | 94.929 | 317.229 | 336.315 | −4.771 | −840.076 | −782.702 | 163.537 |
| 298.15 | 102.878 | 334.663 | 334 663 | 0. | −840.315 | −771.626 | 135.186 |
| 300 | 103.139 | 335.300 | 334 664 | 0.191 | −840.319 | −771.200 | 134.278 |
| 350 | 109.222 | 351.679 | 335.944 | 5.507 | −840.381 | −759.674 | 113.375 |
| 400 | 113.756 | 366.574 | 338.856 | 11.087 | −848.290 | −747.874 | 97.662 |
| 450 | 117.181 | 380.179 | 342.703 | 16.864 | −848.697 | −735.297 | 85.351 |
| 500 | 119.808 | 392.667 | 347.084 | 22.792 | −869.098 | −720.779 | 75.299 |
| 600 | 123.478 | 414.861 | 356.577 | 34.970 | −867.480 | −691.265 | 60.180 |
| 700 | 125.838 | 434.085 | 366.308 | 47.444 | −865.769 | −662.030 | 49 401 |
| 800 | 127.434 | 450.999 | 375.858 | 60.113 | −864 013 | −633.044 | 41.334 |
| 900 | 128.559 | 466.078 | 385.060 | 72.916 | −862.241 | −604.279 | 35.071 |
| 1000 | 129.379 | 479.667 | 393.853 | 85.815 | −860.468 | −575.712 | 30.072 |
| 1100 | 129 994 | 492.029 | 402.224 | 98.785 | −858.705 | −547.322 | 25.990 |
| 1200 | 130.468 | 503.361 | 410.187 | 111.809 | −856.962 | −519.091 | 22.595 |
| 1300 | 130.839 | 513.819 | 417.761 | 124.875 | −855.247 | −491.005 | 19.729 |
| 1400 | 131.135 | 523.526 | 424.974 | 137.974 | −853.568 | −463.050 | 17.277 |
| 1500 | 131.376 | 532.582 | 431.849 | 151 100 | −851.932 | −435.213 | 15.155 |
| 1600 | 131.573 | 541.068 | 438.413 | 164.248 | −850.345 | −407.484 | 13.303 |
| 1700 | 131 738 | 549 049 | 444.688 | 177.414 | −848.810 | −379.852 | 11.671 |
| 1800 | 131.876 | 556.583 | 450.697 | 190.594 | −847.329 | −352.309 | 10.224 |
| 1900 | 131.993 | 563.717 | 456.460 | 203 788 | −845.901 | −324 848 | 8.931 |
| 2000 | 132.093 | 570.490 | 461.993 | 216.993 | −844.519 | −297 460 | 7.769 |
| 2100 | 132 180 | 576.937 | 467.315 | 230.206 | −843.177 | −270 140 | 6.719 |
| 2200 | 132.255 | 583.087 | 472.438 | 243.428 | −841.864 | −242.884 | 5.767 |
| 2300 | 132.320 | 588.968 | 477.378 | 256.657 | −840.569 | −215.686 | 4.898 |
| 2400 | 132.378 | 594.601 | 482.146 | 269.892 | −839.277 | −188.545 | 4.104 |
| 2500 | 132.429 | 600.006 | 486.753 | 283 132 | −837.975 | −161.458 | 3.373 |
| 2600 | 132.474 | 605.200 | 491.209 | 296.378 | −836.649 | −134.423 | 2.701 |
| 2700 | 132.514 | 610.201 | 495.524 | 309.627 | −835.284 | −107.440 | 2.079 |
| 2800 | 132.550 | 615.021 | 499.706 | 322.880 | −833.867 | −80.509 | 1.502 |
| 2900 | 132.583 | 619.673 | 503.763 | 336.137 | −832.387 | −53.629 | 0 966 |
| 3000 | 132.612 | 624.168 | 507.702 | 349.397 | −830.832 | −26.802 | 0 467 |
| 3100 | 132.638 | 628.517 | 511.530 | 362.659 | −829 193 | −0.028 | 0. |
| 3200 | 132.662 | 632.728 | 515.252 | 375.924 | −827.461 | 26.692 | −0.436 |
| 3300 | 132.684 | 636.811 | 518.874 | 389.192 | −825 629 | 53.357 | −0.845 |
| 3400 | 132.704 | 640.772 | 522.401 | 402.461 | −823.693 | 79.964 | −1.228 |
| 3500 | 132.723 | 644.619 | 525.838 | 415.732 | −821.647 | 106.512 | −1.590 |
| 3600 | 132.740 | 648.358 | 529.190 | 429.006 | −819.489 | 133 001 | −1.930 |
| 3700 | 132.755 | 651.995 | 532.460 | 442.280 | −817.216 | 159.428 | −2.251 |
| 3800 | 132.769 | 655.536 | 535.653 | 455.557 | −814.827 | 185.792 | −2.554 |
| 3900 | 132.782 | 658.985 | 538.771 | 468.834 | −812.322 | 212.092 | −2.841 |
| 4000 | 132.795 | 662.347 | 541.818 | 482.113 | −809.700 | 238.326 | −3.112 |
| 4100 | 132.806 | 665.626 | 544.798 | 495.393 | −806.963 | 264.492 | −3.370 |
| 4200 | 132.817 | 668.826 | 547.713 | 508.674 | −804 111 | 290.592 | −3.614 |
| 4300 | 132.826 | 671.952 | 550.567 | 521.956 | −801.146 | 316.621 | −3.846 |
| 4400 | 132.836 | 675.005 | 553.360 | 535.239 | −798.071 | 342.580 | −4.067 |
| 4500 | 132.844 | 677.991 | 556 097 | 548.523 | −794.887 | 368.469 | −4.277 |
| 4600 | 132.852 | 680.911 | 558.778 | 561.808 | −791.596 | 394.285 | −4.477 |
| 4700 | 132.860 | 683.768 | 561.407 | 575.094 | −788.202 | 420.029 | −4.668 |
| 4800 | 132.867 | 686.565 | 563.986 | 588.380 | −784.707 | 445.699 | −4.850 |
| 4900 | 132.873 | 689.305 | 566.515 | 601.667 | −781.114 | 471.295 | −5.024 |
| 5000 | 132 879 | 691.989 | 568.998 | 614.955 | −777.425 | 496.817 | −5.190 |
| 5100 | 132.885 | 694.621 | 571.436 | 628.243 | −773.644 | 522.265 | −5.349 |
| 5200 | 132.891 | 697.201 | 573.830 | 641.532 | −769 772 | 547.638 | −5.501 |
| 5300 | 132.896 | 699.732 | 576.181 | 654.821 | −765.814 | 572.935 | −5 647 |
| 5400 | 132.901 | 702.217 | 578.492 | 668 111 | −761.771 | 598.156 | −5.786 |
| 5500 | 132.906 | 704 655 | 580.764 | 681.401 | −757.647 | 623.301 | −5.920 |
| 5600 | 132.910 | 707.050 | 582.998 | 694.692 | −753.444 | 648.373 | −6.048 |
| 5700 | 132.914 | 709.403 | 585 195 | 707.983 | −749.164 | 673.366 | −6.171 |
| 5800 | 132.918 | 711 714 | 587.356 | 721.275 | −744.811 | 698.285 | −6.289 |
| 5900 | 132.922 | 713 986 | 589 483 | 734.567 | −740.386 | 723.129 | −6.402 |
| 6000 | 132 926 | 716.220 | 591.577 | 747.859 | −735.893 | 747.896 | −6.511 |

PREVIOUS December 1969 (1 atm) CURRENT· December 1969 (1 bar)

# Molybdenum Fluoride ($MoF_5$) IDEAL GAS $M_r$ = 190.932015 Molybdenum Fluoride ($MoF_5$) $F_5Mo_1(g)$

$S^\circ$(298 15 K) = 347.655 ± 8.4 J $K^{-1} \cdot mol^{-1}$

$\Delta_f H^\circ$(0 K) = −1235 878 ± 4.2 kJ$\cdot mol^{-1}$

$\Delta_f H^\circ$(298.15 K) = −1241 393 ± 4.2 kJ$\cdot mol^{-1}$

| Electronic Levels and Quantum Weights | |
|---|---|
| $\epsilon_i$, $cm^{-1}$ | $g_i$ |
| 0 | [2] |
| [1000] | [2] |
| [7500] | [2] |
| [25000] | [4] |

| Vibrational Frequencies and Degeneracies | |
|---|---|
| $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ |
| 759 (1) | 713 (2) |
| 738 (1) | 261 (2) |
| 683 (1) | 112 (2) |
| [500](1) | [200](2) |

Point Group: $[D_{3h}]$ $\sigma$ = [6]

Bond Distance: Mo–F = [1.78] Å

Bond Angle: F–Mo–F = [90]°

Product of the Moments of Inertia: $I_A I_B I_C$ = [3.670258 × $10^{-113}$] $g^3$ $cm^6$

## Enthalpy of Formation

We adopt the enthalpy of formation at 298.15 K derived by Brewer[1] from the high temperature mass spectrometric measurements of equilibria among gaseous molybdenum fluorides by Hildenbrand [1143–1664 K][2] and by Kleinschmidt *et al*. [460–525 K].[8] The value of $\Delta_f H^\circ$(0 K) combined with JANAF data[3] for Mo(g) and F(g) gives $\Delta_a H^\circ$(0 K) = 544.3 ± 4 kcal$\cdot mol^{-1}$ and an average Mo–F bond energy of $\Delta_a H^\circ$(0 K)/5 = 108.9 ± 1 kcal$\cdot mol^{-1}$.

## Heat Capacity and Entropy

Hildenbrand,[4] Douglas,[5] and Krause[6] have calculated somewhat different thermodynamic properties of $MoF_5$(g) monomer All have used the vibrational frequencies, $cm^{-1}$, and degeneracies determined by Acquista and Abramowitz[7] —759,[1] 738,[1] 683,[1] 713,[2] 261,[2] and 112[2] — and an estimated frequency of 500.[1] For the remaining doubly degenerate frequency, Hildenbrand[4] estimated 200 $cm^{-1}$ and both Douglas[5] and Drause[6] estimated 400 $cm^{-1}$. We follow Brewer[1] who has used the determined vibrational frequencies and the estimated frequencies [500][1] and [200],[2] as had Hildenbrand.[4]

From the following analysis, Brewer[1] has attempted to define the electronic contribution more accurately then just a ground state degeneracy of 2[4 5] or 4.[6] $Mo^{5+}$ has only the low–lying electronic state $^2D$ with a spin orbit splitting of 2578 $cm^{-1}$ and a total degeneracy of 10. From the liquid field treatment of $ReF_6$ by Moffitt *et al*.,[9] one might expect an intermediate coupling case with a $t_{3/2}$ quartet ground state and a low–lying $t_{1/2}$ state, with the next quartet state well above 20000 $cm^{-1}$. Peacock and Sleight[10] observed an absorption in liquid $MoF_5$ at 7500 $cm^{-1}$. For $MoF_5$ monomer, the actual levels would be split more. On this basis, the following electronic energy levels, $cm^{-1}$, and quantum weights were assigned.[1] 0,[2] [1000],[2] [7500],[2] and [25000].[4]

The trigonal bipyramid symmetry tentatively assigned by Acquista and Abramowitz[7] is used with the Mo–F distance of 1.78 Å adopted by Brewer.[1] The principal moments of inertia are. $I_A$ = 29 9871 × $10^{-39}$ g $cm^2$, $I_B = I_C$ = 34.9849 × $10^{-39}$ g$\cdot cm^2$.

This table is based on the critical analysis of data existing in 1978 by Brewer [1].

## References

[1] L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, berkeley; personal communication, (September 1978), of preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.

[2] D. L. Hildenbrand, J. Chem. Phys. 65, 614 (1976).

[3] JANAF Thermochemical Tables: Mo(g), 3–31–78; F(g), 9–30–65.

[4] D. L. Hildenbrand, Stanford Research Institute, personal communication to L. Brewer.

[5] T. B. Douglas, J. Chem. Thermodyn. 9, 1165 (1977).

[6] R. F. Krause, Jr., in Proc. Symp. on High Temperature Metal Halide Chemistry, D. L. Hildenbrand and D. D. Cubicciotti, Eds., The Electrochem. Soc., Vol. 78–1, pp. 199–209, (1978).

[7] N. Acquista and S. Abramowitz, J. Chem. Phys. 58, 5484 (1973).

[8] P. D. Kleinschmidt, K H. Lau, and D. L. Hildenbrand, J. Chem. Thermodyn. 11, 765 (1979).

[9] W. Moffitt, G. L. Goodman, M. Fred, and B Weinstock, Molecular Physics 2, 109 (1959) and G. L. Goodman, Ph. D. Thesis, Harvard, (1959).

[10] R. D. Peacock and J. P. Sleight, J Fluorine Chem. 1, 253 (1971).

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p^\circ$ = 0.1 MPa

| | J$\cdot K^{-1}mol^{-1}$ | | | kJ$\cdot mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ - H^\circ(T_r)]/T$ | $H^\circ - H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −21.132 | −1235.878 | −1235.878 | INFINITE |
| 100 | 61.633 | 259.654 | 426.629 | −16.697 | −1239.202 | −1221.872 | 638.241 |
| 200 | 85.339 | 310.140 | 356.534 | −9.279 | −1240.948 | −1203.754 | 314.388 |
| 250 | 94.948 | 330.241 | 349.304 | −4.766 | −1241.309 | −1194.408 | 249.558 |
| 298.15 | 102.763 | 347 655 | 347.655 | 0. | −1241.393 | −1185.363 | 207.671 |
| 300 | 103 034 | 348.291 | 347.657 | 0 190 | −1241.392 | −1185.016 | 206.330 |
| 350 | 109.545 | 364 682 | 348.936 | 5.511 | −1241.257 | −1175.628 | 175 453 |
| 400 | 114.655 | 379.658 | 351.854 | 11.121 | −1240 964 | −1166.271 | 152.299 |
| 450 | 118.614 | 393.401 | 355.718 | 16.957 | −1240.561 | −1156.957 | 134.296 |
| 500 | 121.664 | 406.063 | 360.127 | 22.968 | −1240 081 | −1147.693 | 119.899 |
| 600 | 125.825 | 428.645 | 369.712 | 35.360 | −1238.989 | −1129.316 | 98.316 |
| 700 | 128.324 | 448.245 | 379.562 | 48.078 | −1237.823 | −1111.129 | 82.913 |
| 800 | 129.862 | 465 489 | 389.247 | 60.993 | −1236.652 | −1093.110 | 71.373 |
| 900 | 130.837 | 480.845 | 398.587 | 74.032 | −1235.516 | −1075.236 | 62.405 |
| 1000 | 131.478 | 494.665 | 407.516 | 87.150 | −1234.435 | −1057.485 | 55.237 |
| 1100 | 131.918 | 507.218 | 416.018 | 100.321 | −1233 426 | −1039.840 | 49.378 |
| 1200 | 132.235 | 518.711 | 424.103 | 113.529 | −1232.501 | −1022.282 | 44.499 |
| 1300 | 132.478 | 529.305 | 431.794 | 126.765 | −1231.669 | −1004.799 | 40.373 |
| 1400 | 132.676 | 539.130 | 439.114 | 140.023 | −1230.938 | −987.375 | 36.839 |
| 1500 | 132.847 | 548.290 | 446.090 | 153.300 | −1230.313 | −970.001 | 33 778 |
| 1600 | 133.001 | 556 869 | 452 749 | 166.592 | −1229.799 | −952.664 | 31 101 |
| 1700 | 133.147 | 564 936 | 459.113 | 179.899 | −1229.401 | −935.355 | 28 740 |
| 1800 | 133.285 | 572.551 | 465.206 | 193.221 | −1229.120 | −918.067 | 26.642 |
| 1900 | 133.420 | 579.761 | 471.047 | 206.556 | −1228.959 | −900.792 | 24.764 |
| 2000 | 133.550 | 586 608 | 476.655 | 219.905 | −1228.919 | −883.521 | 23.075 |
| 2100 | 133.676 | 593.127 | 482.047 | 233.266 | −1229.002 | −866.250 | 21.547 |
| 2200 | 133 799 | 599.348 | 487.239 | 246 640 | −1229.208 | −848.972 | 20 157 |
| 2300 | 133 916 | 605.298 | 492.244 | 260.026 | −1229.537 | −831.681 | 18 888 |
| 2400 | 134.028 | 611 000 | 497.074 | 273.423 | −1229.992 | −814.374 | 17.724 |
| 2500 | 134.135 | 616.474 | 501.741 | 286.831 | −1230.573 | −797.045 | 16.653 |
| 2600 | 134.236 | 621.736 | 506.256 | 300.250 | −1231.296 | −779.690 | 15.664 |
| 2700 | 134.331 | 626.804 | 510.627 | 313 678 | −1232.191 | −762.304 | 14.748 |
| 2800 | 134.419 | 631.691 | 514.864 | 327 116 | −1233.313 | −744.881 | 13.896 |
| 2900 | 134.502 | 636.410 | 518.974 | 340.562 | −1270.622 | −727.363 | 13.101 |
| 3000 | 134.579 | 640.971 | 522.965 | 354.016 | −1270.386 | −708.634 | 12.338 |
| 3100 | 134.649 | 645.385 | 526.844 | 367.478 | −1270.077 | −689.915 | 11.625 |
| 3200 | 134.714 | 649.661 | 530.615 | 380.946 | −1269.689 | −671.205 | 10.956 |
| 3300 | 134.774 | 653.807 | 534.286 | 394.420 | −1269.220 | −652.510 | 10.328 |
| 3400 | 134.829 | 657.831 | 537.861 | 407.901 | −1268.666 | −633.830 | 9.738 |
| 3500 | 134.880 | 661.740 | 541.344 | 421.386 | −1268.026 | −615.167 | 9.181 |
| 3600 | 134.926 | 665.541 | 544.742 | 434.876 | −1267.297 | −596.524 | 8.655 |
| 3700 | 134.969 | 669.238 | 548.057 | 448.371 | −1266.480 | −577.902 | 8.159 |
| 3800 | 135.008 | 672.838 | 551.293 | 461.870 | −1265.573 | −559.305 | 7.688 |
| 3900 | 135.044 | 676.345 | 554.455 | 475.373 | −1264.577 | −540.731 | 7.242 |
| 4000 | 135 078 | 679 765 | 557.545 | 488.879 | −1263.492 | −522.184 | 6.819 |
| 4100 | 135.109 | 683.101 | 560.567 | 502.388 | −1262.319 | −503.666 | 6.417 |
| 4200 | 135.138 | 686.357 | 563.523 | 515.900 | −1261.059 | −485.177 | 6.034 |
| 4300 | 135.166 | 689.537 | 566.417 | 529.416 | −1259.713 | −466.720 | 5.670 |
| 4400 | 135.192 | 692.645 | 569.251 | 542.934 | −1258.282 | −448.295 | 5.322 |
| 4500 | 135.217 | 695.683 | 572.027 | 556.454 | −1256.769 | −429.902 | 4.990 |
| 4600 | 135.241 | 698.655 | 574.747 | 569.977 | −1255.174 | −411.545 | 4 673 |
| 4700 | 135.265 | 701.564 | 577.415 | 583.502 | −1253.500 | −393.223 | 4.370 |
| 4800 | 135.288 | 704.412 | 580.031 | 597.030 | −1251.748 | −374.938 | 4.080 |
| 4900 | 135.310 | 707.202 | 582.598 | 610.560 | −1249.921 | −356.690 | 3.802 |
| 5000 | 135.332 | 709.936 | 585.117 | 624.092 | −1839.405 | −332.748 | 3 476 |
| 5100 | 135.354 | 712 616 | 587.591 | 637.626 | −1839.111 | −302.618 | 3.099 |
| 5200 | 135.376 | 715.245 | 590.021 | 651.163 | −1838.894 | −272.493 | 2.737 |
| 5300 | 135.398 | 717.823 | 592.408 | 664.702 | −1838.752 | −242.371 | 2.389 |
| 5400 | 135.420 | 720.355 | 594.754 | 678.243 | −1838.688 | −212.252 | 2.053 |
| 5500 | 135 443 | 722.840 | 597.060 | 691.786 | −1838.698 | −182.133 | 1.730 |
| 5600 | 135.465 | 725.280 | 599.328 | 705.331 | −1838.785 | −152.012 | 1 418 |
| 5700 | 135.488 | 727.678 | 601.559 | 718.879 | −1838.945 | −121.891 | 1.117 |
| 5800 | 135.510 | 730.035 | 603.754 | 732.429 | −1839.179 | −91.766 | 0.826 |
| 5900 | 135.533 | 732.351 | 605.914 | 745.981 | −1839.483 | −61.635 | 0.546 |
| 6000 | 135.556 | 734.629 | 608 040 | 759.535 | −1839.859 | −31.500 | 0.274 |

PREVIOUS: December 1978 (1 atm)    CURRENT: December 1978 (1 bar)

Molybdenum Fluoride ($MoF_5$) $F_5Mo_1(g)$

## Phosphorus Fluoride ($PF_5$) IDEAL GAS $M_r = 125.965775$ Phosphorus Fluoride ($PF_5$) $F_5P_1(g)$

$S°(298.15\ K) = 300.810 \pm 2.1\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -1583.514 \pm 2.9\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298\ 15\ K) = -1594.409 \pm 2.9\ kJ{\cdot}mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|
| 817 (1) | 1025 (2) |
| 640 (1) | 532.5(2) |
| 946.6(1) | 179 (2) |
| 575.1(1) | 514 (2) |

Ground State Quantum Weight: [1] $\sigma = 6$
Point Group: $D_{3h}$
Bond Distances: $P–F_{eq} = 1.534 \pm 0.004$ Å; $P–F_{ax} = 1.577 \pm 0.005$ Å
Bond Angles: $F_{eq}–P–F_{eq} = 120 \pm 0.4°$; $F_{eq}–P–F_{ax} = 74.3 \pm 0.4°$
Product of the Moments of Inertia: $I_AI_BI_C = 1.614 \times 10^{-113}\ g^3{\cdot}cm^6$

### Enthalpy of Formation

Gross *et al.*[1] measured the heat of combustion of α–white phosphorus in fluorine at 25 °C. They reported an enthalpy of formation of $-381.4 \pm 0.8\ kcal{\cdot}mol^{-1}$ (based on α–white phosphorus standard state) calculated from their combustion studies. Similar combustion studies were performed by O'Hare and Hubbard.[2] They reported a enthalpy of formation of $-380.8 \pm 0.3\ kcal{\cdot}mol^{-1}$ (α– white phosphorus standard state), which is in excellent agreement with the work of Gross *et al.*[1] An average value of $-381.1 \pm 0.5\ kcal{\cdot}mol^{-1}$ is adopted for this tabulation. Converting to the P(red,V) standard state with a $\Delta_fH$ trans $= 4.2 \pm 0.2\ kcal{\cdot}mol^{-1}$,[3] we derive, $\Delta_fH°(PF_5, g, 298.15\ K) = -376.9 \pm 0.7\ kcal{\cdot}mol^{-1}$ ($-1576.950 \pm 2.9\ kJ{\cdot}mol^{-1}$).

### Heat Capacity and Entropy

The molecular structure and bond lengths given above for $PF_5$ were recently determined by Hansen and Bartell[4] from electron–diffraction studies. These results indicate that $PF_5$ has a trigonal bipyramid structure with nonequivalent axial and equatorial bonds. Wyatt *et al.*[5] determined rotational constants for $PF_5$ from a study of the infrared vibration–rotation band contour of the $\nu_4$(575 cm$^{-1}$) fundamental. Their analysis led to the following P–F bond lengths which are in excellent agreement with the electron–diffraction results: $r_{eq} = 1.534 \pm 0.024$Å and $r_{ax} = 1.581 \pm 0.025$Å. Individual moments of inertia, calculated from the rotational constants given by Wyatt *et al.*[5] and adopted for this table, are $I_A = 2.230 \times 10^{-38}$ g cm$^2$ and $I_B = I_C = 2.690 \times 10^{-38}$ g cm$^2$. The electron diffraction data lead to a product of moments of inertia of $1.604 \times 10^{-113}\ g^3{\cdot}cm^6$.

Several recent infrared and Raman studies[6,7,8] have been reported for $PF_5$. These data are in good agreement except for the $\nu_7$ fundamental. Griffiths *et al.*[6] originally assigned this fundamental to the 126 cm$^{-1}$ band observed in their infrared spectra. Hoskins[9] later attributed this band to one of the pure rotational lines of hydrogen fluoride, which he felt was present in the sample as an impurity. Further work by Griffiths[10] on the pressure dependence of the infrared spectra of $PF_5$ indicated that the missing fundamental should be assigned to the weak band at 301 cm$^{-1}$. Deiters and Holmes[11] recently showed that this band is not a fundamental of $PF_5$ but a difference band ($\nu_3$–$\nu_2$). Very recently, Levin[8] investigated the Raman spectra of solid phosphorus pentafluoride and assigned the $\nu_7$ fundamental to the 179 cm$^{-1}$ band. Also, Beattie *et al.*[12] investigated the Raman spectra of $PF_5$ in the gas phase at 25°C and 125°C and assigned the $\nu_7$ fundamental to 175 cm$^{-1}$ band which is in excellent agreement with Levin's assignment.[8] The fundamental vibrational frequencies of Holmes and Lord[7] are adopted along with Levin's assignment[8] of the $\nu_7$ fundamental (179 cm$^{-1}$).

### References

[1] P Gross, C. Hayman and M. C. Stuart, Trans. Faraday Soc. 62, 2716 (1966).
[2] P. A. G. O'Hare and W. N Hubbard, Trans. Faraday Soc. 62, 2709 (1966).
[3] JANAF Thermochemical Tables: P(red, v), 6–30–61.
[4] K. W. Hansen and L. S Bartell, Inorg. Chem. 4, 1775 (1965).
[5] R. Wyatt, J T. Roberts, R. E. Wentz and R. M. Wilt, J. Chem. Phys. 50, 2552 (1969).
[6] J. E. Griffiths, R. P. Carter and R. R. Holmes, J. Chem. Phys. 41, 63 (1964).
[7] L. C. Hoskins and R. C. Lord, J Chem. Phys. 46, 2402 (1967).
[8] I. W. Levin, J. Chem. Phys. 50, 1031 (1969).
[9] L. C. Hoskins, J. Chem. Phys. 42, 2631 (1965).
[10] J. E. Griffiths, J. Chem. Phys. 42, 2631 (1965).
[11] R. M. Deiters and R. R. Holmes, J. Chem. Phys. 48, 4796 (1968).
[12] I. R. Beattie, K. M. S. Livingston and D. J. Reynolds, J. Chem. Phys. 51, 4269 (1969).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | S° | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0 | INFINITE | −16.527 | −1583.514 | −1583.514 | INFINITE |
| 100 | 44.341 | 234.160 | 362.483 | −12.832 | −1587.974 | −1567.029 | 818.532 |
| 200 | 65 173 | 270.951 | 307.973 | −7 404 | −1592.132 | −1544.571 | 403.401 |
| 250 | 75.849 | 286.661 | 302.158 | −3.874 | −1593.450 | −1532.521 | 320.203 |
| 298.15 | 84.836 | 300.810 | 300.810 | 0. | −1594.409 | −1520.695 | 266.419 |
| 300 | 85.152 | 301.336 | 300.811 | 0.157 | −1594.441 | −1520.237 | 264.697 |
| 350 | 92.905 | 315.064 | 301.878 | 4.615 | −1595.891 | −1507.738 | 225 018 |
| 400 | 99.238 | 327.897 | 304.337 | 9.424 | −1596.474 | −1495.102 | 195.240 |
| 450 | 104.373 | 339.893 | 307.629 | 14.519 | −1596.864 | −1482.405 | 172.073 |
| 500 | 108.537 | 351.113 | 311.423 | 19.845 | −1597.100 | −1469.673 | 153.536 |
| 600 | 114.710 | 371.484 | 319.771 | 31.028 | −1597.234 | −1444.169 | 125.726 |
| 700 | 118.917 | 389.503 | 328.471 | 42.722 | −1597.051 | −1418.669 | 105.862 |
| 800 | 121.874 | 405.586 | 337.124 | 54.770 | −1596.660 | −1393.211 | 90.967 |
| 900 | 124.015 | 420.071 | 345.549 | 67.070 | −1596.127 | −1367.811 | 79.386 |
| 1000 | 125.608 | 433.224 | 353.669 | 79.555 | −1595.500 | −1342.475 | 70.124 |
| 1100 | 126.821 | 445.255 | 361.456 | 92.179 | −1594.808 | −1317.206 | 62.549 |
| 1200 | 127 763 | 456.332 | 368.906 | 104.910 | −1657.647 | −1290.923 | 56.192 |
| 1300 | 128.509 | 466.589 | 376.031 | 117.725 | −1656.113 | −1260.424 | 50.644 |
| 1400 | 129 109 | 476.135 | 382.844 | 130.607 | −1654.570 | −1230.045 | 45.894 |
| 1500 | 129.598 | 485.060 | 389.364 | 143.543 | −1653.027 | −1199.776 | 41.780 |
| 1600 | 130.002 | 493.437 | 395.610 | 156.524 | −1651.488 | −1169.609 | 38.184 |
| 1700 | 130.339 | 501.329 | 401.599 | 169.541 | −1649.958 | −1139.538 | 35.014 |
| 1800 | 130.623 | 508.787 | 407.348 | 182.590 | −1648.435 | −1109.557 | 32.199 |
| 1900 | 130.865 | 515.856 | 412.875 | 195.664 | −1646.919 | −1079.662 | 29.682 |
| 2000 | 131.072 | 522.574 | 418.193 | 208.762 | −1645.406 | −1049.845 | 27.419 |
| 2100 | 131.251 | 528.973 | 423.317 | 221.878 | −1643.891 | −1020.104 | 25.374 |
| 2200 | 131.407 | 535.083 | 428.260 | 235.011 | −1642.367 | −990.436 | 23.516 |
| 2300 | 131.543 | 540.927 | 433.032 | 248.159 | −1640.827 | −960.836 | 21.821 |
| 2400 | 131.663 | 546.528 | 437.645 | 261.319 | −1639.264 | −931.305 | 20.269 |
| 2500 | 131.769 | 551.905 | 442.109 | 274.491 | −1637.670 | −901.840 | 18.843 |
| 2600 | 131.863 | 557.075 | 446.432 | 287.672 | −1636.036 | −872.439 | 17.528 |
| 2700 | 131.947 | 562.053 | 450.623 | 300.863 | −1634.356 | −843.101 | 16.311 |
| 2800 | 132.022 | 566.853 | 454.688 | 314.061 | −1632.622 | −813.827 | 15.182 |
| 2900 | 132.090 | 571.487 | 458.637 | 327.267 | −1630.828 | −784.616 | 14.132 |
| 3000 | 132.151 | 575.966 | 462.473 | 340.479 | −1628.968 | −755.468 | 13.154 |
| 3100 | 132.206 | 580.300 | 466.205 | 353.697 | −1627.036 | −726.383 | 12.239 |
| 3200 | 132.257 | 584.499 | 469.836 | 366.920 | −1625.030 | −697.361 | 11.383 |
| 3300 | 132.303 | 588.569 | 473.373 | 380.148 | −1622.944 | −668.403 | 10.580 |
| 3400 | 132.345 | 592.519 | 476.819 | 393.381 | −1620.777 | −639.510 | 9.825 |
| 3500 | 132.383 | 596.356 | 480.180 | 406.617 | −1618.525 | −610.682 | 9.114 |
| 3600 | 132.418 | 600.086 | 483.459 | 419.857 | −1616.188 | −581.919 | 8.443 |
| 3700 | 132 451 | 603.715 | 486.660 | 433.101 | −1613.765 | −553.223 | 7.810 |
| 3800 | 132 481 | 607.247 | 489.788 | 446.347 | −1611.254 | −524.593 | 7.211 |
| 3900 | 132.508 | 610.689 | 492.844 | 459.597 | −1608.657 | −496.030 | 6 644 |
| 4000 | 132.534 | 614.044 | 495.832 | 472.849 | −1605.972 | −467.535 | 6.105 |
| 4100 | 132.558 | 617.317 | 498.755 | 486 103 | −1603.202 | −439.109 | 5.594 |
| 4200 | 132.580 | 620.512 | 501.616 | 499.360 | −1600.346 | −410.750 | 5.108 |
| 4300 | 132.601 | 623.632 | 504.418 | 512.619 | −1597.407 | −382.462 | 4.646 |
| 4400 | 132.620 | 626.680 | 507.162 | 525.880 | −1594.384 | −354.242 | 4.205 |
| 4500 | 132.638 | 629.661 | 509.851 | 539.143 | −1591.281 | −326.091 | 3.785 |
| 4600 | 132.655 | 632.576 | 512 487 | 552 408 | −1588.099 | −298.011 | 3.384 |
| 4700 | 132.670 | 635.429 | 515.073 | 565.674 | −1584.839 | −270.000 | 3.001 |
| 4800 | 132.685 | 638.223 | 517.610 | 578.942 | −1581.503 | −242.060 | 2.634 |
| 4900 | 132.699 | 640.959 | 520 099 | 592.211 | −1578.094 | −214.190 | 2.283 |
| 5000 | 132.712 | 643.640 | 522.543 | 605 482 | −1574.613 | −186.391 | 1.947 |
| 5100 | 132.725 | 646.268 | 524 943 | 618.754 | −1571.062 | −158 661 | 1.625 |
| 5200 | 132 736 | 648.845 | 527.301 | 632.027 | −1567.443 | −131.002 | 1.316 |
| 5300 | 132.747 | 651.374 | 529.619 | 645.301 | −1563.759 | −103.413 | 1.019 |
| 5400 | 132.758 | 653.855 | 531.896 | 658.576 | −1560.011 | −75.895 | 0.734 |
| 5500 | 132.767 | 656.291 | 534.136 | 671.852 | −1556.201 | −48.447 | 0.460 |
| 5600 | 132.777 | 658.683 | 536.339 | 685.130 | −1552.332 | −21.067 | 0.197 |
| 5700 | 132.785 | 661.034 | 538.506 | 698.408 | −1548 404 | 6.241 | −0.057 |
| 5800 | 132.794 | 663.343 | 540.638 | 711.687 | −1544.420 | 33.481 | −0.302 |
| 5900 | 132.802 | 665.613 | 542 737 | 724.966 | −1540.382 | 60.653 | −0.537 |
| 6000 | 132.809 | 667.845 | 544.804 | 738.247 | −1536.291 | 87.754 | −0.764 |

PREVIOUS. December 1969 (1 atm) CURRENT· December 1969 (1 bar)

## Sulfur Fluoride ($SF_5$) IDEAL GAS $M_r = 127.052015$ Sulfur Fluoride ($SF_5$) $F_5S_1(g)$

$\Delta_fH°(0\ K) = -898.295 \pm 15.1\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = [304.752 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = -908.447 \pm 15.1\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

| $\epsilon_i$, cm | $g_i$ | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
|---|---|---|---|
| 0 | [2] | [25000] | [2] |
| [10000] | [2] | [30000] | [2] |
| [20000] | [2] | | |

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|---|
| [800](1) | [550](1) | 812 (2) |
| [600](1) | [400](1) | 552 (2) |
| [550](1) | [450](1) | [350] (2) |

Point Group: $C_{4v}$ $\sigma = 4$
Bond Distances: S–F* = [1.58]Å; S–F** = [1.51]Å
Bond Angles: F*–S–F* = [90]°; F**–S–F* = [90]°
(* = equatorial, ** = axial)
Product of the Moments of Inertia: $I_AI_BI_C = [1.415983 \times 10^{-113}]\ g^3 \cdot cm^6$

### Enthalpy of Formation

$\Delta_fH°(0\ K)$ is calculated from the bond dissociation process $SF_6(g) = SF_5(g) + F(g)$ with $D_0° = 92.0 \pm 3.0\ kcal \cdot mol^{-1}$ and JANAF auxiliary enthapies of formation.[1] The information which was considered in arriving at the selected $D_0°$ value is reviewed below. Another recent review[2] of the thermodynamics of $SF_5$ led to selected values of $D_0°(SF_5–F) = 92.6 \pm 3.0\ kcal \cdot mol^{-1}$ and $\Delta_fH°(298.15\ K) = -218 \pm\ 3\ kcal\ mol^{-1}$ which agree with the results adopted here.

The electron–impact appearance potential of $F^-$ from $SF_6$ has been reported as approximately zero by Harland and Thynne[3] and Curran.[4] In addition, Curran[4] measured the kinetic energy of the negative ion and found K.E. (Total) = 0.23 ± 0.05 eV. Combining these results with EA(F) = 3.399 eV,[1] we obtain an upper limit value for $D_0°$ of <3.2 eV (73.1 kcal·mol$^{-1}$).

Modica[5] performed shock tube measurements on mixtures of $SF_6/Ar$, $SF_5Cl/Ar$, and $SF_6/H_2$ and analyzed the equilibrium data with a thermochemical equilibrium computer program. With $\Delta_fH°(SF_4, g, 0\ K) = -172.2\ kcal \cdot mol^{-1}$, Modica [5] adjusted the value of $\Delta_fH°$ for $SF_5$ to bring the calculated and experimental $SF_4/HF$ concentrations into good agreement. These results suggest $\Delta_fH°(SF_5, g, 0\ K) = -241.7\ kcal \cdot mol^{-1}$ or $D_0°(SF_5–F) = 65.2\ kcal \cdot mol^{-1}$. We are unable to reanalyze these shock tube equilibrium data but presumably the $\Delta_fH°$ and $D_0°$ values should be adjusted for the changes in $\Delta_fH°$ of $SF_4$.[1]

Bott and Jacobs[6] used infrared and ultraviolet absorption techniques to study the thermal (1650–2050 K) dissociation of $SF_6$ in a shock tube. They interpreted their rate data in terms of the RRK theory and showed that the results were consistent with $D_0°(SF–F) = 75.9 \pm 4.0\ kcal\ mol^{-1}$. Lyman[7] has re-evaluated the $SF_6$ dissociation data in terms of the more complete RRKM unimolecular reaction rate theory and presented evidence which indicates that the $D_0°(SF_5–F)$ is considerably higher than previously reported. His analysis of the rate data yielded a $D_0°$ value of 92 kcal·mol$^{-1}$ which we adopt.

The enthalpy of atomization and mean bond dissociation energy are calculated to be 372.2 kcal·mol$^{-1}$ and 74.4 kcal·mol$^{-1}$, respectively. $\Delta_fH°(0\ K)$ combined with that for $SF_5^+$ [1] gives IP = 11.14 eV which appears reasonable in comparison with IP values for the other sulfur fluorides.[1]

### Heat Capacity and Entropy

We assume that the five fluorine atoms form a tetragonal pyramid around the central sulfur atom based on evidence from an EPR study[8] which shows that four of the fluorine atoms are equivalent. This structure is further supported by recent SCF MO calculations[9] which predict that the F**–S–F* bond angle is near 90°. The geometry optimized bond lengths[9] appear to be about 0.2Å too large in comparison with experimentally measured S–F bond lengths for other sulfur–fluorine species.[1] We assume that the S–F* bond length is the same as that reported for $SF_6$ and $S_2F_{10}$.[1] The axial bond length is taken to be slightly shorter than the equatorial bonds, in accordance with the pattern followed in the related molecules $ClF_5$[12] and $TeF_5^-$.[10] The principal moments of inertia are: $I_A = 30\ 7102 \times 10^{-39}$ and $I_B = I_C = 21.4728 \times 10^{-39}\ g \cdot cm^2$.

Smardzewski and Fox[11] reported the matrix infrared spectra of $SF_5$ formed during the vacuum ultraviolet photolysis of $SF_6$ and its derivatives, $SF_5X$ (X=F, Cl, Br, $SF_5$), in argon matrices at 8 K. Values of $\nu_7$ and $\nu_8$ are taken from this study. The other seven fundamentals are estimated by analogy with those for $SF_5^{-1}$ and $ClF_5$.[12] Double ($\nu_1$ and $\nu_7$) and triple ($\nu_3$, $\nu_4$ and $\nu_8$) coincidences are predicted at about 800 cm$^{-1}$ and 550 cm$^{-1}$, respectively, based on the infrared spectra of $ClF_5$.[12] The four upper electronic levels are estimated from those observed for $SF_6^+$ [13] and are assummed to be doublets.

Our thermal functions essentially update and extend those previously reported by O'Hare.[14] Wilkins[15] has also calculated functions covering the temperature range 50–6000 K. He assumed that the structure of the radical was a trigonal bipyramid ($D_{3h}$ symmetry). We cannot completely rule out this structure but consider it to be unlikely.

### References

[1] JANAF Thermochemical Tables: $SF_6(g)$, $SF_4(g)$, $SF_3(g)$, $SF_2(g)$ and SF(g), 6–30–76; F(g), 9–30–65; $F^-(g)$, 12–31–71; $S_2F_{10}(g)$, $S_2F_{10}(g)$, $SF_5^+(g)$ and $SF_5^-(g)$, 12–31–77; $ClF_5(g)$, 6–30–66.
[2] S. W. Benson, Chem. Rev. (to be published).
[3] P. Harland and J. C. J. Thynne, J. Phys. Chem. 73, 4031 (1969).
[4] R. K. Curran, J. Chem. Phys. 34, 1069 (1961).

Continued on page 1217

Enthalpy Reference Temperature = $T_r$ = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −16.323 | −898.295 | −898.295 | INFINITE |
| 100 | 38.347 | 238.884 | 367.958 | −12.907 | −902.837 | −882.881 | 461.170 |
| 200 | 66.342 | 273.589 | 312.273 | −7.737 | −906.631 | −861.295 | 224.947 |
| 250 | 79.469 | 289.850 | 306.174 | −4.081 | −907.751 | −849.822 | 177.561 |
| 298.15 | 89.642 | 304.752 | 304.752 | 0 | −908.447 | −838.597 | 146.919 |
| 300 | 89.986 | 305.308 | 304 754 | 0 166 | −908.468 | −838.163 | 145.937 |
| 350 | 98.138 | 319.818 | 305.881 | 4.878 | −908.894 | −826.409 | 123.335 |
| 400 | 104.412 | 333.351 | 308 479 | 9 949 | −911.330 | −814.521 | 106.365 |
| 450 | 109.265 | 345.941 | 311.950 | 15.296 | −912.076 | −802.382 | 93.138 |
| 500 | 113.054 | 357.657 | 315.942 | 20.857 | −912.764 | −790.154 | 82.547 |
| 600 | 118.445 | 378.782 | 324.695 | 32.452 | −913.437 | −765.557 | 66.648 |
| 700 | 121.973 | 397.324 | 333 774 | 44.485 | −913.630 | −740.890 | 55.286 |
| 800 | 124.386 | 413.778 | 342.765 | 56.810 | −913.540 | −716.217 | 46.764 |
| 900 | 126.101 | 428.533 | 351.490 | 69.339 | −966.403 | −690.485 | 40.075 |
| 1000 | 127.359 | 441.888 | 359.872 | 82.015 | −964.808 | −659.913 | 34.470 |
| 1100 | 128.309 | 454.073 | 367.890 | 94.801 | −963.194 | −629.501 | 29.893 |
| 1200 | 129.044 | 465.270 | 375.545 | 107.670 | −961.577 | −599.237 | 26.084 |
| 1300 | 129.627 | 475.623 | 382.850 | 120.604 | −959.968 | −569.107 | 22.867 |
| 1400 | 130.102 | 485.247 | 389.824 | 133.592 | −958.375 | −539.101 | 20.114 |
| 1500 | 130.497 | 494.237 | 396.489 | 146.622 | −956.804 | −509.208 | 17.732 |
| 1600 | 130.836 | 502.670 | 402.864 | 159.689 | −955.257 | −479.419 | 15.651 |
| 1700 | 131.134 | 510.611 | 408.971 | 172.788 | −953.735 | −449.725 | 13.818 |
| 1800 | 131.403 | 518.114 | 414.828 | 185.915 | −952.233 | −420.121 | 12.192 |
| 1900 | 131.652 | 525.226 | 420.453 | 199.068 | −950.750 | −390 600 | 10.738 |
| 2000 | 131.887 | 531.985 | 425.862 | 212.245 | −949.277 | −361 156 | 9.432 |
| 2100 | 132.112 | 538.425 | 431.070 | 225 445 | −947.807 | −331 787 | 8.253 |
| 2200 | 132.331 | 544.576 | 436.091 | 238 667 | −946.331 | −302 487 | 7.182 |
| 2300 | 132.545 | 550.463 | 440.936 | 251.911 | −944.840 | −273.255 | 6.206 |
| 2400 | 132.757 | 556.108 | 445.618 | 265.176 | −943.324 | −244.088 | 5.312 |
| 2500 | 132.966 | 561.532 | 450.147 | 278.462 | −941.773 | −214.985 | 4.492 |
| 2600 | 133 174 | 566.751 | 454.532 | 291.769 | −940.177 | −185.945 | 3.736 |
| 2700 | 133.380 | 571.781 | 458.782 | 305.097 | −938.528 | −156.967 | 3.037 |
| 2800 | 133.584 | 576.635 | 462.905 | 318.445 | −936.816 | −128.051 | 2.389 |
| 2900 | 133.787 | 581.327 | 466.908 | 331.814 | −935.035 | −99.198 | 1.787 |
| 3000 | 133.988 | 585.866 | 470.798 | 345.202 | −933.178 | −70.407 | 1.226 |
| 3100 | 134.187 | 590.262 | 474.581 | 358.611 | −931.239 | −41.680 | 0.702 |
| 3200 | 134.384 | 594.526 | 478.263 | 372.040 | −929.213 | −13.017 | 0.212 |
| 3300 | 134.578 | 598.664 | 481.849 | 385.488 | −927.097 | 15.582 | −0.247 |
| 3400 | 134.769 | 602.684 | 485.344 | 398.955 | −924.886 | 44.115 | −0.678 |
| 3500 | 134.958 | 606.594 | 488.753 | 412.442 | −922.580 | 72.582 | −1.083 |
| 3600 | 135.143 | 610.398 | 492.079 | 425.947 | −920.175 | 100.982 | −1.465 |
| 3700 | 135.326 | 614.103 | 495.328 | 439.470 | −917.672 | 129.313 | −1.826 |
| 3800 | 135.505 | 617.715 | 498.501 | 453.012 | −915.070 | 157.574 | −2.166 |
| 3900 | 135.682 | 621.237 | 501.603 | 466.571 | −912.369 | 185.767 | −2.488 |
| 4000 | 135.855 | 624.674 | 504.637 | 480.148 | −909.569 | 213.889 | −2.793 |
| 4100 | 136.026 | 628.031 | 507.606 | 493.742 | −906.672 | 241.940 | −3.082 |
| 4200 | 136.193 | 631.311 | 510.512 | 507.353 | −903.679 | 269.919 | −3.357 |
| 4300 | 136.357 | 634.517 | 513.359 | 520.981 | −900.592 | 297.825 | −3.618 |
| 4400 | 136.518 | 637.654 | 516.148 | 534.624 | −897.411 | 325.659 | −3.866 |
| 4500 | 136.675 | 640.724 | 518.883 | 548.284 | −894.140 | 353.420 | −4.102 |
| 4600 | 136.830 | 643.729 | 521.564 | 561 959 | −890.780 | 381.106 | −4.328 |
| 4700 | 136.982 | 646.674 | 524.195 | 575.650 | −887.334 | 408.719 | −4.542 |
| 4800 | 137.131 | 649.559 | 526.777 | 589.356 | −883.803 | 436.257 | −4.747 |
| 4900 | 137.277 | 652.388 | 529.311 | 603.076 | −880.191 | 463.721 | −4.943 |
| 5000 | 137.419 | 655.163 | 531.801 | 616.811 | −876.499 | 491.111 | −5.131 |
| 5100 | 137.559 | 657.886 | 534.246 | 630.560 | −872.730 | 518.425 | −5.310 |
| 5200 | 137.696 | 660.558 | 536.650 | 644.323 | −868.887 | 545.666 | −5.481 |
| 5300 | 137.830 | 663.182 | 539.013 | 658.099 | −864.971 | 572.832 | −5.646 |
| 5400 | 137.961 | 665.760 | 541.336 | 671.888 | −860.985 | 599.923 | −5.803 |
| 5500 | 138.088 | 668.292 | 543.621 | 685.691 | −856.931 | 626.939 | −5.954 |
| 5600 | 138.213 | 670.782 | 545.870 | 699.506 | −852.812 | 653.882 | −6.099 |
| 5700 | 138.335 | 673.229 | 548.083 | 713.333 | −848.630 | 680.749 | −6.238 |
| 5800 | 138.454 | 675.636 | 550.261 | 727.173 | −844.387 | 707.543 | −6.372 |
| 5900 | 138.569 | 678.004 | 552.406 | 741.024 | −840.085 | 734.265 | −6.501 |
| 6000 | 138.681 | 680.334 | 554.519 | 754.887 | −835.726 | 760.911 | −6.624 |

PREVIOUS: December 1977 (1 atm) CURRENT. December 1977 (1 bar)

## Sulfur Fluoride, Ion ($SF_5^+$) IDEAL GAS $M_r$ = 127.051466 Sulfur Fluoride, Ion ($SF_5^+$) $F_5S_1^+(g)$

$S°$(298.15 K) = [298.151 ± 8.4] J·K$^{-1}$·mol$^{-1}$

$\Delta_fH°$(0 K) = 176.574 ± 20.9 kJ·mol$^{-1}$
$\Delta_fH°$(298 15 K) = [172.644] kJ·mol$^{-1}$

| Electronic Levels and Quantum Weights | | | |
|---|---|---|---|
| $\epsilon_i$, cm$^{-1}$ | $g_i$ | $\epsilon_i$, cm$^{-1}$ | $g_i$ |
| 0 | [1] | 29036 | [1] |
| 9275 | [1] | 37101 | [1] |
| 17341 | [1] | | |

| Vibrational Frequencies and Degeneracies | | |
|---|---|---|
| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
| [800](1) | [550](1) | [800](2) |
| [600](1) | [400](1) | [550](2) |
| [550](1) | [450](1) | [350](2) |

Point Group: [$C_{4v}$] $\sigma$ = [4]
Bond Distances: S–F* = [1.50] Å; S–F** = [1.46] Å
Bond Angles: F**–S–F* = [90]°; F*–S–F* = [90]°
(* – equatorial ** – axial)
Product of the Moments of Inertia: $I_AI_BI_C$ = [1.126194 × 10$^{-113}$] g$^3$·cm$^6$

### Enthalpy of Formation

The threshold energy for the formation of $SF_5^+$ from $SF_6$ has been measured by photoionization,[1] electron–impact,[2-5] and photoelectron spectroscopy.[4 6-8] Presented below is a summary of the reported appearance potentials (AP) along with results arrived at from an analysis of the data. Also included in the summary are results derived from an electron–impact study[9] on the formation of $SF_5^+$ from $SF_5Cl$. All auxiliary data are from the most recent JANAF tables[10] with the exception of the value for $\Delta_fH°$(0 K) of $SF_5Cl$. We use $\Delta_fH°$($SF_5Cl$, g, 0 K) = −247.4 kcal·mol$^{-1}$.

| Source | Method | AP[a], eV | $\Delta_fH°$(0K) kcal·mol$^{-1}$ | IP, eV |
|---|---|---|---|---|
| 1 | Photoionization | <15.29 | <45.88 | <11.3 |
| 2 | Electron–Impact | 15.9 ± 0.2 | <59.94 | <11.9 |
| 3 | Electron–Impact | 15.85 ± 0.15 | <59.79 | <11.9 |
| 4 | RPD | 15.75 ± 0.05 | <56.48 | <11.8 |
| | Photoelectron Spectroscopy | 15 30 | 46.11 | 11.31 |
| 5 | Electron–Impact | 15.50 ± 0.1 | <50.72 | <11.5 |
| 6 | Photoelectron Spectroscopy | 15.35 ± 0.2 | 47.26 | 11.36 |
| 7 | Photoelectron Spectroscopy | 15.15 | 42.65 | 11.16 |
| 8 | Photoelectron Spectroscopy | 14.72 | 32 73 | 10.73 |
| 9 | Electron–Impact | 13.2 ± 0.2[b] | <28.33 | <10.5 |

[a] $SF_6(g) + e^- = SF_5^+(g) + F(g) + 2e^-$ [b] $SF_5Cl(g) + e^- = SF_5^+(g) + Cl(g) + 2e^-$

No study has been made of the kinetic energies of the fragments produced by photoionization or electron–impact of $SF_6$ and $SF_5Cl$. As a result, the ionization potentials (IP) derived from these studies[1-5,9] represent upper limits to the true value. $SF_5^+$ is produced in the photoionization of $SF_6$ by rapid dissociation of $SF_6^+$ whose ground state is expected to exhibit Jahn–Teller instability.[1] As a result of this, an accurate determination of the threshold energy for the dissociation process is difficult. We choose to adopt a mean $\Delta_fH°$(0 K) value of 42.2 ± 5.0 kcal·mol$^{-1}$ based on the results measured in four photoelectron spectroscopic studies[4 6-8] of the $SF_6/SF_5^+$ dissociation. Our adopted enthalpies of formation correspond to IF($SF_5$) = 11.14 ± 0.37 eV which is in agreement with the limiting values of 9.25<IP<12.05 eV.[13]

$\Delta_fH°$ is calculated to be 41.263 kcal·mol$^{-1}$ at 298.15 K. Using JANAF data,[10] we find that the primary bond dissociation energy, $D_0°(SF_4^+-F)$, is 75.4 kcal·mol$^{-1}$. This value appears reasonable in comparison with $D_0°$ values for other even–electron positive and negative S–F species,[10] providing some additional support for our adopted results.

### Heat Capacity and Entropy

By anolog with $SF_5$[14, 15] and $SF_5^-$,[10] we adopt a tetragonal pyramidal structure ($C_{4v}$ symmetry). The $SF_4$ part of this configuration is predicted to be planar as a result of a reduction in the repulsive forces[16] upon ionization. The four equatorial S–F bond lengths are assumed equal to that for $SF_3^+$.[10] The axial bond length is assumed to be slightly shorter than the equatorial bonds, in accordance with the pattern followed in the related molecules $ClF_5$[10] and $TeF_5^-$.[17] The individual moments of inertia are. $I_A$ = 28.3933 × 10$^{-39}$ and $I_B = I_C$ = 19.9158 × 10$^{-39}$ g·cm$^2$. We estimate vibrational frequencies from those for $SF_5$,[10] $SF_5^-$ [10] and $ClF_5$.[18] Double ($\nu_1$ and $\nu_7$) and triple ($\nu_3$, $\nu_4$, and $\nu_8$) coincidences are predicted at 800 cm$^{-1}$ and 550 cm$^{-1}$, respectively, based on the infrared spectra of $ClF_5$.[18] The electronic levels are calculated from the RPD measurements of Delwiche.[4] We do not include levels predicted to lie above 40,000 cm$^{-1}$ since these have a negligible effect on the thermal functions. The existence of the first two excited states is verified by an independent RPD study.[3]

Continued on page 1217

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −16.347 | 176.574 | | |
| 100 | 38.358 | 232.170 | 361.488 | −12.932 | | | |
| 200 | 66.479 | 266.918 | 305.689 | −7.754 | | | |
| 250 | 79.653 | 283.215 | 299.576 | −4.090 | | | |
| 298.15 | 89 842 | 298 151 | 298.151 | 0. | 172.644 | 238.207 | −41.733 |
| 300 | 90.187 | 298 708 | 298.153 | 0.167 | 172.662 | 238.614 | −41.546 |
| 350 | 98.336 | 313.250 | 299.283 | 4.889 | 173.286 | 249.560 | −37.245 |
| 400 | 104.598 | 326.808 | 301.886 | 9.969 | 171.898 | 260.490 | −34.017 |
| 450 | 109.434 | 339 419 | 305.364 | 15.325 | 172.200 | 271.538 | −31.519 |
| 500 | 113.207 | 351.152 | 309.363 | 20.894 | 172.560 | 282.560 | −29.519 |
| 600 | 118.567 | 372.303 | 318.131 | 32.503 | 173.979 | 304.438 | −26.504 |
| 700 | 122.071 | 390.861 | 327.223 | 44.547 | 175.875 | 326.036 | −24.329 |
| 800 | 124.466 | 407.327 | 336.226 | 56.881 | 178.053 | 347.341 | −22.679 |
| 900 | 126.167 | 422.091 | 344.961 | 69 417 | 127.276 | 369.443 | −21 442 |
| 1000 | 127.415 | 435.451 | 353.352 | 82.099 | 130.955 | 396.154 | −20.693 |
| 1100 | 128.358 | 447.642 | 361.378 | 94.890 | 134.653 | 422.495 | −20.063 |
| 1200 | 129.091 | 458.843 | 369.040 | 107.764 | 138.354 | 448.499 | −19.523 |
| 1300 | 129.676 | 469.200 | 376.351 | 120 703 | 142.047 | 474.195 | −19.053 |
| 1400 | 130.156 | 478.828 | 383.331 | 133.695 | 145 723 | 499.606 | −18.641 |
| 1500 | 130.561 | 487.822 | 390.001 | 146.732 | 149.378 | 524 756 | −18.274 |
| 1600 | 130.914 | 496.259 | 396.381 | 159.806 | 153.011 | 549.662 | −17.945 |
| 1700 | 131.229 | 504.206 | 402.492 | 172.913 | 156.621 | 574.343 | −17.647 |
| 1800 | 131.519 | 511.715 | 408.353 | 186.051 | 160.211 | 598.811 | −17.377 |
| 1900 | 131 791 | 518.833 | 413.982 | 199.216 | 163 786 | 623.080 | −17.130 |
| 2000 | 132.050 | 525.600 | 419.395 | 212.408 | 167.353 | 647.161 | −16.902 |
| 2100 | 132.301 | 532.049 | 424.608 | 225.626 | 170.919 | 671.063 | −16.692 |
| 2200 | 132.547 | 538.209 | 429.632 | 238.869 | 174 494 | 694 796 | −16.497 |
| 2300 | 132.789 | 544 106 | 434.482 | 252.135 | 178.086 | 718.366 | −16.315 |
| 2400 | 133.027 | 549.763 | 439.168 | 265.426 | 181.707 | 741.779 | −16.144 |
| 2500 | 133.263 | 555.198 | 443.702 | 278.741 | 185.365 | 765.041 | −15.985 |
| 2600 | 133 496 | 560.429 | 448.091 | 292.079 | 189.070 | 788.154 | −15.834 |
| 2700 | 133.727 | 565.472 | 452.346 | 305.440 | 192.831 | 811.125 | −15.692 |
| 2800 | 133 954 | 570.339 | 456.473 | 318.824 | 196.657 | 833.955 | −15.558 |
| 2900 | 134.179 | 575 044 | 460.481 | 332.231 | 200.555 | 856.647 | −15.430 |
| 3000 | 134.399 | 579.596 | 464.376 | 345.660 | 204.531 | 879.203 | −15.308 |
| 3100 | 134 616 | 584.007 | 468.165 | 359.110 | 208.590 | 901.625 | −15.192 |
| 3200 | 134 829 | 588.284 | 471.852 | 372.583 | 212.739 | 923.916 | −15.081 |
| 3300 | 135.037 | 592.436 | 475.443 | 386.076 | 216.979 | 946.075 | −14.975 |
| 3400 | 135.240 | 596.470 | 478 944 | 399.590 | 221.315 | 968.103 | −14.873 |
| 3500 | 135 437 | 600.393 | 482.358 | 413.124 | 225 747 | 990 004 | −14.775 |
| 3600 | 135.630 | 604.212 | 485.690 | 426.677 | 230.279 | 1011.776 | −14.680 |
| 3700 | 135.816 | 607 930 | 488 944 | 440.249 | 234.909 | 1033.421 | −14.589 |
| 3800 | 135.997 | 611.555 | 492.123 | 453.840 | 239.639 | 1054.938 | −14.501 |
| 3900 | 136.172 | 615.089 | 495.231 | 467.449 | 244.468 | 1076.331 | −14.416 |
| 4000 | 136.341 | 618.539 | 498.271 | 481.074 | 249.395 | 1097.599 | −14.333 |
| 4100 | 136.504 | 621.908 | 501.245 | 494.717 | 254.419 | 1118.741 | −14.253 |
| 4200 | 136.662 | 625 199 | 504.157 | 508.375 | 259.538 | 1139.761 | −14.175 |
| 4300 | 136 813 | 628 417 | 507.010 | 522.049 | 264 751 | 1160.657 | −14.099 |
| 4400 | 136.959 | 631.564 | 509.805 | 535.738 | 270.054 | 1181.431 | −14.025 |
| 4500 | 137.099 | 634.643 | 512.545 | 549.440 | 275 447 | 1202.084 | −13.953 |
| 4600 | 137.233 | 637.658 | 515.232 | 563.157 | 280 927 | 1222.615 | −13.883 |
| 4700 | 137.361 | 640.611 | 517.869 | 576.887 | 286.491 | 1243.027 | −13.815 |
| 4800 | 137.485 | 643.504 | 520.456 | 590.629 | 292.137 | 1263.320 | −13.748 |
| 4900 | 137.603 | 646.340 | 522.996 | 604.384 | 297.862 | 1283.493 | −13.682 |
| 5000 | 137.715 | 649.121 | 525.491 | 618.150 | 303.663 | 1303.549 | −13.618 |
| 5100 | 137.823 | 651.849 | 527.942 | 631.926 | 309.539 | 1323.489 | −13.555 |
| 5200 | 137.926 | 654.526 | 530.351 | 645 714 | 315.486 | 1343.313 | −13.494 |
| 5300 | 138.024 | 657.155 | 532.718 | 659.512 | 321.502 | 1363.021 | −13.433 |
| 5400 | 138.118 | 659.735 | 535.047 | 673.319 | 327.584 | 1382.616 | −13.374 |
| 5500 | 138.208 | 662.271 | 537.337 | 687.135 | 333.730 | 1402.096 | −13.316 |
| 5600 | 138.293 | 664.762 | 539.590 | 700.960 | 339.937 | 1421.466 | −13.259 |
| 5700 | 138.374 | 667.210 | 541.808 | 714.793 | 346.204 | 1440.722 | −13.203 |
| 5800 | 138.451 | 669.617 | 543.991 | 728.635 | 352.528 | 1459.869 | −13.148 |
| 5900 | 138.524 | 671.985 | 546.140 | 742.484 | 358.906 | 1478.908 | −13.093 |
| 6000 | 138.594 | 674.313 | 548.257 | 756.339 | 365.337 | 1497.836 | −13.040 |

PREVIOUS· December 1977 (1 atm) CURRENT: December 1977 (1 bar)

# Sulfur Fluoride, Ion ($SF_5^-$) IDEAL GAS $M_r$ = 127.052564 Sulfur Fluoride, Ion ($SF_5^-$) $F_5S_1^-(g)$

$\Delta_aH°(0\ K) = 1586.154 \pm 41.8\ kJ\cdot mol^{-1}$
$S°(298.15\ K) = [315.571 \pm 2.1]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_fH°(0\ K) = -1255.192 \pm 33.5\ kJ\cdot mol^{-1}$
$\Delta_fH°(298\ 15\ K) = [-1268\ 706]\ kJ\cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ |
|---|---|---|
| 796(1) | 435(1) | 595 (2) |
| 522(1) | 269(1) | [435](2) |
| 470(1) | 342(1) | 241 (2) |

Ground State Quantum Weight. [1] $\sigma = 4$
Point Group: $C_{4v}$
Bond Distances: S–F* = [1.56] Å, S–F** = [1.46] Å
Bond Angles: F**–S–F* = [85]°, F*–S–F* = 90°
(* – equatorial ** – axial)
Product of the Moments of Inertia: $I_AI_BI_C = [1.256203 \times 10^{-113}]\ g^3\cdot cm^6$

## Enthalpy of Formation

The threshold energy for the dissociative electron attachment process $e^- + SF_6(g) = SF_5^-(g) + F(g)$ has been measured directly by means of mass spectrometry.[1-4] In addition, mass spectrometric studies[5] have been reported on various electron transfer reactions which provide independent estimates of the enthalpy for the above process. Presented below is a summary of the results derived from these measurements. Also included in the summary are results obtained from an electron–impact study[1] of the process $e^- + SF_5Cl(g) = SF_5^-(g) + Cl(g)$. We assume that the fragment–ions are formed in each process with no excess or kinetic energies. As a result, the derived electron affinities represent lower limits to the true value. Other reported values of EA($SF_5$) include >1.465 eV,[9] 3.2 eV[5] and 3.66 ± 0 04 eV.[10] The first two results are based on charge–transfer studies[5-9] while the latter value represents a direct measurement of EA using the magnetron technique.[10]

| Source | Reaction | Method | AP or $\Delta_rH°(0\ K)$ kcal·mol⁻¹ | $\Delta_fH°(SF_5^-, g, 0\ K)$[a] kcal·mol⁻¹ | EA($SF_5$)[a] eV |
|---|---|---|---|---|---|
| [1] | A | Electron–impact | 2.31 | −304.41 | >3.89 |
| [2] | A | RPD | 1.15 | −305.56 | >3.94 |
| [3] | A | RPD | 5.77 | −300.95 | >3 74 |
| [4] | A | Electron–impact | –0 | −308.72 | >3.99 |
| [5] | A | Electron transfer | 11.53 | −295.19 | >3.49 |
| [6] | A | Collisional ionization | 11.45 | −295.07 | >3.49 |
| [1] | B | Electron–impact | 4.61 | −271.45 | >2.46 |

Reactions: (A) $e^- + SF_6(g) = SF_5^-(g) + F(g)$
(B) $e^- + SF_5(g) = SF_5^-(g) + Cl(g)$

[a] Auxiliary $\Delta_fH°(0\ K)$ data (in kcal $mol^{-1}$): $SF_6$,[7] − 288 36 ± 0 2, F,[7] 18.36 ± 0.4; Cl,[7] 28.587; $SF_5Cl$,[8] −247.48, $SF_5$,[7] −214.7 ± 3.6.

We reject the electron–impact results on the dissociative electron attachment process for $SF_5Cl$ since Harland and Thynne[1] also reported results for $SF_3^-$ and $SF_4^-$ which lead to EA that are too low.[7] The other results are reasonably consistent with the mean EA value of 3.7 ± 0.2 eV. This value corresponds to $\Delta_fH°(SF_5^-, g, 0\ K) = -300\ 0 \pm 8.0\ kcal\cdot mol^{-1}$ which we adopt.

$\Delta_fH°$ (298.15 K) is −303.228 $kcal\cdot mol^{-1}$ and the fluoride–ion affinity is IA($SF_4$) = 59 1 $kcal\cdot mol^{-1}$.

## Heat Capacity and Entropy

The infrared and Raman spectra[11,12] of the solid adduct $CsFSF_4$ are consistent with a slightly distorted tetragonal pyramidal structure for the $SF_5^-$ anion. We adopt this configuration assuming the length of the four equivalent bonds is the same as that in $SF_6$.[7] The axial bond length is taken to be slightly shorter (0.1–) than the equatorial bonds, in accordance with the pattern followed in the related molecules $ClF_5$[7] and $TeF_5^-$.[13] The F**–S–F* bond angle has been estimated by Drullinger and Griffiths.[11] The principal moments of inertia are: $I_A = 30.4769 \times 10^{-39}$ and $I_B = I_C = 20.3023 \times 10^{-39}\ g\cdot cm^2$.

Smardzewski and Fox[14] reported the matrix infrared spectra of $SF_5^-$ formed during the vacuum ultraviolet photolysis of $SF_6$and $SD_2F_{10}$ in argon matrices at 8 K. Values of $\nu_1$, $\nu_3$ and $\nu_7$ are taken from this recent study. The other six fundamentals are those measured by Christe *et al.*[12] for the $SF_5^-$ anion observed in the Raman spectra of the solid adduct $CsFSF_4$. An independent set[11] of vibrational frequencies for the $SF_5^-$ anion show good agreement with those adopted here except for $\nu_8$. Drullinger and Griffiths[11] observed a weak band at 388 $cm^{-1}$ in the infrared spectra of solid $Cs^+SF_5^-$ which they assigned to $\nu_8$. This band does not appear in the spectrum reported by Christe *et al.*[12] who assumed a double coincidence between $\nu_4$ and $\nu_8$ as observed for the related molecule $ClF_5$.[12] We adopt this latter assignment.

Drullinger and Griffiths[11] have previously evaluated thermal functions for $SF_5^-$ at selected temperatures in the range 200–2000 K. Using the bond lengths estimated by Drullinger and Griffiths[11] and their vibrational frequencies, we calculate entropies which are about 0.8 cal $K^{-1}\cdot mol^{-1}$ lower than those reported. The reason for this discrepancy is not apparent.

Continued on page 1217

Enthalpy Reference Temperature = $T_r$ = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

|  | J·K⁻¹mol⁻¹ |  |  | kJ·mol⁻¹ |  |  |  |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | S° | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0 | INFINITE | −19.158 | −1255.192 |  |  |
| 100 | 46.921 | 235 666 | 390 718 | −15.505 |  |  |  |
| 200 | 80.815 | 279.023 | 324.282 | −9.052 |  |  |  |
| 250 | 92.943 | 298.427 | 317.198 | −4.693 |  |  |  |
| 298.15 | 101.535 | 315.571 | 315.571 | 0. | −1268.706 | −1195.827 | 209.504 |
| 300 | 101.815 | 316.200 | 315.573 | 0.188 | −1268 743 | −1195.375 | 208.133 |
| 350 | 108.286 | 332.407 | 316.838 | 5.449 | −1269.660 | −1183.072 | 176.564 |
| 400 | 113.061 | 347.194 | 319.722 | 10.989 | −1272.666 | −1170.559 | 152.859 |
| 450 | 116.644 | 360.727 | 323.537 | 16.735 | −1274.052 | −1157.721 | 134.385 |
| 500 | 119.381 | 373.165 | 327.887 | 22.639 | −1275.437 | −1144.718 | 119.58 |
| 600 | 123.187 | 395.294 | 337.324 | 34.782 | −1277.641 | −1118.359 | 97.362 |
| 700 | 125.627 | 414.480 | 347.006 | 47.231 | −1279.496 | −1091.662 | 81.461 |
| 800 | 127.273 | 431.369 | 356.517 | 59.881 | −1281.160 | −1064 713 | 69.519 |
| 900 | 128.432 | 446 430 | 365 686 | 72.670 | −1335.842 | −1036.482 | 60.156 |
| 1000 | 129.276 | 460.008 | 374.450 | 85.557 | −1336.114 | −1003.206 | 52.402 |
| 1100 | 129.910 | 472.360 | 382.798 | 98.518 | −1336.403 | −969.901 | 46.057 |
| 1200 | 130.396 | 483.686 | 390.740 | 111.534 | −1336.717 | −936.569 | 40.768 |
| 1300 | 130.778 | 494.139 | 398.297 | 124.594 | −1337.062 | −903.209 | 36.291 |
| 1400 | 131.083 | 503.842 | 405.494 | 137.688 | −1337.441 | −869.822 | 32.453 |
| 1500 | 131.330 | 512.894 | 412.355 | 150.809 | −1337.858 | −836.407 | 29.126 |
| 1600 | 131.533 | 521.377 | 418.907 | 163.952 | −1338.314 | −802.962 | 26.214 |
| 1700 | 131.702 | 529.356 | 425.171 | 177.114 | −1338.806 | −769.487 | 23.643 |
| 1800 | 131 844 | 536 888 | 431 171 | 190.292 | −1339.333 | −735 983 | 21.358 |
| 1900 | 131.965 | 544 020 | 436 924 | 203.482 | −1339.890 | −702.449 | 19.312 |
| 2000 | 132.068 | 550.792 | 442.450 | 216.684 | −1340.471 | −668.884 | 17.469 |
| 2100 | 132.157 | 557.238 | 447.763 | 229.895 | −1341.069 | −635.290 | 15.802 |
| 2200 | 132.234 | 563.387 | 452.880 | 243.115 | −1341.674 | −601.668 | 14.285 |
| 2300 | 132.301 | 569.267 | 457.814 | 256.342 | −1342.279 | −568.017 | 12.900 |
| 2400 | 132.360 | 574.899 | 462.576 | 269.575 | −1342.873 | −534.341 | 11.630 |
| 2500 | 132.412 | 580.303 | 467.178 | 282.814 | −1343.448 | −500.640 | 10.460 |
| 2600 | 132.459 | 585 497 | 471.629 | 296.057 | −1343.994 | −466.917 | 9.380 |
| 2700 | 132.500 | 590 497 | 475.940 | 309.305 | −1344.503 | −433.173 | 8.380 |
| 2800 | 132.537 | 595.317 | 480.118 | 322.557 | −1344.967 | −399.412 | 7.451 |
| 2900 | 132.571 | 599.968 | 484.171 | 335.813 | −1345.377 | −365.634 | 6.586 |
| 3000 | 132.601 | 604.463 | 488.106 | 349.071 | −1345.729 | −331.844 | 5.778 |
| 3100 | 132.628 | 608.811 | 491.930 | 362.333 | −1346.016 | −298.043 | 5.022 |
| 3200 | 132.652 | 613.022 | 495.648 | 375.597 | −1346.234 | −264.234 | 4.313 |
| 3300 | 132.675 | 617.105 | 499.267 | 388.863 | −1346.377 | −230.419 | 3.647 |
| 3400 | 132.696 | 621.066 | 502.792 | 402.132 | −1346.444 | −196.601 | 3.020 |
| 3500 | 132.714 | 624.913 | 506.226 | 415.402 | −1346.432 | −162.782 | 2.429 |
| 3600 | 132.732 | 628 651 | 509.575 | 428.674 | −1346.339 | −128.964 | 1.871 |
| 3700 | 132.748 | 632.288 | 512.843 | 441.948 | −1346.164 | −95.150 | 1.343 |
| 3800 | 132.762 | 635.829 | 516.033 | 455.224 | −1345.906 | −61.343 | 0.843 |
| 3900 | 132.776 | 639.278 | 519.149 | 468.501 | −1345.566 | −27.542 | 0.369 |
| 4000 | 132.788 | 642.639 | 522.194 | 481 779 | −1345.144 | 6.248 | −0.082 |
| 4100 | 132.800 | 645.918 | 525 172 | 495.058 | −1344.640 | 40.026 | −0.510 |
| 4200 | 132.811 | 649.119 | 528.085 | 508.339 | −1344.056 | 73.792 | −0.918 |
| 4300 | 132.821 | 652.244 | 530.937 | 521.621 | −1343.393 | 107.542 | −1.306 |
| 4400 | 132.830 | 655.297 | 533.728 | 534.903 | −1342.653 | 141.277 | −1.677 |
| 4500 | 132.839 | 658.283 | 536.463 | 548 187 | −1341.836 | 174.994 | −2.031 |
| 4600 | 132.847 | 661.202 | 539.143 | 561.471 | −1340.946 | 208.691 | −2.370 |
| 4700 | 132.855 | 664.059 | 541.771 | 574.756 | −1339.984 | 242.369 | −2.694 |
| 4800 | 132.862 | 666.857 | 544.348 | 588.042 | −1338.952 | 276.025 | −3.004 |
| 4900 | 132.869 | 669.596 | 546.876 | 601.329 | −1337.852 | 309.659 | −3.301 |
| 5000 | 132.875 | 672.281 | 549.357 | 614.616 | −1336.686 | 343.270 | −3.586 |
| 5100 | 132.881 | 674.912 | 551.794 | 627 904 | −1335.457 | 376.857 | −3.860 |
| 5200 | 132 887 | 677.492 | 554.186 | 641.192 | −1334.166 | 410.420 | −4.123 |
| 5300 | 132.892 | 680.024 | 556.537 | 654.481 | −1332.816 | 443.957 | −4.375 |
| 5400 | 132.898 | 682.508 | 558.846 | 667.770 | −1331.409 | 477.467 | −4.619 |
| 5500 | 132.902 | 684.946 | 561.117 | 681.060 | −1329.947 | 510.951 | −4.853 |
| 5600 | 132.907 | 687.341 | 563.350 | 694.351 | −1328.431 | 544.409 | −5.078 |
| 5700 | 132 911 | 689 693 | 565.546 | 707.642 | −1326.864 | 577.838 | −5.295 |
| 5800 | 132.915 | 692.005 | 567.706 | 720.933 | −1325.247 | 611.239 | −5.505 |
| 5900 | 132 919 | 694.277 | 569.832 | 734.225 | −1323.583 | 644.614 | −5.707 |
| 6000 | 132.923 | 696.511 | 571.925 | 747.517 | −1321.873 | 677.958 | −5.902 |

PREVIOUS: December 1977 (1 atm)   CURRENT· December 1977 (1 bar)

## Hydrogen Fluoride ($H_6F_6$) IDEAL GAS $M_r = 120.038058$ Hydrogen Fluoride ($H_6F_6$) $F_6H_6(g)$

$\Delta_fH°(0 K) = -1791.171 \pm 8.4 kJ·mol^{-1}$

$S°(298.15 K) = [466.420 \pm 25.1] J·K^{-1}·mol^{-1}$ $\Delta_fH°(298.15 K) = -1807.655 \pm 8.4 kJ·mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, cm $^{-1}$ |
|---|
| [202](5) |
| [53](4) |
| [962](5) |
| [552](5) |
| [3060](5) |

Ground State Quantum Weight: 1 $\sigma = [6]$

Point Group: [$C_6$]

Bond Distance: F–F = [2.5] Å

Product of the Moments of Inertia: $I_AI_BI_C = [4.833984 \times 10^{-112}] g^3·cm^6$

| Enthalpy Reference Temperature = $T_r$ = 298.15 K | | | | | | | Standard State Pressure = $p°$ = 0.1 MPa |
|---|---|---|---|---|---|---|---|
| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −35.392 | −1791.171 | −1791 171 | INFINITE |
| 100 | 107.705 | 318.614 | 597.486 | −27.887 | −1801.385 | −1751.917 | 915.107 |
| 200 | 142.277 | 404.563 | 481.012 | −15.290 | −1805.656 | −1700.530 | 444.133 |
| 250 | 156.333 | 437.855 | 469.123 | −7.817 | −1806.879 | −1674.097 | 349.783 |
| 298.15 | 168.056 | 466.420 | 466.420 | 0. | −1807.655 | −1648.447 | 288.801 |
| 300 | 168 470 | 467.461 | 466.423 | 0.311 | −1807.678 | −1647 459 | 286.848 |
| 350 | 178.673 | 494.221 | 468.513 | 8.998 | −1808.105 | −1620.717 | 241.879 |
| 400 | 187.132 | 518.649 | 473.276 | 18.149 | −1808.215 | −1593.937 | 208.147 |
| 450 | 194.152 | 541.108 | 479.582 | 27.687 | −1808.060 | −1567.159 | 181.911 |
| 500 | 200.051 | 561.878 | 486.786 | 37.546 | −1807.684 | −1540.410 | 160.926 |
| 600 | 209.552 | 599.229 | 502.484 | 58.047 | −1806.391 | −1487.066 | 129.461 |
| 700 | 217.186 | 632.122 | 518.701 | 79.395 | −1804.511 | −1433 987 | 107.005 |
| 800 | 223.740 | 661.561 | 534.750 | 101.448 | −1802.144 | −1381.211 | 90.184 |
| 900 | 229.555 | 688.256 | 550.346 | 124.119 | −1799.360 | −1328.757 | 77.119 |
| 1000 | 234.768 | 712.716 | 565.377 | 147.340 | −1796.220 | −1276.633 | 66.684 |
| 1100 | 239.440 | 735.316 | 579.812 | 171.054 | −1792.782 | −1224.839 | 58.163 |
| 1200 | 243.615 | 756.332 | 593.656 | 195.211 | −1789.098 | −1173.368 | 51.075 |
| 1300 | 247.332 | 775.981 | 606.934 | 219.762 | −1785.217 | −1122.214 | 45.091 |
| 1400 | 250.632 | 794 434 | 619.674 | 244.664 | −1781.180 | −1071.365 | 39.973 |
| 1500 | 253.559 | 811.827 | 631.910 | 269.876 | −1777.023 | −1020.808 | 35.548 |
| 1600 | 256.153 | 828.276 | 643.674 | 295.364 | −1772.775 | −970.532 | 31.685 |
| 1700 | 258.454 | 843.876 | 654.995 | 321.097 | −1768.458 | −920.523 | 28.284 |
| 1800 | 260 497 | 858.708 | 665.904 | 347.046 | −1764.090 | −870.770 | 25.269 |
| 1900 | 262.315 | 872.842 | 676.427 | 373.189 | −1759.682 | −821.262 | 22.578 |
| 2000 | 263.936 | 886.339 | 686.587 | 399.503 | −1755.241 | −771.986 | 20.162 |
| 2100 | 265.384 | 899.252 | 696.409 | 425.970 | −1750.771 | −722.933 | 17.982 |
| 2200 | 266.681 | 911.628 | 705.912 | 452.575 | −1746.271 | −674.094 | 16.005 |
| 2300 | 267.846 | 923.509 | 715.116 | 479.302 | −1741.741 | −625 460 | 14.205 |
| 2400 | 268.895 | 934.931 | 724.039 | 506.140 | −1737.177 | −577.023 | 12.559 |
| 2500 | 269.842 | 945.927 | 732.696 | 533.078 | −1732.574 | −528.778 | 11.048 |
| 2600 | 270.699 | 956.527 | 741.102 | 560.105 | −1727.926 | −480.718 | 9.658 |
| 2700 | 271.476 | 966.758 | 749.271 | 587.215 | −1723.228 | −432.838 | 8.374 |
| 2800 | 272.183 | 976.644 | 757.216 | 614.398 | −1718.476 | −385.132 | 7.185 |
| 2900 | 272.828 | 986.207 | 764.949 | 641.649 | −1713.663 | −337.597 | 6.081 |
| 3000 | 273 416 | 995.466 | 772.479 | 668.962 | −1708.786 | −290.230 | 5.053 |
| 3100 | 273.956 | 1004.441 | 779.818 | 696.331 | −1703.841 | −243.027 | 4.095 |
| 3200 | 274.451 | 1013.146 | 786 974 | 723.752 | −1698.824 | −195.983 | 3.199 |
| 3300 | 274.906 | 1021.599 | 793.956 | 751.220 | −1693.733 | −149.097 | 2.360 |
| 3400 | 275.325 | 1029.812 | 800 773 | 778.732 | −1688.567 | −102.368 | 1.573 |
| 3500 | 275 712 | 1037.798 | 807.432 | 806.284 | −1683.325 | −55 791 | 0.833 |
| 3600 | 276.070 | 1045.570 | 813.939 | 833.873 | −1678.006 | −9.365 | 0.136 |
| 3700 | 276.402 | 1053.139 | 820.302 | 861.497 | −1672.610 | 36.912 | −0.521 |
| 3800 | 276.710 | 1060.514 | 826.527 | 889.153 | −1667.139 | 83.042 | −1.141 |
| 3900 | 276 996 | 1067 706 | 832.619 | 916.838 | −1661.592 | 129.028 | −1.728 |
| 4000 | 277 263 | 1074.722 | 838.584 | 944.551 | −1655.973 | 174.870 | −2.284 |
| 4100 | 277.511 | 1081.572 | 844.428 | 972.290 | −1650.281 | 220.570 | −2.810 |
| 4200 | 277.744 | 1088.262 | 850.154 | 1000.053 | −1644.521 | 266.132 | −3.310 |
| 4300 | 277.961 | 1094.800 | 855.768 | 1027.838 | −1638.692 | 311.554 | −3.785 |
| 4400 | 278 164 | 1101.192 | 861.273 | 1055.645 | −1632.798 | 356.841 | −4.236 |
| 4500 | 278.355 | 1107 446 | 866.674 | 1083.471 | −1626.841 | 401.993 | −4.666 |
| 4600 | 278.534 | 1113.565 | 871.975 | 1111.315 | −1620.822 | 447.011 | −5.076 |
| 4700 | 278 702 | 1119.557 | 877.179 | 1139.177 | −1614.745 | 491.899 | −5.467 |
| 4800 | 278 861 | 1125.427 | 882.290 | 1167.055 | −1608.610 | 536.658 | −5.840 |
| 4900 | 279.010 | 1131.178 | 887.311 | 1194.949 | −1602.420 | 581.286 | −6.197 |
| 5000 | 279.151 | 1136.816 | 892.245 | 1222.857 | −1596.176 | 625.789 | −6.538 |
| 5100 | 279.284 | 1142.346 | 897.095 | 1250 779 | −1589.880 | 670.164 | −6.864 |
| 5200 | 279.409 | 1147.770 | 901.864 | 1278.713 | −1583.533 | 714.419 | −7.176 |
| 5300 | 279.528 | 1153.093 | 906.554 | 1306.660 | −1577.136 | 758.549 | −7.476 |
| 5400 | 279.641 | 1158.319 | 911.168 | 1334.619 | −1570.690 | 802.558 | −7.763 |
| 5500 | 279 748 | 1163.452 | 915.708 | 1362.588 | −1564.196 | 846.446 | −8.039 |
| 5600 | 279.849 | 1168.493 | 920.177 | 1390.568 | −1557.654 | 890.218 | −8.304 |
| 5700 | 279.945 | 1173.447 | 924.577 | 1418.558 | −1551.064 | 933.871 | −8.558 |
| 5800 | 280 037 | 1178.317 | 928 910 | 1446.557 | −1544.426 | 977.409 | −8.803 |
| 5900 | 280.124 | 1183 105 | 933.178 | 1474.565 | −1537.741 | 1020.831 | −9.038 |
| 6000 | 280 207 | 1187.813 | 937.383 | 1502.582 | −1531.007 | 1064 139 | −9.264 |

PREVIOUS: June 1977 (1 atm) CURRENT June 1977 (1 bar)

### Enthalpy of Formation

The enthalpy of 6 HF(g) → $H_6F_6$(g) was taken as the mean of 3rd law values which were determined from the equilibrium data of two investigations. Briegleb and Strohmeier[1] measured the vapor density of associated HF between 20 and 60°C and between 50 and 650 torr. Franck and Meyer[2] measured $C_p°$ between −20 and 100°C and between 100 and 700 torr. Each investigation evaluated $K_p$ at $n = 2, 3, 4, ...$ for the reactions n(HF) → $(HF)_n$ and reported 2nd law values of $\Delta_fH$ and $\Delta_fS$. At $n = 6$ their 2nd and 3rd law values differed by 0.8 kcal mol$^{-1}$, which was taken as an estimate of error, while the calculated 3rd law values differed by 0.6 kcal moll$^{-1}$ Using $\Delta_fH°(298.15 K) = -41.20$ kcal·mol$^{-1}$ and auxiliary JANAF data[3] gives the enthalpy of formation of $H_6F_6$(g).

### Heat Capacity and Entropy

The molecular structure of $H_6F_6$ was assumed as planar with the F atoms forming the vertices of a regular hexagon and with the H atoms also lying on the circumscribed circle. That rings are more stable than open chains was confirmed by Del Bene and Pople's[4] theoretical molecular-orbital studies on HF polymers. The length of side (F–F axis) was taken from Atoji and Lipscomb's[5] X-ray studies of solid HF(F–F = 2.49 Å) and agrees with the 2.52 Å which Janzen and Bartell[6] determined for HF gaseous polymers by electron diffraction. The low F-bending frequency (53 cm$^{-1}$) was taken from Boutin *et al.*[7] The other vibrational frequencies were taken from Kittelberger and Hornig's[8] work on crystalline HF Huong and Couzi[9] and Smith[10] have made spectral studies of the gas phase in the range from 350 to 4000 cm$^{-1}$.

The National Bureau of Standards prepared this table[11] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_fH°$ selected by NBS,[11] we recalculate the table in terms of 1973 fundamental constants,[12] 1975 atomic weights,[13] and current JANAF reference states for the elements.

### References

[1] G. Briegleb and W. Strohmeier, Z. Elektrochem. 57, 668 (1953).
[2] E. U. Franck and F. Meyer, Z. Electrochem. 63, 571 (1959).
[3] JANAF Thermochemical Tables: HF(g), 6–30–77.
[4] J. E. Del Bene and J. A. Pole, J Chem. Phys. 55, 2296 (1971).
[5] M. Atoji and W. N. Lipscomb, Acta Cryst. 7, 173 (1954).
[6] J. Janzen and L. S. Bartell, J. Chem. Phys. 50 3611 (1969).
[7] H Boutin, G. J. Safford, and V. Brajovic, J. Chem. Phys. 39, 3135 (1963).
[8] J. S. Kittelberger and D. F. Hornig, J. Chem. Phys. 46, 3099 (1967).
[9] P. V. Huong and M. Couzi, J Chim. Phys. 66, 1309 (1969).
[10] D. F. Smith, J. Chem. Phys. 28, 1040 (1958), 48, 1429 (1968).
[11] S Abramowitz *et al.*, U. S. Nat. Bur Stand. Report 10904, 239, (1972).
[12] CODATA Task Group on Fundamental Constants, CODATA Bulletin 11, (December 1973).
[13] IUPAC Commission on Atomic Weights, Pure Appl. Chem. 47, 75 (1976).

# Molybdenum Fluoride ($MoF_6$) LIQUID $M_r = 209.930418$ Molybdenum Fluoride ($MoF_6$) $F_6Mo_1(l)$

$S°(298.15\ K) = 259.693 \pm 0.25\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{trs} = 263.5 \pm 0.02\ K$
$T_{fus} = 290.76 \pm 0.02\ K$

$\Delta_fH°(298.15\ K) = -1585.656 \pm 0.11\ kJ{\cdot}mol^{-1}$
$\Delta_{trs}H° = 8.171 \pm 0.008\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 4.326 \pm 0.004\ kJ{\cdot}mol^{-1}$

## Enthalpy of Formation

The adopted $\Delta_fH°(MoF_6,\ l,\ 298.15\ K) = -378.98 \pm 0.25\ kcal{\cdot}mol^{-1}(-1585.657 \pm 0.11\ kJ{\cdot}mol^{-1})$ is calculated from $\Delta_fH°(MoF_6,\ g,\ 298.15\ K) = -372.29 \pm 0.22\ kcal{\cdot}mol^{-1}$[1] minus $\Delta_{vap}H°(298.15\ K) = 6.69 \pm 0.03\ kcal{\cdot}mol^{-1}$ from our 3rd law analysis of vapor pressure data.

The enthalpy of reaction of $MoF_6(l)$ with excess of $OH^-(aq)$ has been measured by Myers and Brady[2] and by Nuttall *et al.*;[3] the derived $\Delta_fH°(MoF_6,\ l,\ 298.15\ K)$ is $-393.2$ and $-380.81 \pm 1.3$-1 0 kcal $mol^{-1}$, respectively. The agreement of the latter value with the adopted value is not quite within the assigned uncertainties.

## Heat Capacity and Entropy

The heat capacity of $MoF_6$ has been measured by Brady *et al*. (50–300 K, 4) and by Osborne et al. (4–350 K, 5).

We adopt the more extensive data of Osborne *et al.*[5] extrapolating $C_p°$ linearly with temperature outside the observed range. $S°(298.15\ K) = 62.07 \pm 0.06\ cal\ K^{-1}{\cdot}mol^{-1}$ is derived from heat capacity, heat of transition, and heat of melting data and $S°(5\ K) = 0.024\ cal\ K^{-1}{\cdot}mol^{-1}$ from the $T^3$ extrapolation of Osborne *et al.*[5]

## Transition Data

Osborne *et al.*[5] confirmed the solid state transition ($263.5 \pm 0.02$ K, $\Delta_{trs}H° = 1.953 \pm 0.002\ kcal{\cdot}mol^{-1}$ found by Brady *et al*. (263.6 K, $\Delta_{trs}H° = 1.957 \pm 0.010\ kcal{\cdot}mol^{-1}$)[4].

## Fusion Data

Melting point and enthalpy of fusion data have been reported by several investigators. These results are summarized below

| Source | Method | $T_{fus}$/K | $\Delta_{fus}H°$, $kcal{\cdot}mol^{-1}$ |
|---|---|---|---|
| 4 | Calorimetric | 290.7 | 1.059 ± 0.010 |
| 5 | Calorimetric | 290.76 ± 0.02 | 1.034 ± 0.001 |
| 6 | Vap Pressure | 290.65 | 0.858* |
| 7 | Vap Pressure | 290.55 | 0.902* |
| 8 | Vap Pressure | 290.95 | 0.987* |

*Calculated as the difference between the 2nd law heat of sublimation at 291 K and the adopted 3rd law $\Delta_{vap}H°(298.15\ K)$ corrected to 291 K.

We adopt the calorimetric values of Osborne *et al*[5]

## Vaporization Data

Our 2nd and 3rd law analysis of four sets of vapor pressure data produces the following results. The second virial coefficient determined by Osborne *et al.*[5] is used to convert all four vapor pressure data sets to ideal gas fugacity.

| Source | T/K | Data Points | $\Delta_{vap}H°(298.15\ K)$, $kcal{\cdot}mol^{-1}$ 2nd law | 3rd law | Drift cal $K^{-1}{\cdot}mol^{-1}$ |
|---|---|---|---|---|---|
| 6 | 291-295 | 4 | 5.981 ± 0.467 | 6.691 ± 0.012 | 2.42 ± 1.59 |
| 7 | 291-307 | Eqn | 6.737 | 6.692 ± 0.002 | −0.15 |
| 5 | 291-320 | 21 | 6.691 ± 0.002 | 6.691 ± 0.000 | 0.00 ± 0.01 |
| 8 | 291-335 | Eqn | 6.696 | 6.691 ± 0.001 | −0.02 |

The agreement in 3rd law values is excellent and we adopt $\Delta_{vap}H°(298.15\ K) = 6.69 \pm 0.03\ kcal{\cdot}mol^{-1}$. $T_{vap} = 308.0$ K and $\Delta_{vap}H°(308\ K) = 6.57\ kcal{\cdot}mol^{-1}$ are calculated for a fugacity of one atmosphere for the process $MoF_6(l) = MoF_6(g)$. For vaporization to the real gas, $T_{vap} = 307.04$ K and $\Delta_{vap}H°(307\ K) = 6.51\ kcal{\cdot}mol^{-1}$.

This table is based on the critical analysis of data existing in 1978 by Brewer.[9]

## References

[1] JANAF Thermochemical Tables: $MoF_6(g)$, 9-30-78.
[2] O. E. Myers and A. P. Brady, J. Phys. Chem. 64, 591 (1960).
[3] R. L. Nuttall, K. L. Churney and M. V. Kilday, J. Res. Nat. Bur. Stand. 83, 335 (1978).

Continued on page 1217

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

|  | $J{\cdot}K^{-1}mol^{-1}$ |  |  | $kJ{\cdot}mol^{-1}$ |  |  |  |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 |  |  |  |  |  |  |  |
| 100 |  |  |  |  |  |  |  |
| 200 | 152.720 | 195.532 | 274.669 | −15.827 | −1590.266 | −1511.085 | 394.655 |
| 298 15 | 169.795 | 259.693 | 259.693 | 0. | −1585.656 | −1473.170 | 258.093 |
| 300 | 170.117 | 260.744 | 259.696 | 0.314 | −1585.560 | −1472.473 | 256.380 |
| 400 | 187.512 | 312.066 | 266.576 | 18 196 | −1579.792 | −1435.615 | 187.472 |
| 500 | 204 907 | 355.777 | 280.143 | 37.817 | −1572.817 | −1400.351 | 146.294 |
| 600 | 222.302 | 394.673 | 296.044 | 59.177 | −1564.493 | −1366 617 | 118.975 |
| 700 | 239.697 | 430.247 | 312.709 | 82.277 | −1554.721 | −1334.389 | 99.573 |
| 800 | 257.092 | 463.390 | 329.494 | 107.117 | −1543.431 | −1303.665 | 85 121 |
| 900 | 274.487 | 494.675 | 346.125 | 133.696 | −1530.581 | −1274.450 | 73.967 |
| 1000 | 291.882 | 524.496 | 362.482 | 162.014 | −1516.145 | −1246.750 | 65.124 |

PREVIOUS: June 1970 CURRENT September 1978

## Molybdenum Fluoride ($MoF_6$) IDEAL GAS $M_r = 209.930418$ Molybdenum Fluoride ($MoF_6$) $F_6Mo_1(g)$

$\Delta_fH°(0\ K) = -1550.595 \pm 0.92\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 350.710 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = -1557.661 \pm 0.92\ kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies | |
|---|---|
| $\nu$, cm $^{-1}$ | $\nu$, cm $^{-1}$ |
| 741.8(1) | 264(3) |
| 652.0(2) | 317(3) |
| 742 (3) | 117(3) |

Ground State Quantum Weight. 1 $\sigma = 24$

Point Group· $O_h$

Bond Distance: Mo–F = 1.82 ± 0.01 Å

Bond Angle F–Mo–F = 90°

Product of the Moments of Inertia: $I_AI_BI_C = 7.303442 \times 10^{-113}\ g^3 \cdot cm^6$

### Enthalpy of Formation

The adopted $\Delta_fH°(MoF_6, g, 298\ 15\ K) = -372.29 \pm 0\ 22\ kcal \cdot mol^{-1}$ is from the measurements of the direct combination of the elements by Settle *et al.*[1] with the minor corrections[2] for a change in atomic weights and new values for the enthalpy of formation of $MoF_5(cr)$ and $NiF_2(cr)$.

Burgess *et al.*[3] reacted $MoF_6(g)$ with excess NaOH solution and derived $\Delta_fH°(MoF_6, g, 298.15\ K) = -373.8\ kcal \cdot mol^{-1}$. The result of the direct measurement of Settle *et al.*[1] is preferred. The value of $\Delta_fH°(0\ K)$ combined with JANAF data[15] for Mo(g) and F(g) gives $\Delta_aH°(0\ K) = 637.9 \pm 1.5\ kcal \cdot mol^{-1}$ and an average Mo–F bond energy of $\Delta_aH°(0\ K)/6 = 106.3 \pm 0.3\ kcal \cdot mol^{-1}$.

### Heat Capacity and Entropy

From the Raman spectra of liquid $MoF_6$, Tanner and Duncan[4] concluded that the structure of the molecule was a regular octahedron with $O_h$ symmetry rather than the unsymmetrical structure deduced by Braune and Pinnow[5] from electron diffraction studies This discrepancy was explained by Glauber and Schomaker [6]

Values of the Mo–F bond distance vary from 1.84 Å from electron diffraction[7] to 1.80 Å from x–ray diffraction of the cubic solid.[8] Seip and Seip[9] calculated a bond distance of 1 82 Å from electron diffraction measurements. We adopt this value with an uncertainty of ±0.01 Å.[10] The individual moments of inertia are $I_A = I_B = I_C = 41.8000 \times 10^{-39}\ g \cdot cm^2$.

The vibrational frequencies are those adopted by Brewer[10] from the assignment by Weinstock and Goodman[11] and the more recent studies of Claasen *et al.*[12] and McDowell *et al.*[13]

$S°(MoF_6, g, 298.15\ K) = 83.796\ cal\ K^{-1} \cdot mol^{-1}$ calculated from the molecular data is in excellent agreement with $S°(MoF_6, l, 298.15\ K) = 62.068\ cal\ K^{-1} \cdot mol^{-1}$ plus $\Delta_{vap}\ S°(298\ 15\ K) = 21.727\ cal\ K^{-1} \cdot mol^{-1}$ to give $S°(MoF_6, g, 298.15\ K) = 83.795 \pm 0.10\ cal\ K^{-1} \cdot mol^{-1}$ based on our analysis of the data of Osborne *et al.*[14]

This table is based on the critical analysis of data existing in 1978 by Brewer.[10]

### References

[1] J. L. Settle, H. M. Feder and W. N. Hubbard, J. Phys. Chem. 65, 1337 (1961).

[2] R. L. Nuttall, K. L. Churney and M. V. Kilday, J. Res Nat. Bur. Stand. 83, 335 (1978).

[3] J. Burgess, I. Haigh and R. D. Peacock, J. Chem. Soc., Dalton Trans. 1062 (1974).

[4] K. N. Tanner and A. B. F. Duncan, J. Amer. Chem. Soc 73, 1164 (1951).

[5] H. Braune and P. Pinnow, Z. Phys 35B, 239 (1937).

[6] R. Glauber and V. Schomaker, Phys. Rev. 89, 667 (1953).

[7] G. M. Nazarian, Ph. D. Thesis, California Institute of Technology, (1957).

[8] J. H. Levy, P. L. Sanger, J C. Taylor and P W. Wilson, Acta Cryst. B31, 1065 (1965).

[9] H. M. Seip and R Seip, Acta Chem. Scand. 20, 2698 (1966); Select Top. Struct. Chem., 26 (1967).

[10] L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication, (September 1978), of preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.

[11] B. Weinstock and G. L. Goodman, Advan. Chem. Phys 9, 169 (1965).

[12] H. H. Claasen, G. L. Goodman, J H Halloway and H. J Selig, J. Chem. Phys. 53, 341 (1970).

[13] R. S. McDowell, R. J. Sherman, B. Asprey and R J Kennedy, J. Chem. Phys. 62, 3974 (1975).

[14] D. W. Osborne, F. Schreiner, J G. Malm, H. Selig and L. Rochester, J Chem. Phys. 44, 2802 (1966).

[15] JANAF Thermochemical Tables Mo(g), 3–31–78, F(g), 9–30–65.

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
|---|---|---|---|---|---|---|---|
| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
| 0 | 0. | 0. | INFINITE | −23.993 | −1550.595 | −1550.595 | INFINITE |
| 100 | 67.247 | 249 179 | 442.877 | −19.370 | −1555.184 | −1528.288 | 798.296 |
| 200 | 99.881 | 306.715 | 361.123 | −10.882 | −1557.325 | −1500.381 | 391.859 |
| 250 | 111.452 | 330.294 | 352.644 | −5.587 | −1557.656 | −1486.099 | 310.503 |
| 298.15 | 120.276 | 350.710 | 350.710 | 0. | −1557.661 | −1472.312 | 257.943 |
| 300 | 120.574 | 351.455 | 350.713 | 0.223 | −1557.657 | −1471.782 | 256.260 |
| 350 | 127.635 | 370.596 | 352.208 | 6.436 | −1557.424 | −1457.486 | 217.518 |
| 400 | 133.077 | 388.010 | 355 611 | 12.959 | −1557.033 | −1443.234 | 188.467 |
| 450 | 137.291 | 403.938 | 360.109 | 19.723 | −1556.536 | −1429.038 | 165.878 |
| 500 | 140.585 | 418.580 | 365.234 | 26.673 | −1555.965 | −1414.902 | 147.814 |
| 600 | 145.275 | 444.658 | 376.352 | 40.984 | −1554.692 | −1386.806 | 120.732 |
| 700 | 148.347 | 467.299 | 387.763 | 55 675 | −1553.328 | −1358.932 | 101.405 |
| 800 | 150.448 | 487.253 | 398.977 | 70.621 | −1551.932 | −1331.257 | 86 922 |
| 900 | 151.941 | 505.064 | 409.793 | 85.744 | −1550.537 | −1303.756 | 75.668 |
| 1000 | 153.036 | 521.132 | 420.137 | 100.996 | −1549.168 | −1276.410 | 66.673 |
| 1100 | 153.861 | 535 759 | 429 993 | 116.342 | −1547.844 | −1249.199 | 59.320 |
| 1200 | 154.497 | 549.175 | 439.373 | 131.762 | −1546.581 | −1222.105 | 53.197 |
| 1300 | 154 997 | 561.562 | 448.302 | 147.237 | −1545.394 | −1195.114 | 48.020 |
| 1400 | 155.398 | 573 063 | 456.808 | 162.758 | −1544.295 | −1168.212 | 43.587 |
| 1500 | 155.723 | 583.796 | 464.920 | 178.314 | −1543.295 | −1141.384 | 39.747 |
| 1600 | 155.991 | 593.855 | 472.667 | 193.901 | −1542.403 | −1114.620 | 36.389 |
| 1700 | 156.214 | 603.319 | 480.077 | 209.511 | −1541.624 | −1087.907 | 33.427 |
| 1800 | 156.401 | 612.253 | 487 174 | 225.142 | −1540.963 | −1061.238 | 30.796 |
| 1900 | 156.560 | 620.714 | 493.982 | 240.790 | −1540.425 | −1034.602 | 28.443 |
| 2000 | 156.696 | 628.748 | 500.521 | 256.453 | −1540.012 | −1007.991 | 26.326 |
| 2100 | 156.814 | 636.396 | 506.811 | 272.129 | −1539.724 | −981 398 | 24.411 |
| 2200 | 156.916 | 643 693 | 512.868 | 287.816 | −1539.562 | −954.815 | 22.670 |
| 2300 | 157.005 | 650.671 | 518.709 | 303.512 | −1539.525 | −928.236 | 21 081 |
| 2400 | 157.084 | 657.354 | 524.348 | 319.216 | −1539.613 | −901.657 | 19.624 |
| 2500 | 157.153 | 663.768 | 529 797 | 334.928 | −1539.829 | −875.072 | 18.284 |
| 2600 | 157.214 | 669.933 | 535.069 | 350.647 | −1540.182 | −848.475 | 17.046 |
| 2700 | 157.269 | 675.868 | 540.175 | 366.371 | −1540.705 | −821.862 | 15.900 |
| 2800 | 157.318 | 681.588 | 545.124 | 382.100 | −1541.449 | −795.225 | 14.835 |
| 2900 | 157.363 | 687.109 | 549 925 | 397.834 | −1578.373 | −768.507 | 13.842 |
| 3000 | 157 402 | 692.445 | 554.587 | 413.573 | −1577.744 | −740.592 | 12.895 |
| 3100 | 157.439 | 697.607 | 559.118 | 429.315 | −1577.031 | −712.698 | 12.009 |
| 3200 | 157.471 | 702 606 | 563.524 | 445.060 | −1576.229 | −684.829 | 11.179 |
| 3300 | 157.501 | 707 452 | 567.813 | 460.809 | −1575.333 | −656.986 | 10.399 |
| 3400 | 157.528 | 712 154 | 571.989 | 476.560 | −1574.340 | −629.172 | 9.666 |
| 3500 | 157.553 | 716.721 | 576.059 | 492.314 | −1573.247 | −601.389 | 8 975 |
| 3600 | 157.576 | 721.159 | 580.029 | 508.071 | −1572.052 | −573.638 | 8.323 |
| 3700 | 157.597 | 725 477 | 583.902 | 523.830 | −1570.753 | −545.922 | 7.707 |
| 3800 | 157.617 | 729 680 | 587.683 | 539.590 | −1569.349 | −518.243 | 7.124 |
| 3900 | 157.635 | 733 775 | 591.377 | 555.353 | −1567.842 | −490 601 | 6.571 |
| 4000 | 157.652 | 737.766 | 594 987 | 571.117 | −1566.230 | −462.999 | 6.046 |
| 4100 | 157.667 | 741.659 | 598.517 | 586.883 | −1564.514 | −435.440 | 5.548 |
| 4200 | 157.682 | 745 459 | 601.970 | 602.651 | −1562.696 | −407.923 | 5.073 |
| 4300 | 157.695 | 749.169 | 605.350 | 618.420 | −1560.778 | −380 452 | 4.622 |
| 4400 | 157.707 | 752 794 | 608.660 | 634.190 | −1558.759 | −353.025 | 4.191 |
| 4500 | 157.719 | 756.339 | 611.903 | 649.961 | −1556.643 | −325.645 | 3 780 |
| 4600 | 157 730 | 759.805 | 615.081 | 665.734 | −1554.431 | −298.314 | 3.387 |
| 4700 | 157.740 | 763.198 | 618.196 | 681.507 | −1552.126 | −271.032 | 3.012 |
| 4800 | 157.750 | 766.519 | 621.252 | 697.282 | −1549.730 | −243 799 | 2.653 |
| 4900 | 157 759 | 769.771 | 624.250 | 713.057 | −1547.244 | −216.618 | 2.309 |
| 5000 | 157 767 | 772.959 | 627.192 | 728.833 | −2136.057 | −183.758 | 1.920 |
| 5100 | 157.775 | 776 083 | 630.081 | 744.610 | −2135.079 | −144.722 | 1.482 |
| 5200 | 157.783 | 779.147 | 632.918 | 760.388 | −2134.166 | −105 703 | 1.062 |
| 5300 | 157.790 | 782.152 | 635 706 | 776.167 | −2133.317 | −66.703 | 0 657 |
| 5400 | 157 797 | 785.102 | 638.445 | 791.946 | −2132.534 | −27.718 | 0 268 |
| 5500 | 157.803 | 787 997 | 641.138 | 807 726 | −2131.815 | 11.253 | −0 107 |
| 5600 | 157.809 | 790.841 | 643.786 | 823.507 | −2131.161 | 50.213 | −0.468 |
| 5700 | 157 815 | 793 634 | 646.390 | 839.288 | −2130.571 | 89.159 | −0 817 |
| 5800 | 157.820 | 796.379 | 648.953 | 855 070 | −2130.046 | 128.097 | −1 154 |
| 5900 | 157.825 | 799.077 | 651.475 | 870.852 | −2129.581 | 167.027 | −1.479 |
| 6000 | 157.830 | 801.729 | 653.957 | 886.635 | −2129.180 | 205.948 | −1.793 |

PREVIOUS· September 1978 (1 atm) CURRENT September 1978 (1 bar)

Molybdenum Fluoride ($MoF_6$) $F_6Mo_1(g)$

## Sulfur Fluoride (SF$_6$)    IDEAL GAS    $M_r = 146.050418$ Sulfur Fluoride (SF$_6$)    $F_6S_1(g)$

$\Delta_f H°(0\ K) = -1206.501 \pm 0.8\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = 291.535 \pm 0.4\ J{\cdot}K^{-1}{\cdot}mol^{-1}$    $\Delta_f H°(298.15\ K) = -1220.473 \pm 0.8\ kJ{\cdot}mol^{-1}$

| Vibrational Frequencies and Degeneracies<br>$\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|---|
| 773.5(1) | 947.5(3) | 525.0(3) |
| 641.7(2) | 615.5(3) | 347.0(3) |

Ground State Quantum Weight: 1    $\sigma = 24$
Point Group: $O_h$
Bond Distance. S–F = 1.564 ± 0.01 A
Bond Angle· F–S–F = 90°
Product of the Moments of Inertia: $I_A I_B I_C = 2.941168 \times 10^{-113}\ g^3{\cdot}cm^6$

### Enthalpy of Formation

The calorimetric measurement of $\Delta_f H°$ by direct combination of the elements has been the subject of numerous investigations.[1-6] O'Hare *et al.*[1] performed six combustion experiments on a sample of rhombic sulfur which contained 60 ppm oxygen as the major impurity. The sulfur (~0.5 gram) was burned in 5–6 atmospheres of fluorine which had a purity of 99.97%. Spectrometric and gas chromatographic analyses of the product gases indicated that the sole combustion product was SF$_6$. We adjust their result $\Delta_f H°(298.15\ k) = -271.7 \pm 0.24\ kcal{\cdot}mol^{-1}$ to correspond to an atomic weight of sulfur equal to 32.06, and we obtain $\Delta_f H°(SF_6, g, 298.15\ k) = -291.7_3 \pm 0.2\ kcal{\cdot}mol^{-1}$. The rounded value of $-291.7 \pm 0.2\ kcal{\cdot}mol^{-1}$ is adopted in this tabulation. Less extensive measurements (3 determinations) by Schroder and Sieben[2] on a portion of the same sample used by O'Hare *et al.*[1] gave $\Delta_f H°(SF_6, g, 298.15\ K) = -291.4\ kcal{\cdot}mol^{-1}$ which provides confirmation for our selected value.

Other reported $\Delta_f H°$ values which are consistently less negative than the value selected here include (in kcal·mol$^{-1}$) −291.0 ± 0.3,[3] −288.9 ± 0.7,[4] −288.5 ± 0.7[5] and −262.0[6] The fluorine used by Leonidov *et al.*[3] contained 0.13 wt. % oxygen, and this impurity may be responsible for their low results. Gross *et al.*[4] studied the sulfur fluorination reaction in a glass apparatus and also applied their technique to titanium. Their reported $\Delta_f H°$ value for TiF$_4$ is in satisfactory agreement ( ±0.8 kcal·mol$^{-1}$) with JANAF data.[7] Insufficient information has been reported[4] to resolve the discrepancy for SF$_6$.

Our adopted $\Delta_f H°$ value is essentially the same as that recently selected by NBS.[8] The earlier NBS selection[9] of −289.0 kcal mol$^{-1}$ based on the work of Gross *et al.*,[4,5] is unreliable.

### Heat Capacity and Entropy

The product of the moments of inertia is calculated for a structure in which the fluorine atoms lie at the corners of a regular octahedran. This structure belongs to the highest symmetry point group $O_h$ ($\sigma = 24$) and is consistent with observations made from electron diffraction,[10-12] Raman[13-15] and infrared[16-18] studies. The bond length and angle are from the electron diffraction work of Ewing and Sutton.[10] Earlier and less precise work[11-12] led to $r_e$(S–F) values which are only slightly different from the adopted value. The individual moments of inertia are: $I_A = I_B = I_C = 30.8679 \times 10^{-39}\ g\ cm^2$.

The SF$_6$ molecule has been extensively characterized by vibrational spectroscopy. Weinstock and Goodman[19] reviewed work prior to 1965. Recent studies include gas–phase Raman,[13-14] matrix–isolation Raman,[15] and gas–phase infrared.[16-18] These spectrometric results are in good agreement; the largest deviation arising in the Raman and infrared inactive fundamental $\nu_6$. Weinstock and Goodman[19] obtained $\nu_6 = 349\ cm^{-1}$ from the combination (2 + 6) band. Claassen *et al.*[13] reported $\nu_6 = 347\ cm^{-1}$ from the overtone $2\nu_6$ band, and Holzer and Ouillon[14] have directly observed this forbidden fundamental in the collision–induced Raman spectra at 336 cm$^{-1}$. Rosenberg and Birnbaum[20] recorded the far–infrared absorption spectrum of gaseous SF$_6$ and assigned a band centered at 173 cm$^{-1}$ to $\nu_5$–$\nu_6$. The difference band gives $\nu_6 = 352\ cm^{-1}$ with $\nu_5 = 525\ cm^{-1}$ [13] and supports the higher value for $\nu_6$. All frequencies used in this tabulation except for the two infrared active ($\nu_3$ and $\nu_4$) fundamentals are taken from the work of Claassen *et al.*[13] Values for the infrared active frequencies are from Abramowitz and Levin.[16] Recent MO calculations[21] predict a singlet ground state with no low–lying electronic levels, and are supported by the x–ray emission[22] and absorption[22, 23] spectra of gaseous SF$_6$. Gianturco[28] has presented a description of the electronic properties.

Kelley and King[24] analyzed $C_p°$ data (13–230 K) reported by Eucken and Schroder[25] and obtained $S°(298.15\ K) = 70.3 \pm 0.7\ cal\ K^{-1}{\cdot}mol^{-1}$ for the gas phase. This value is in reasonable agreement with the spectroscopic result ($69.7 \pm 0.1\ cal\ K^{-1}{\cdot}mol^{-1}$). Our thermal functions essentially extend and update those reported in the literature.[1 26, 27]

### References

[1] P. A. G. O'Hare, J. L. Settle and W. N. Hubbard, Trans. Faraday Soc. 62, 558 (1966).
[2] J. Schroder and F. J. Sieben, Chem. Ber. 103, 76 (1970).
[3] V. Ya. Leonidov, V. S. Pervov, O. M. Gaisinskaya and L. I. Klyuev, Dokl. Akad. Nauk SSSR, 211, 901 (1973).
[4] P. Gross, Bull. Chem. Thermodyan., No. 3, 14 (1960).
[5] P. Gross, Bull. Chem. Thermodyn., No. 3, 14 (1960).
[6] D. M. Yost and W. H. Claassen, J. Amer. Chem. Soc. 55, 885 (1933).
[7] JANAF Thermochemical Tables: TiF$_4$(cr), 9–30–67.
[8] V. B. Parker, D. D. Wagman and D. Garvin, NBSIR 75–968, 1976.
[9] U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).
[10] V. C. Ewing and L. E. Sutton, Trans. Faraday Soc. 59, 1241 (19630.

Continued on page 1217

Enthalpy Reference Temperature = $T_r$ = 298.15 K    Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −16.915 | −1206.501 | −1206.501 | INFINITE |
| 100 | 38.721 | 223.132 | 358.027 | −13.490 | −1212.486 | −1182.436 | 617.641 |
| 200 | 68.822 | 258.508 | 299.562 | −8.211 | −1217.637 | −1150.220 | 300.407 |
| 250 | 84.315 | 275.568 | 293.063 | −4.374 | −1219.327 | −1133.158 | 236.760 |
| 298.15 | 96.960 | 291.535 | 291.535 | 0. | −1220.473 | −1116.451 | 195.598 |
| 300 | 97.398 | 292.136 | 291.537 | 0.180 | −1220.509 | −1115.806 | 194.279 |
| 350 | 107.968 | 307.974 | 292.763 | 5.324 | −1221.297 | −1098.288 | 163.911 |
| 400 | 116.373 | 322.962 | 295.610 | 10 940 | −1224.003 | −1080.591 | 141.111 |
| 450 | 123.040 | 337.068 | 299.441 | 16.932 | −1224.938 | −1062.615 | 123.345 |
| 500 | 128.351 | 350.317 | 303.873 | 23.222 | −1225.747 | −1044.532 | 109.122 |
| 600 | 136.069 | 374.450 | 313.667 | 36.470 | −1226.504 | −1008.204 | 87.772 |
| 700 | 141.228 | 395.838 | 323 907 | 50.351 | −1226 624 | −971.804 | 72.517 |
| 800 | 144.808 | 414.944 | 334.114 | 64.663 | −1226.352 | −935.416 | 61.076 |
| 900 | 147.375 | 432.156 | 344.068 | 79.279 | −1278.955 | −897.998 | 52.118 |
| 1000 | 149.272 | 447.786 | 353.670 | 94.116 | −1277.044 | −855.771 | 44.701 |
| 1100 | 150.709 | 462.084 | 362.885 | 109.118 | −1275.073 | −813 739 | 38.641 |
| 1200 | 151.822 | 475.247 | 371.707 | 124.247 | −1273.069 | −771.888 | 33.599 |
| 1300 | 152.700 | 487.435 | 380.147 | 139.475 | −1271.051 | −730.204 | 29.340 |
| 1400 | 153.404 | 498.778 | 388.220 | 154.782 | −1269.035 | −688.677 | 25.695 |
| 1500 | 153.978 | 509.382 | 395.948 | 170.152 | −1267.030 | −647.293 | 22.541 |
| 1600 | 154 450 | 519.335 | 403.352 | 185.574 | −1265.042 | −606.042 | 19.785 |
| 1700 | 154.844 | 528 711 | 410.453 | 201.039 | −1263.075 | −564.914 | 17.358 |
| 1800 | 155 176 | 537.571 | 417.271 | 216.540 | −1261.130 | −523.902 | 15.203 |
| 1900 | 155.458 | 545.969 | 423.825 | 232.073 | −1259.203 | −482.998 | 13.279 |
| 2000 | 155.700 | 553.949 | 430.134 | 247 631 | −1257.289 | −442.195 | 11.549 |
| 2100 | 155.908 | 561.551 | 436.212 | 263.211 | −1255.382 | −401 487 | 9 986 |
| 2200 | 156.089 | 568.808 | 442.076 | 278.811 | −1253.473 | −360.870 | 8.568 |
| 2300 | 156.248 | 575 750 | 447 738 | 294.428 | −1251.553 | −320.340 | 7.275 |
| 2400 | 156.387 | 582.403 | 453.211 | 310.060 | −1249.612 | −279.894 | 6.092 |
| 2500 | 156.510 | 588.789 | 458.507 | 325.705 | −1247.639 | −239.529 | 5.005 |
| 2600 | 156.620 | 594.930 | 463.637 | 341.362 | −1245.625 | −199.245 | 4.003 |
| 2700 | 156.717 | 600.843 | 468.610 | 357.029 | −1243.560 | −159 038 | 3.077 |
| 2800 | 156.805 | 606.544 | 473.435 | 372.705 | −1241.434 | −118.910 | 2.218 |
| 2900 | 156.883 | 612.048 | 478.120 | 388.390 | −1239.240 | −78.858 | 1.420 |
| 3000 | 156.954 | 617.368 | 482.674 | 404.082 | −1236.970 | −38.883 | 0.677 |
| 3100 | 157.019 | 622.515 | 487 102 | 419.780 | −1234.619 | 1.014 | −0.017 |
| 3200 | 157.077 | 627.501 | 491.412 | 435.485 | −1232.180 | 40.835 | −0.667 |
| 3300 | 157.130 | 632.336 | 495.610 | 451.195 | −1229 649 | 80.578 | −1.275 |
| 3400 | 157.179 | 637.027 | 499.700 | 466.911 | −1227.022 | 120.242 | −1.847 |
| 3500 | 157.224 | 641.584 | 503.689 | 482.631 | −1224.298 | 159.828 | −2.385 |
| 3600 | 157.264 | 646.014 | 507.582 | 498.356 | −1221.473 | 199.336 | −2.892 |
| 3700 | 157.302 | 650.323 | 511.381 | 514.084 | −1218.547 | 238.762 | −3.371 |
| 3800 | 157.337 | 654.519 | 515.093 | 529.816 | −1215.520 | 278.108 | −3.823 |
| 3900 | 157.369 | 658.606 | 518.721 | 545.551 | −1212.391 | 317.374 | −4.251 |
| 4000 | 157.399 | 662.590 | 522.268 | 561.290 | −1209.161 | 356.558 | −4.656 |
| 4100 | 157.426 | 666.477 | 525.738 | 577.031 | −1205.831 | 395.659 | −5.041 |
| 4200 | 157.452 | 670.271 | 529.134 | 592 775 | −1202.403 | 434.680 | −5.406 |
| 4300 | 157.476 | 673.976 | 532.460 | 608.521 | −1198.877 | 473.615 | −5.753 |
| 4400 | 157.498 | 677.597 | 535.718 | 624.270 | −1195.256 | 512.469 | −6.084 |
| 4500 | 157.519 | 681.137 | 538.910 | 640.021 | −1191.542 | 551.240 | −6.399 |
| 4600 | 157.539 | 684.599 | 542.040 | 655.774 | −1187.737 | 589.926 | −6.699 |
| 4700 | 157.557 | 687.987 | 545.109 | 671.528 | −1183.843 | 628.530 | −6.985 |
| 4800 | 157.574 | 691.305 | 548.120 | 687.285 | −1179.864 | 667 049 | −7.259 |
| 4900 | 157.590 | 694.554 | 551.076 | 703.043 | −1175.801 | 705.484 | −7.521 |
| 5000 | 157.605 | 697.738 | 553 977 | 718.803 | −1171.658 | 743.836 | −7.771 |
| 5100 | 157.620 | 700.859 | 556.827 | 734.564 | −1167.436 | 782 104 | −8.010 |
| 5200 | 157.633 | 703.920 | 559.626 | 750.327 | −1163.138 | 820.289 | −8.240 |
| 5300 | 157.646 | 706.922 | 562.377 | 766.091 | −1158.767 | 858.390 | −8.460 |
| 5400 | 157.658 | 709.869 | 565.081 | 781.856 | −1154.325 | 896.408 | −8.671 |
| 5500 | 157.669 | 712.762 | 567.740 | 797.622 | −1149.815 | 934.342 | −8.874 |
| 5600 | 157.680 | 715.603 | 570.355 | 813.390 | −1145.239 | 972.196 | −9.068 |
| 5700 | 157.690 | 718.394 | 572.928 | 829.158 | −1140.599 | 1009.965 | −9.255 |
| 5800 | 157.700 | 721.137 | 575.460 | 844.928 | −1135.898 | 1047.653 | −9.435 |
| 5900 | 157 709 | 723.833 | 577.952 | 860.698 | −1131.137 | 1085.261 | −9.608 |
| 6000 | 157.718 | 726.483 | 580.405 | 876.470 | −1126.320 | 1122.785 | −9.775 |

PREVIOUS· June 1976 (1 atm)    CURRENT June 1976 (1 bar)

## Sulfur Fluoride, Ion ($SF_6^-$) IDEAL GAS $M_r$ = 146.050967 Sulfur Fluoride, Ion ($SF_6^-$) $F_6S_1^-(g)$

$S°(298.15\ K) = [302.860 \pm 2.1]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -1322.282 \pm 29.3\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -1341.876 \pm 29.3\ kJ{\cdot}mol^{-1}$

| Vibrational Frequencies and Degeneracies | | |
|---|---|---|
| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
| [700](1) | [925](3) | [500](3) |
| [625](2) | 594(3) | [325](3) |

Ground State Quantum Weight: 2 $\sigma = 24$
Point Group: $O_h$
Bond Distance: S–F = [1.72] Å
Bond Angle: F–S–F = 90°
Product of the Moments of Inertia: $I_AI_BI_C = [5.203193 \times 10^{-113}]\ g^3{\cdot}cm^6$

### Enthalpy of Formation

We calculate the enthalpy of formation at 0 K as the difference between $\Delta_fH°(SF_6, g) = -288.36 \pm 0.2\ kcal{\cdot}mol^{-1}$ [1] and the selected value of the electron affinity (EA) equal to 1.2 ± 0.3 eV (27.67 kcal·mol$^{-1}$) There have been numerous values proposed for EA($SF_6$). Franklin and Harland[2] have recently reviewed several of the published values; other values of EA not included in the review are tabulated below. The only direct measurement of EA = 1.49 eV by the magnetron technique[3] is suspect since mass spectral studies[4] have shown that $SF_5$ rather than $SF_6$ is the predominant ion formed under conditions used in the magnetron experiments. An EA = 1.2 eV is consistent with most of the available information and is adopted here as the best current value.

| Source | Method | EA($SF_6$), eV |
|---|---|---|
| 5 | Electron Transfer | <1.18 |
| 6 | Collisional Ionization Cs/$SF_6$ | >0.54 |
| 7 | Rate Measurements | >0.7 |
| 8 | Electron Transfer | >0.43<br><1.47 |
| 9 | Solution Electron Transfer | 0.6 |
| 10 | MO Calculation | 1.7 |

From the adopted results, we calculate the primary bond dissociation energy $D_0°(SF_6^- {-} F)$ to be 34.4 kcal mol$^{-1}$ which agrees with the value of 24.2 kcal·mol$^{-1}$ obtained from threshold energies for $SF_6^-$ and $SF_5^-$ measured in collisional ionization studies[6] on the Cs/$SF_6$ system. $\Delta_fH°(298.15\ K)$ is −320.7 kcal·mol$^{-1}$, and the fluoride ion affinity (IA) is IA = 41.3 kcal·mol$^{-1}$.

### Heat Capacity and Entropy

The six fluorine atoms are assumed to form a regular octahedron around the central sulfur atom, in accordance with observations[11] on the ESR spectrum of $SF_6^-$. The value of the bond length is taken from theoretical calculations.[11] This value (1.72 Å) is intermediate between the bond lengths for $SF_6$[1] and $XeF_6$[12] and therefore appears to be a reasonable estimate. The principal moments of inertia are: $I_A = I_B = I_C = 37.3328 \times 10^{-39}\ g{\cdot}cm^2$.

MO calculations[11] in the INDO approximation indicate that the unpaired electron occupies a totally symmetric antibonding orbital ($A_{1g}$). Thus, we predict that the bonding in $SF_6^-$ is somewhat weaker than that in the neutral molecule. Additional support for this is provided by the fact that the mean S–F bond energy (products S(g)+F (g) + 5F(g)) in $SF_6^-$ is 8.5 kcal·mol$^{-1}$ less than that in $SF_6$.[1] Due to the weaker bonding in $SF_6^-$, all vibrational frequencies are expected to show a lowering relative to those for $SF_6$.[1] Very recently, Barefield and Guillory[13] have assigned an absorption band at 594 cm$^{-1}$ observed in the matrix isolated infrared spectra of NO, Na, and K photoionized in the presence of $SF_6$ as the $\nu_4$ fundamental of $SF_6^-$. This represents a lowering of 21.3 cm$^{-1}$ from the gas phase frequency for $SF_6$.[1] The other infrared active mode ($\nu_3$) for $SF_6^-$ expected to lie near 925 cm$^{-1}$ was not observed but was believed to be hidden beneath the matrix isolated $\nu_3$ band (937 cm$^{-1}$) of $SF_6$. We estimate the eight unobserved fundamental from the gas phase values for $SF_6$.[1]

MO calculations[11] indicate that the ground state electronic configuration is $A_{1g}$. There is, however, little information available on the excited states for $SF_6^-$ or for isoelectronic molecules such as ClF,6 and $BrF_6$. Indirect experimental evidence for the existence of an excited state at 0.5 eV (4033 cm$^{-1}$) has been reported by Lifshitz *et al.*[14] from mass spectral studies of charge–transfer reactions. As shown by Fehsenfeld,[15] *stable excited states are expected to exist only if* $D_0°(SF_5^- {-} F) > EA(SF_6)$. Our adopted results give a difference in $D_0°(SF_5^- {-} F)$ and EA($SF_6$) of only 0.053 eV, suggesting that perhaps the $SF_6^-$ ion observed by Lifshitz *et al.*[14] was vibrationally rather than electronically excited. We prefer not to include this level, but if it does exist, our entropies should be increased by 0.41 and 1.0 cal K$^{-1}$·mol$^{-1}$ at 2000 K and 4500 K.

### References

[1] JANAF Thermochemical Tables: $SF_6(g)$, 6–30–76.
[2] J. L. Franklin and P. W. Marland, Ann. Rev. Phys. Chem. 25, 485 (1974).
[3] J. Kay and F. M. Page, Trans. Faraday Soc. 60, 1042 (1964).
[4] J. T. Herron, H. M. Rosenstock and W. R. Shields, Nature, 206, 611 (1965).
[5] C. Lifshitz, B. M. Hughes and T. O. Tiernan, Chem. Phys. Letters, 7, 469 (1970).
[6] R. N. Compton and C. D. Cooper, J. Chem. Phys. 59, 4140 (1973).

Continued on page 1217

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −17.490 | −1322.282 | | |
| 100 | 39.970 | 231.635 | 371.985 | −14.035 | | | |
| 200 | 71.908 | 268.576 | 311.174 | −8.520 | | | |
| 250 | 87.504 | 286.343 | 304.439 | −4.524 | | | |
| 298.15 | 99.984 | 302.860 | 302.860 | 0. | −1341.876 | −1234.976 | 216.363 |
| 300 | 100.413 | 303.480 | 302.862 | 0.185 | −1341.945 | −1234.313 | 214.913 |
| 350 | 110.698 | 319.762 | 304.124 | 5.473 | −1343.629 | −1216.236 | 181.513 |
| 400 | 118.794 | 335.094 | 307.047 | 11.219 | −1347.245 | −1197.851 | 156.423 |
| 450 | 125.168 | 349.469 | 310.971 | 17.324 | −1349.105 | −1179.072 | 136.863 |
| 500 | 130.218 | 362.928 | 315.501 | 23.713 | −1350.854 | −1160.082 | 121.193 |
| 600 | 137.516 | 387.362 | 325.485 | 37.126 | −1353.525 | −1121.663 | 97.649 |
| 700 | 142.367 | 408.948 | 335.897 | 51.136 | −1355.595 | −1082.850 | 80.803 |
| 800 | 145.720 | 428.191 | 346.253 | 65.550 | −1357.300 | −1043 766 | 68.151 |
| 900 | 148.119 | 445.500 | 356.335 | 80.248 | −1411.899 | −1003.403 | 58.236 |
| 1000 | 149.889 | 461.202 | 366.049 | 95.153 | −1411.999 | −958.009 | 50.041 |
| 1100 | 151.228 | 475.554 | 375.361 | 110.212 | −1412.050 | −912.607 | 43.336 |
| 1200 | 152.264 | 488.758 | 384.268 | 125.388 | −1412.076 | −867.202 | 37.748 |
| 1300 | 153.080 | 500.980 | 392.782 | 140.657 | −1412.097 | −821.795 | 33.020 |
| 1400 | 153.735 | 512.349 | 400.921 | 155.999 | −1412.123 | −776.387 | 28.967 |
| 1500 | 154.268 | 522.974 | 408.707 | 171.400 | −1412.166 | −730.975 | 25.455 |
| 1600 | 154.707 | 532.945 | 416.164 | 186.850 | −1412.229 | −685.561 | 22.381 |
| 1700 | 155.072 | 542.335 | 423.312 | 202.339 | −1412.317 | −640.141 | 19.669 |
| 1800 | 155.380 | 551.208 | 430.173 | 217.862 | −1412.429 | −594.716 | 17.258 |
| 1900 | 155.642 | 559 616 | 436.767 | 233.414 | −1412.561 | −549.284 | 15.101 |
| 2000 | 155.866 | 567.605 | 443.111 | 248.989 | −1412.708 | −503.844 | 13.159 |
| 2100 | 156.059 | 575.215 | 449.222 | 264.586 | −1412.864 | −458.398 | 11.402 |
| 2200 | 156.227 | 582.479 | 455.115 | 280.200 | −1413.019 | −412.943 | 9.805 |
| 2300 | 156.374 | 589.427 | 460.805 | 295.830 | −1413.164 | −367.482 | 8.346 |
| 2400 | 156.504 | 596.085 | 466.303 | 311.475 | −1413.290 | −322.015 | 7.008 |
| 2500 | 156.618 | 602.476 | 471.623 | 327.131 | −1413.385 | −276.543 | 5.778 |
| 2600 | 156.719 | 608.620 | 476.775 | 342.798 | −1413.439 | −231.068 | 4.642 |
| 2700 | 156.810 | 614.537 | 481.768 | 358.474 | −1413.442 | −185.592 | 3.590 |
| 2800 | 156.891 | 620.241 | 486.613 | 374.159 | −1413.386 | −140.117 | 2.614 |
| 2900 | 156.964 | 625.748 | 491.316 | 389.852 | −1413.262 | −94.645 | 1.705 |
| 3000 | 157.029 | 631.070 | 495.886 | 405.552 | −1413.064 | −49.178 | 0.856 |
| 3100 | 157.089 | 636.220 | 500.331 | 421.258 | −1412.784 | −3.720 | 0.063 |
| 3200 | 157.143 | 641.208 | 504.656 | 436.969 | −1412.416 | 41.728 | −0.681 |
| 3300 | 157.192 | 646.045 | 508.867 | 452.686 | −1411.957 | 87.163 | −1.380 |
| 3400 | 157.238 | 650.738 | 512.971 | 468.408 | −1411.403 | 132.583 | −2.037 |
| 3500 | 157.279 | 655.297 | 516.973 | 484.134 | −1410.752 | 177.985 | −2.656 |
| 3600 | 157.317 | 659.728 | 520.877 | 499.863 | −1410.001 | 223.368 | −3.241 |
| 3700 | 157.352 | 664.039 | 524.688 | 515.597 | −1409.148 | 268.727 | −3.794 |
| 3800 | 157.384 | 668.235 | 528.411 | 531.334 | −1408.195 | 314.062 | −4.317 |
| 3900 | 157.414 | 672.324 | 532.049 | 547.074 | −1407.140 | 359.372 | −4.813 |
| 4000 | 157 441 | 676.310 | 535.606 | 562.816 | −1405.984 | 404.653 | −5.284 |
| 4100 | 157.467 | 680.198 | 539.085 | 578.562 | −1404.729 | 449.903 | −5.732 |
| 4200 | 157.490 | 683.992 | 542.490 | 594.310 | −1403.375 | 495.122 | −6.158 |
| 4300 | 157.513 | 687.699 | 545.824 | 610.060 | −1401.924 | 540.306 | −6.563 |
| 4400 | 157.533 | 691.320 | 549.090 | 625.812 | −1400.378 | 585.457 | −6.950 |
| 4500 | 157.553 | 694.860 | 552.290 | 641.566 | −1398.739 | 630.572 | −7.319 |
| 4600 | 157.571 | 698.323 | 555.427 | 657.323 | −1397.009 | 675.649 | −7.672 |
| 4700 | 157.588 | 701.712 | 558.504 | 673.080 | −1395.191 | 720.687 | −8.010 |
| 4800 | 157.603 | 705.030 | 561.522 | 688.840 | −1393.288 | 765.686 | −8.332 |
| 4900 | 157.618 | 708.280 | 564.484 | 704.601 | −1391.301 | 810.644 | −8.642 |
| 5000 | 157.632 | 711.465 | 567.392 | 720.364 | −1389.233 | 855.561 | −8.938 |
| 5100 | 157.646 | 714.586 | 570.247 | 736.128 | −1387.087 | 900.435 | −9.222 |
| 5200 | 157.658 | 717.647 | 573.053 | 751.893 | −1384.865 | 945.268 | −9.495 |
| 5300 | 157.670 | 720.651 | 575.809 | 767.659 | −1382.570 | 990.056 | −9.758 |
| 5400 | 157.681 | 723.598 | 578.519 | 783.427 | −1380.204 | 1034.800 | −10.010 |
| 5500 | 157.692 | 726.491 | 581.183 | 799.195 | −1377.770 | 1079.500 | −10.252 |
| 5600 | 157.702 | 729.333 | 583.803 | 814.965 | −1375.271 | 1124.156 | −10.486 |
| 5700 | 157.711 | 732.124 | 586.381 | 830.736 | −1372.707 | 1168.765 | −10.711 |
| 5800 | 157.720 | 734.867 | 588.918 | 846.507 | −1370.083 | 1213.329 | −10.927 |
| 5900 | 157.728 | 737.563 | 591.414 | 862.280 | −1367.399 | 1257.849 | −11.136 |
| 6000 | 157.737 | 740.214 | 593.872 | 878.053 | −1364.659 | 1302.321 | −11.338 |

PREVIOUS: June 1977 (1 atm) CURRENT June 1977 (1 bar)

## Tungsten Fluoride ($WF_6$) LIQUID $M_r = 297.840418$ Tungsten Fluoride ($WF_6$) $F_6W_1(l)$

$S°(298.15\ K) = 249.216 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$

$T_{fus} = 275.2\ K$

$\Delta_f H°(298.15\ K) = -1748.368 \pm 2.1\ kJ \cdot mol^{-1}$

$\Delta_{fus} H° = 4.100\ kJ \cdot mol^{-1}$

### Enthalpy of Formation

The adopted enthalpy of formation, $-417.87\ kcal \cdot mol^{-1}$, is calculated from the chosen $\Delta_{vap}H°(290.3\ K) = 6.465 \pm 0.08\ kcal \cdot mol^{-1}$ with $\Delta_f H°(WF_6,\ g,\ 298.15\ K) = -411.5 \pm 0.4\ kcal \cdot mol^{-1}$. The value of $\Delta_{vap}H°(290.3\ K)$ is obtained by corrected 2nd law analysis of vapor pressure data[6, 7, 8] which are given in the vaporization section of this table.

Myers and Brady[1] measured calorimetrically $\Delta_r H°(298.15\ K) = -150.1\ kcal \cdot mol^{-1}$ for the reaction $WF_6(l) + 8\ NaOH(aq,\ 500\ H_2O) \rightarrow Na_2WO_4(aq,\ 4900\ H_2O) + 4\ H_2O(l) + 6\ NaF(aq,\ 800\ H_2O)$. Spitsyn and Patsukova[2] measurd calorimetrically $\Delta_r H°(298.15\ K) = -13.8\ kcal \cdot mol^{-1}$ for the reaction $WO_3(cr) + 2\ NaOH_4(aq,\ 66\ H_2O) \rightarrow Na_2WO_4(aq,\ 4200\ H_2O) + H_2O(l)$. Based on these data and auxiliary data for NaOH(aq),[3, 9] NaF(aq)[3, 10] and $Na_2WO_4(aq)$[4] we obtain $\Delta_r H°(298.15\ K) = -136.2\ kcal \cdot mol^{-1}$ for $WF_6(l) + 6\ NaOH(aq,\ \infty) \rightarrow WO_3(cr) + 3\ H_2O(l) + 6\ NaF(aq,\ \infty)$. This leads to $\Delta_f H°(WF_6,\ l,\ 298.15\ K) = -416.9 \pm 1\ kcal \cdot mol^{-1}$ which is in good agreement with the value adopted.

### Heat Capacity and Entropy

The heat capacity, $40.5\ cal\ K^{-1} \cdot mol^{-1}$, is obtained from a graph of the $C_p°$ versus temperature curve determined calorimetrically by Westrum.[5]

The entropy, $S°(298.15\ K) = 59.564\ cal\ K^{-1} \cdot mol^{-1}$, is calculated from the chosen $\Delta_{vap}H°(290.3) = 6.465\ kcal \cdot mol^{-1}$ with $S°(WF_6,\ g,\ 298.15\ K) = 81.50\ cal\ K^{-1} \cdot mol^{-1}$.

### Fusion Data

The melting point and heat of melting have been reported by the following investigators, and their results are summarized below. Ruff and Ascher's value, $2.40\ kcal \cdot mol^{-1}$, is too high because they did not know of the existence of a solid–solid transition[5] at 264.7 K with $\Delta_{trs} H° = 2.067\ kcal \cdot mol^{-1}$. Westrum's data are adopted in the tabulation.

| Source | Method | $T_{fus}/K$ | $\Delta_{fus}H°$ $kcal \cdot mol^{-1}$ |
|---|---|---|---|
| 5 | Calorimetric | 275.2 | 0.980 |
| 7 | Vapor pressure | 275.4 | 2.400* |
| 8 | Warming curve | 275.1 | 0.500 |
| 6 | Vapor pressure | 275.2 | 0.420* |

*This value is the difference between the 2nd law heats of sublimation and vaporization without correction for $\Delta C_p°$ for both processes.

### Vaporization Data

2nd law analyses of the data,[6,7,8] neglecting corrections for nonideality of the vapor, are summarized below. The value of $\Delta_{vap}H°(298.15\ K) = 6.37\ kcal \cdot mol^{-1}$ ($\Delta_{vap}H°(290.3\ K) = 6.465\ kcal \cdot mol^{-1}$ is selected in the tabulation.

### References

[1] O. E. Myers and A. P. Brady, J. Phys. Chem. 64, 591 (1960).

[2] V. I. Spitsyn and N. N. Patsukova, Russ. J. Inorg. Chem. 10, 1304 (1965).

[3] V. B. Parker, U.S. Nat. Bur. Stand., NSRDS–NBS 2, (1965).

[4] We have assumed $\Delta_{dil}H° = 0$ for $Na_2WO_4(aq,\ 4200\ H_2O) \rightarrow Na_2WO_4(aq,\ 4900\ H_2O)$ based on the dilution data of R. L. Graham and L. G. Hepler, J. Amer. Chem. Soc. 80, 3538 (1958).

[5] E. F. Westrum, Jr., Pure & Appl. Chem. 8, 187 (1964); J. Chem. Ed. 39, 443 (1962).

[6] G. H. Cady and G. B. Hargreaves, J. Chem. Soc., 1563 (1961).

[7] O. Ruff and E. Ascher, Z. anorg. allg. Chem. 196, 413 (1931).

[8] E. J. Barber and G. H. Cady, J. Phys. Chem. 60, 505 (1956).

[9] JANAF Thermochemical Table: NaOH(cr), 3–31–66.

[10] U. S. Nat. Bur. Stand. Tech. Note 270–1, (1965).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | $J \cdot K^{-1} mol^{-1}$ | | | $kJ \cdot mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 169.452 | 249.216 | 249.216 | 0. | −1748.368 | −1631.549 | 285.841 |
| 300 | 169.452 | 250.264 | 249.219 | 0.313 | −1748.273 | −1630.825 | 283.952 |
| 400 | 169.452 | 299.012 | 255.866 | 17.259 | −1743.449 | −1592.418 | 207.948 |
| 500 | 169.452 | 336.824 | 268.417 | 34.204 | −1739.116 | −1555 170 | 162.468 |
| 600 | 169.452 | 367.719 | 282.471 | 51.149 | −1735.148 | −1518.759 | 132.220 |
| 700 | 169 452 | 393.840 | 296.563 | 68.094 | −1731.459 | −1482.989 | 110.662 |
| 800 | 169.452 | 416.467 | 310.168 | 85.039 | −1727.987 | −1447.733 | 94.527 |
| 900 | 169.452 | 436.426 | 323.110 | 101.985 | −1724.693 | −1412.900 | 82.003 |
| 1000 | 169.452 | 454.280 | 335.350 | 118.930 | −1721.552 | −1378.426 | 72.002 |

PREVIOUS: December 1963 CURRENT· March 1967

$\Delta_f H°(0\ K) = -1713.009 \pm 1.7\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 341.127\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -1721.716 \pm 1.7\ kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies | |
|---|---|
| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
| 769 (1) | 256 (3) |
| 670 (2) | 322 (3) |
| 712 (3) | 216 (3) |

Ground State Quantum Weight: 1 $\sigma = 24$
*Point Group*: $O_h$
Bond Distance: W–F = 1.83 Å
Bond Angle: F–W–F = 90°
Product of the Moments of Inertia: $I_A I_B I_C = 7.547547 \times 10^{-113}\ g^3 \cdot cm^6$

## Enthalpy of Formation

O'Hare and Hubbard[7] determined the enthalpy of formation, $\Delta_f H°(WF_6,\ g,\ 298.15\ K) = -411.5 \pm 0.4\ kcal \cdot mol^{-1}$, by combustion of tungsten in fluorine in a bomb calorimeter. This value is adopted in the tabulation.

## Heat Capacity and Entropy

The molecular configuration and vibrational frequencies were obtained from the infrared and Raman spectroscopic studies by Gaunt,[1] Burke *et al*[2] and Tanner and Duncan.[3]

The bond distance was reported by Claasen,[4] based on the preliminary result of Schomaker *et al.*[5] who determined the bond distance by electron diffraction. Gaunt[6] derived W–F = 1.89 Å from correlations with other hexafluorides and a valence force constant calculation. The three principal moments of inertia are $I_A = I_B = I_C = 42.2606 \times 10^{-39}\ g \cdot cm^2$.

## References

[1] J. Gaunt, Trans. Faraday Soc 49, 1122 (1953).
[2] T. G Burke, D. F. Smith and A. H. Nielsen, J. Chem. Phys. 20, 447 (1952).
[3] K. N. Tanner and A. B. F Duncan, J. Am. Chem. Soc. 73, 1164 (1951).
[4] H. H. Classen, J Chem. Phys. 30, 968 (1959).
[5] V Schomaker, M. Kimura and B. Weinstock, Proceedings of 2nd U.N. International Conference on Peaceful Uses of Atomic Energy, Geneva, 28, 125 (1958).
[6] J. Gaunt, Trans. Faraday Soc. 50, 546 (1954).
[7] P. A. G. O'Hare and W. N. Hubbard, J. Phys. Chem. 70, 3353 (1966).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log K$_f$ |
| 0 | 0 | 0. | INFINITE | −22.741 | −1713.009 | −1713.009 | INFINITE |
| 100 | 59.529 | 243.924 | 430.923 | −18.700 | −1718.341 | −1690.661 | 883.111 |
| 200 | 97.058 | 297 911 | 351.387 | −10.695 | −1721.131 | −1661.668 | 433.983 |
| 250 | 109.635 | 320.979 | 343.037 | −5.515 | −1721.615 | −1646.736 | 344.067 |
| 298.15 | 119.029 | 341 127 | 341.127 | 0. | −1721 716 | −1632.301 | 285.972 |
| 300 | 119.343 | 341.865 | 341.130 | 0.220 | −1721.714 | −1631.746 | 284.112 |
| 350 | 126.763 | 360.844 | 342.612 | 6.382 | −1721.544 | −1616.762 | 241.288 |
| 400 | 132 434 | 378.158 | 345.989 | 12.868 | −1721.188 | −1601.815 | 209.176 |
| 450 | 136.800 | 394.020 | 350.457 | 19.603 | −1720.706 | −1586.921 | 184.205 |
| 500 | 140.200 | 408 616 | 355.553 | 26.532 | −1720.136 | −1572.086 | 164.235 |
| 600 | 145.020 | 434 637 | 366.619 | 40.811 | −1718.835 | −1542.596 | 134.295 |
| 700 | 148.166 | 457.244 | 377.986 | 55.481 | −1717.421 | −1513.333 | 112.926 |
| 800 | 150.313 | 477 178 | 389 164 | 70.411 | −1715.964 | −1484.277 | 96.913 |
| 900 | 151 836 | 494.975 | 399.950 | 85.523 | −1714.503 | −1455.404 | 84.469 |
| 1000 | 152 952 | 511.033 | 410.268 | 100.765 | −1713.065 | −1426.693 | 74.523 |
| 1100 | 153.793 | 525.652 | 420.103 | 116 104 | −1711.664 | −1398.124 | 66.391 |
| 1200 | 154.440 | 539.063 | 429.466 | 131.517 | −1710.314 | −1369.680 | 59.621 |
| 1300 | 154.950 | 551.446 | 438.378 | 146.987 | −1709.021 | −1341.347 | 53.896 |
| 1400 | 155.357 | 562.944 | 446.870 | 162.503 | −1707 793 | −1313.111 | 48.993 |
| 1500 | 155 688 | 573.674 | 454.970 | 178.056 | −1706.634 | −1284.960 | 44 746 |
| 1600 | 155 960 | 583.731 | 462.707 | 193.639 | −1705.548 | −1256.885 | 41.033 |
| 1700 | 156.186 | 593.193 | 470.107 | 209.247 | −1704.533 | −1228.874 | 37.759 |
| 1800 | 156.377 | 602 126 | 477.195 | 224.875 | −1703.589 | −1200.922 | 34.850 |
| 1900 | 156.538 | 610.585 | 483.995 | 240.521 | −1702.711 | −1173.021 | 32.249 |
| 2000 | 156.677 | 618 618 | 490.527 | 256.182 | −1701.894 | −1145.163 | 29.909 |
| 2100 | 156.796 | 626.265 | 496.810 | 271.856 | −1701 131 | −1117.346 | 27.792 |
| 2200 | 156.900 | 633.562 | 502.862 | 287.541 | −1700.414 | −1089.564 | 25.870 |
| 2300 | 156.990 | 640.539 | 508.697 | 303.235 | −1699.733 | −1061.813 | 24.115 |
| 2400 | 157.070 | 647.222 | 514.331 | 318.938 | −1699.078 | −1034.091 | 22.506 |
| 2500 | 157.140 | 653 635 | 519.776 | 334.649 | −1698.439 | −1006.397 | 21.028 |
| 2600 | 157.203 | 659.800 | 525.043 | 350.366 | −1697.804 | −978.728 | 19.663 |
| 2700 | 157.259 | 665.733 | 530.145 | 366.089 | −1697.190 | −951.083 | 18.400 |
| 2800 | 157.308 | 671.454 | 535.090 | 381.818 | −1696.623 | −923.460 | 17.227 |
| 2900 | 157.353 | 676 974 | 539.888 | 397.551 | −1696.133 | −895.855 | 16.136 |
| 3000 | 157.394 | 682.310 | 544.547 | 413.288 | −1695.741 | −868.267 | 15.118 |
| 3100 | 157.430 | 687.471 | 549.075 | 429.029 | −1695 484 | −840.689 | 14.166 |
| 3200 | 157.464 | 692.470 | 553.478 | 444 774 | −1695.387 | −813.117 | 13.273 |
| 3300 | 157 494 | 697.316 | 557.764 | 460.522 | −1695.472 | −785.545 | 12.434 |
| 3400 | 157.522 | 702.018 | 561.938 | 476.273 | −1695.770 | −757.968 | 11.645 |
| 3500 | 157.547 | 706.584 | 566.006 | 492.026 | −1696.342 | −730.378 | 10.900 |
| 3600 | 157.570 | 711.023 | 569.972 | 507.782 | −1697.283 | −702.766 | 10 197 |
| 3700 | 157.592 | 715.341 | 573.843 | 523.540 | −1733.457 | −674.932 | 9.528 |
| 3800 | 157.612 | 719.544 | 577.622 | 539.300 | −1731.845 | −646.345 | 8.885 |
| 3900 | 157.630 | 723.638 | 581.314 | 555.063 | −1730.128 | −617.801 | 8.275 |
| 4000 | 157.647 | 727.629 | 584.922 | 570.826 | −1728.308 | −589.302 | 7.696 |
| 4100 | 157 663 | 731.522 | 588.451 | 586.592 | −1726.384 | −560.852 | 7.145 |
| 4200 | 157 677 | 735.321 | 591.903 | 602.359 | −1724.357 | −532.448 | 6.622 |
| 4300 | 157.691 | 739 032 | 595.281 | 618.127 | −1722.229 | −504.095 | 6.124 |
| 4400 | 157.703 | 742.657 | 598.590 | 633.897 | −1720.002 | −475.791 | 5.648 |
| 4500 | 157.715 | 746.201 | 601.831 | 649.668 | −1717.677 | −447.539 | 5 195 |
| 4600 | 157 726 | 749.668 | 605.007 | 665 440 | −1715.257 | −419.341 | 4.762 |
| 4700 | 157.737 | 753.060 | 608.121 | 681.213 | −1712.743 | −391.195 | 4.348 |
| 4800 | 157.747 | 756.381 | 611.175 | 696.987 | −1710.137 | −363.104 | 3.951 |
| 4900 | 157.756 | 759.634 | 614.172 | 712.762 | −1707.443 | −335.069 | 3.572 |
| 5000 | 157.764 | 762.821 | 617.113 | 728.538 | −1704.662 | −307.090 | 3.208 |
| 5100 | 157.772 | 765.945 | 620.001 | 744.315 | −1701.796 | −279.167 | 2.859 |
| 5200 | 157.780 | 769 009 | 622.837 | 760.093 | −1698.848 | −251.300 | 2.524 |
| 5300 | 157 787 | 772.014 | 625.623 | 775.871 | −1695.821 | −223.491 | 2.203 |
| 5400 | 157 794 | 774 964 | 628.362 | 791.650 | −1692.716 | −195.741 | 1.893 |
| 5500 | 157 801 | 777.859 | 631.054 | 807.430 | −1689.536 | −168.049 | 1.596 |
| 5600 | 157.807 | 780.703 | 633.701 | 823.210 | −1686.284 | −140.414 | 1.310 |
| 5700 | 157.813 | 783.496 | 636.304 | 838.991 | −1682.960 | −112.840 | 1.034 |
| 5800 | 157.818 | 786.240 | 638.866 | 854.773 | −1679.569 | −85.324 | 0.768 |
| 5900 | 157.823 | 788.938 | 641.387 | 870.555 | −1676 111 | −57.865 | 0.512 |
| 6000 | 157.828 | 791.591 | 643 868 | 886.338 | −1672.589 | −30.467 | 0.265 |

PREVIOUS March 1967 (1 atm) CURRENT March 1967 (1 bar)

$S°(298.15\ K) = [523\ 432 \pm 29.3]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -2083.834 \pm 37.7\ kJ\ mol^{-1}$

$\Delta_f\,H°(298.15\ K) = -2102.544 \pm 37.7\ kJ{\cdot}mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, $cm^{-1}$ |
|---|
| [202](7) |
| [53](8) |
| [962](7) |
| [552](7) |
| [3060](7) |

Ground State Quantum Weight: 1 σ = [7]

Point Group: [$C_7$]

Interatomic Distance: F–F = [2.5]Å

Product of the Moments of Inertia: $I_AI_BI_C = [1.797733 \times 10^{-111}]\ g^3{\cdot}cm^6$

## Enthalpy of Formation

The enthalpy of 7 HF(g) → $H_7F_7$(g) was taken as the mean of 3rd law values which were determined from the equilibrium data of two investigations. Briegleb and Strohmeier[1] measured the vapor density of associated HF between 20 and 60°C and between 50 and 650 torr. Franck and Meyer[2] measured $C_p°$ between −20 and 100°C and between 100 and 700 torr. Each investigation evaluated $K_p$ at $n$ = 2, 3, 4, ... for the reactions n(HF) → (HF) and reported 2nd law values of $\Delta H$ and $\Delta S$. At $n$ = 7 their 2nd law values differed by 7.3 $kcal{\cdot}mol^{-1}$, which was taken as an estimate of error, while the calculated 3rd law values differed by 6.4 $kcal{\cdot}mol^{-1}$ Using $\Delta_fH°$(298 15 K) = 046.54 $kcal{\cdot}mol^{-1}$ and auxiliary JANAF data[3] gives the enthalpy of formation of $H_7F_7$(g).

## Heat Capacity and Entropy

The molecular structure of $H_7F_7$ was assumed as planar with the F atoms forming the vertices of a regular heptagon and the H atoms also lying on the circumscribed circle. That rings are more stable than open chains was confirmed by Del Bene and Pople's[4] theoretical molecular orbital studies on HF polymers. The length of side (F–F axis) was taken from Atoji and Lipscomb's[5] X-ray studies of solid HF (F–F = 2.49 Å) and agrees with the 2.52 Å which Janzen and Bartell[6] determined for HF gaseous polymers by electron diffraction. The low F bending frequency (53 $cm^{-1}$) was taken from Boutin *et al.*[7] The other vibrational frequencies were taken from Kittelberger and Hornig's[8] work on crystalline HF. Huong and Couzi[9] and Smith[10] have made spectral studies of the gas phase in the range from 350 to 4000 $cm^{-1}$.

The National Bureau of Standards prepared this table[11] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_fH°$ selected by NBS,[11] we recalculate the table in terms of 1973 fundamental constants,[12] 1975 atomic weights[13] and current JANAF reference states for the elements.

## References

[1] G. Briegleb and W. Strohmeier, Z. Elektrochem. 57, 668 (1953).
[2] E. U. Franck and F. Meyer, Z. Elektrochem. 63, 571 (1959).
[3] JANAF Thermochemical Tables: HF(g), 6–30–77.
[4] J. E. Del Bene and J. A. Pople, J. Chem. Phys. 55, 2296 (1971).
[5] M. Atoji and W. N. Lipscomb, Acta Cryst. 7, 173 (1954).
[6] J. Janzen and L. S. Bartell, J. Chem. Phys. 50, 3611 (1969).
[7] H. Boutin, G. J. Safford, and V. Brajovic, J. Chem. Phys. 39, 3135 (1963).
[8] J. S. Kittelberger and D. F. Hornig, J. Chem. Phys. 46, 3099 (1967).
[9] P. V. Huong and M. Couzi, J. Chim. Phys. 66, 1309 (1969).
[10] D. F. Smith, J. Chem. Phys. 28, 1040 (1958); 48, 1429 (1968).
[11] S. Abramowitz *et al.*, U. S. Nat. Bur. Stand. Report 10904, 239, (1972).
[12] CODATA Task Group on Fundamental Constants, CODATA Bulletin 11, (December 1973).
[13] IUPAC Commission on Atomic Weights, Pure Appl. Chem. 47, 75 (1976).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | $J{\cdot}K^{-1}mol^{-1}$ | | | $kJ{\cdot}mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T/K$ | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −41.813 | −2083.834 | −2083.834 | INFINITE |
| 100 | 128.036 | 348.140 | 678.718 | −33.058 | −2095.751 | −2035 680 | 1063.330 |
| 200 | 168.661 | 450.187 | 540.705 | −18.104 | −2100.476 | −1973.468 | 515.417 |
| 250 | 185.096 | 489.628 | 526.631 | −9.251 | −2101.769 | −1941.556 | 405.666 |
| 298.15 | 198.792 | 523.432 | 523.432 | 0. | −2102.544 | −1910.622 | 334.733 |
| 300 | 199.275 | 524.663 | 523.436 | 0.368 | −2102.565 | −1909.431 | 332.461 |
| 350 | 211.190 | 556.305 | 525.908 | 10.639 | −2102.927 | −1877.208 | 280.158 |
| 400 | 221.067 | 585.171 | 531.538 | 21.453 | −2102.918 | −1844.959 | 240.927 |
| 450 | 229.262 | 611.697 | 538.991 | 32.718 | −2102.600 | −1812.730 | 210.416 |
| 500 | 236.149 | 636.218 | 547.503 | 44.358 | −2102.023 | −1780.551 | 186.013 |
| 600 | 247.237 | 680.297 | 566.046 | 68.551 | −2100.239 | −1716.411 | 149.427 |
| 700 | 256.147 | 719.099 | 585.194 | 93.733 | −2097.769 | −1652.627 | 123.321 |
| 800 | 263.796 | 753.813 | 604.139 | 119.739 | −2094.731 | −1589.236 | 103.766 |
| 900 | 270.581 | 785.283 | 622.545 | 146.464 | −2091.207 | −1526.256 | 88.582 |
| 1000 | 276.663 | 814.112 | 640.280 | 173.832 | −2087.267 | −1463.692 | 76.455 |
| 1100 | 282.115 | 840.741 | 657.308 | 201.776 | −2082.979 | −1401.539 | 66.554 |
| 1200 | 286.986 | 865.501 | 673.638 | 230.236 | −2078.404 | −1339.789 | 58.320 |
| 1300 | 291.323 | 888.647 | 689.297 | 259.155 | −2073.599 | −1278.432 | 51.368 |
| 1400 | 295.174 | 910.380 | 704.320 | 288.484 | −2068.612 | −1217.451 | 45.424 |
| 1500 | 298.588 | 930.864 | 718.747 | 318.175 | −2063.486 | −1156.832 | 40.284 |
| 1600 | 301.615 | 950.233 | 732.615 | 348.189 | −2058.252 | −1096.559 | 35.799 |
| 1700 | 304.300 | 968.600 | 745 961 | 378.487 | −2052.939 | −1036.615 | 31.851 |
| 1800 | 306.684 | 986.062 | 758.819 | 409.038 | −2047.566 | −976 986 | 28.351 |
| 1900 | 308.805 | 1002.702 | 771.220 | 439.815 | −2042.146 | −917.658 | 25.228 |
| 2000 | 310.696 | 1018.590 | 783.194 | 470.792 | −2036.688 | −858.614 | 22.425 |
| 2100 | 312.385 | 1033.791 | 794.768 | 501 947 | −2031.196 | −799.846 | 19.895 |
| 2200 | 313.899 | 1048.359 | 805 966 | 533.263 | −2025.670 | −741.340 | 17.602 |
| 2300 | 315.258 | 1062.343 | 816.811 | 564.722 | −2020.108 | −683.085 | 15.513 |
| 2400 | 316.482 | 1075.786 | 827.324 | 596.310 | −2014.506 | −625.074 | 13.604 |
| 2500 | 317.586 | 1088.728 | 837.523 | 628.014 | −2008.858 | −567.297 | 11.853 |
| 2600 | 318.586 | 1101.204 | 847.426 | 659.824 | −2003.158 | −509.747 | 10.241 |
| 2700 | 319 493 | 1113.245 | 857.049 | 691.729 | −1997 401 | −452.417 | 8.753 |
| 2800 | 320.318 | 1124.879 | 866.408 | 723.720 | −1991.579 | −395.302 | 7 374 |
| 2900 | 321.070 | 1136.133 | 875.516 | 755 790 | −1985.687 | −338.395 | 6.095 |
| 3000 | 321.757 | 1147.029 | 884.386 | 787.932 | −1979.720 | −281.694 | 4.905 |
| 3100 | 322.386 | 1157.590 | 893.029 | 820 139 | −1973.673 | −225.193 | 3.794 |
| 3200 | 322 963 | 1167.835 | 901.458 | 852.407 | −1967.543 | −168.888 | 2.757 |
| 3300 | 323 494 | 1177 781 | 909.681 | 884.730 | −1961.327 | −112.775 | 1.785 |
| 3400 | 323.984 | 1187.446 | 917.709 | 917.105 | −1955.023 | −56.853 | 0.873 |
| 3500 | 324.435 | 1196.844 | 925.551 | 949.526 | −1948.630 | −1.118 | 0.017 |
| 3600 | 324.853 | 1205.989 | 933.214 | 981.990 | −1942.147 | 54.435 | −0.790 |
| 3700 | 325.240 | 1214.895 | 940.707 | 1014.495 | −1935.575 | 109.805 | −1.550 |
| 3800 | 325.599 | 1223.574 | 948.038 | 1047.038 | −1928.915 | 164 996 | −2.268 |
| 3900 | 325.933 | 1232.036 | 955.212 | 1079.614 | −1922.167 | 220.012 | −2.947 |
| 4000 | 326.244 | 1240.292 | 962.236 | 1112.223 | −1915.334 | 274.852 | −3.589 |
| 4100 | 326.534 | 1248.351 | 969 116 | 1144.863 | −1908.417 | 329.521 | −4.198 |
| 4200 | 326.805 | 1256.223 | 975.859 | 1177.530 | −1901.418 | 384.022 | −4.776 |
| 4300 | 327.059 | 1263.916 | 982.469 | 1210.223 | −1894.341 | 438.352 | −5.325 |
| 4400 | 327.296 | 1271.438 | 988.951 | 1242.941 | −1887.188 | 492.519 | −5.847 |
| 4500 | 327.519 | 1278.795 | 995.311 | 1275.682 | −1879.961 | 546.522 | −6.344 |
| 4600 | 327.727 | 1285 996 | 1001.552 | 1308.444 | −1872.662 | 600.362 | −6.817 |
| 4700 | 327.924 | 1293 047 | 1007.679 | 1341.227 | −1865.294 | 654.045 | −7.269 |
| 4800 | 328.109 | 1299.952 | 1013.696 | 1374.029 | −1857.860 | 707.571 | −7.700 |
| 4900 | 328.283 | 1306.720 | 1019.608 | 1406.848 | −1850.361 | 760.938 | −8.112 |
| 5000 | 328.447 | 1313.353 | 1025.417 | 1439.685 | −1842.799 | 814.155 | −8.505 |
| 5100 | 328.602 | 1319.859 | 1031.126 | 1472.537 | −1835.177 | 867.217 | −8.882 |
| 5200 | 328.749 | 1326.241 | 1036.740 | 1505.405 | −1827.495 | 920 132 | −9.243 |
| 5300 | 328.888 | 1332.505 | 1042.262 | 1538.287 | −1819.754 | 972.897 | −9.588 |
| 5400 | 329.019 | 1338.654 | 1047.694 | 1571.182 | −1811.957 | 1025.515 | −9.920 |
| 5500 | 329 144 | 1344.692 | 1053.039 | 1604.091 | −1804.103 | 1077.987 | −10.238 |
| 5600 | 329.262 | 1350.624 | 1058.300 | 1637.011 | −1796.194 | 1130.319 | −10.543 |
| 5700 | 329.374 | 1356.453 | 1063.480 | 1669.943 | −1788.228 | 1182.506 | −10.836 |
| 5800 | 329.481 | 1362.182 | 1068.581 | 1702.886 | −1780.207 | 1234.555 | −11.118 |
| 5900 | 329.583 | 1367.815 | 1073.605 | 1735.839 | −1772.131 | 1286.464 | −11.389 |
| 6000 | 329.679 | 1373.355 | 1078.555 | 1768.802 | −1763.998 | 1338.235 | −11.650 |

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15 K) = 347.740 \pm 1.3 J·K^{-1}·mol^{-1}$

$\Delta_fH°(0 K) = -947.050 \pm 2.5 kJ·mol^{-1}$
$\Delta_fH°(298.15 K) = -961.065 \pm 2.5 kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies

| $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ |
|---|---|---|
| 676(1) | 746(2) | 510(2) |
| 635(1) | 425(2) | 352(2) |
| 670(1) | 257(2) | 310(2) |
| 365(1) | | [340](2) |

Ground State Quantum Weight: [1] $\sigma = 10$
Point Group: $D_{5h}$
Bond Distances: I-F(equatorial) = 1.86 Å; I-F(axial) = 1.76 Å
Bond Angles: F(eq)-I-F(ax) = 90°; F(eq)-I-F(eq) = 72°
Product of the Moments of Inertia: $I_AI_BI_C = 1\ 196821 \times 10^{-112}\ g^3·cm^6$

## Enthalpy of Formation

Settle *et al.*[1] derived $\Delta_fH° = 229.7 \pm 0.6$ kcal·mol$^{-1}$ for $IF_7(g)$ at 298.15 K from treatment of their calorimetric data on combustion of iodine in fluorine. The combustion products, consisting of mixtures of $IF_5$ and $IF_7$, were expanded, treated to remove excess fluorine, and then hydrolyzed. The solutions were analyzed for iodate and the sum of iodate plus periodate. Since the recovery of iodine was not complete (about 70 to 99%), it was necessary to try various assumptions about the form of the unrecovered iodine. Consistent results were obtained only by assigning the unrecovered iodine to $IF_7$, the less volatile product. This treatment indicated that $IF_7$ was formed in yields ranging from about 1 to 70%.

$\Delta_rH°$ for the reaction $IF_7(g) \rightarrow IF_5(g) + F_2(g)$ may be checked via equilibrium data.[2] Using six points read from Figure 2 of Bernstein and Katz, we obtain $\Delta_rH°$(3rd law) = 29.36 ± 0.2 kcal·mol$^{-1}$ and $\Delta_rH°$(2nd law) = 29.53 ± 0.7 kcal·mol$^{-1}$, both at 298.15 K. The entropy test, $\Delta_rS°$(2nd law) $\Delta_rS°$(JANAF Functions) = 0.3 ± 1.4 cal K$^{-1}$·mol$^{-1}$, indicates consistency with the JANAF functions. Combination of $\Delta_rH°$(3rd law) with $\Delta_fH°$ for $IF_5(g)$ yields $\Delta_fH°(IF_7, g) = -230.2 \pm 0.6$ kcal·mol$^{-1}$ In deriving the uncertainty, we assume that $\Delta_rH°$(3rd law) is uncertain by ±0.5 kcal·mol$^{-1}$ due to an estimated uncertainty of about 1.0 cal K$^{-1}$·mol$^{-1}$ in the JANAF value of $\Delta_rS°$ at 500 K.

## Heat Capacity and Entropy

Recent evidence favors $D_{5h}$ symmetry and a pentagonal bipyramidal structure for the heptafluoride. Claassen *et al.*[3] review the earlier debate about structure of lower symmetry. They provide convincing evidence of $D_{5h}$ symmetry from the first observation of Raman spectra of the vapor state and re examination of the infrared spectra. Their data including five fundamentals in Raman (two polarized), five fundamentals in infrared, no coincidences between Raman and infrared, and one fundamental inactive are consistent only with $D_{5h}$ symmetry. This is confirmed by Falconer *et al.*[4] who interpret their electric deflection experiments as indicating a symmetry forbidden dipole moment. Extended Huckel molecular orbital calculations[5] also predict $D_{5h}$ symmetry. The adopted structural parameters are from our approximate analysis of the electron diffraction data of Thompson and Bartell.[6] The authors gave a radial distribution curve and suggested only a gross (unrefined) structure because of the probable presence of a fluorocarbon impurity in their sample Principal moments of inertia are $I_A = I_B = 46.8306 \times 10^{-39}$ and $I_C = 54.5719 \times 10^{-39}$ g·cm$^2$.

Observed vibrational fundamentals are from Claassen *et al.*[3] The inactive fundamental is estimated from the calculations of Khanna.[7]

## References

[1] J. L. Settle, J. H. E. Jeffes, P. A. G. O'Hare and W. N. Hubbard, presented at the 23rd Annual Calorimetry Conference, Midland, Mich., (August 1968).
[2] R. B Bernstein and J. J. Katz, J. Phys. Chem. 56, 885 (1952).
[3] H. H. Claassen, E. L. Gasner and H. Selig, J. Chem. Phys. 49, 1803 (1968).
[4] W. E. Falconer, A. Buchler, J. L. Stauffer and W. Klemperer, J. Chem. Phys. 48, 312 (1968).
[5] R. L. Oakland and G. H. Duffey, J. Chem. Phys. 46, 19 (1967).
[6] H. B. Thompson and L. S. Bartell, Trans Amer. Crystallogr. Assoc. 2, 190 (1966).
[7] R. K. Khanna, J. Mol. Spectrosc. 8, 134 (1962).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_fH°$ | $\Delta_fG°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −23.471 | −947.050 | −947.050 | INFINITE |
| 100 | 52.248 | 247.318 | 444.637 | −19.732 | −955.010 | −917 063 | 479.024 |
| 200 | 103.461 | 300.045 | 359.173 | −11.826 | −959.821 | −876.878 | 229.017 |
| 250 | 121.537 | 325.173 | 349.886 | −6.178 | −960.746 | −856.020 | 178.856 |
| 298.15 | 134 451 | 347.740 | 347.740 | 0. | −961.065 | −835.814 | 146.431 |
| 300 | 134.875 | 348.573 | 347.743 | 0.249 | −961.069 | −835.037 | 145.393 |
| 350 | 144 688 | 370.140 | 349.424 | 7.251 | −961.034 | −814.031 | 121.487 |
| 400 | 151.979 | 389.959 | 353.269 | 14.676 | −968.728 | −792.774 | 103.526 |
| 450 | 157.478 | 408.192 | 358.373 | 22.419 | −968.837 | −770.771 | 89 469 |
| 500 | 161.694 | 425.012 | 364.207 | 30.403 | −988.880 | −746.865 | 78.024 |
| 600 | 167.580 | 455.054 | 376.906 | 46.889 | −986.428 | −698.688 | 60.826 |
| 700 | 171.367 | 481.191 | 389.978 | 63.850 | −983.782 | −650.938 | 48.574 |
| 800 | 173.928 | 504.252 | 402.849 | 81.122 | −981.032 | −603.576 | 39.409 |
| 900 | 175.733 | 524.848 | 415.281 | 98.610 | −978.229 | −556.562 | 32.302 |
| 1000 | 177.050 | 543.434 | 427.182 | 116.252 | −975.402 | −509.861 | 26.632 |
| 1100 | 178.038 | 560.358 | 438.531 | 134.009 | −972.573 | −463.444 | 22.007 |
| 1200 | 178.798 | 575.883 | 449.339 | 151.853 | −969.756 | −417.284 | 18.164 |
| 1300 | 179.395 | 590.219 | 459.632 | 169 763 | −966.966 | −371.358 | 14.921 |
| 1400 | 179.871 | 603.531 | 469.440 | 187.727 | −964.212 | −325.646 | 12.150 |
| 1500 | 180.257 | 615.955 | 478.799 | 205.734 | −961.506 | −280.129 | 9.755 |
| 1600 | 180.575 | 627.599 | 487.739 | 223.777 | −958.853 | −234.791 | 7.665 |
| 1700 | 180.839 | 638.554 | 496.291 | 241.848 | −956.258 | −189.616 | 5.826 |
| 1800 | 181.061 | 648.897 | 504.485 | 259.943 | −953.723 | −144.593 | 4.196 |
| 1900 | 181.249 | 658.692 | 512.345 | 278.059 | −951.244 | −99.710 | 2.741 |
| 2000 | 181.410 | 667.993 | 519.897 | 296.192 | −948.815 | −54.955 | 1.435 |
| 2100 | 181.549 | 676.847 | 527.162 | 314.340 | −946.425 | −10.321 | 0.257 |
| 2200 | 181.670 | 685.296 | 534.159 | 332.501 | −944.062 | 34.200 | −0.812 |
| 2300 | 181.775 | 693.374 | 540.907 | 350 674 | −941.712 | 78.614 | −1.785 |
| 2400 | 181.868 | 701.112 | 547.422 | 368.856 | −939.356 | 122.925 | −2.675 |
| 2500 | 181.950 | 708.538 | 553.719 | 387.047 | −936.978 | 167.138 | −3 492 |
| 2600 | 182.022 | 715.676 | 559.812 | 405.245 | −934.560 | 211.256 | −4.244 |
| 2700 | 182.087 | 722.547 | 565.713 | 423.451 | −932.086 | 255.279 | −4.939 |
| 2800 | 182.145 | 729.170 | 571.433 | 441.663 | −929.539 | 299.209 | −5.582 |
| 2900 | 182.197 | 735.562 | 576.983 | 459.880 | −926.904 | 343.046 | −6.179 |
| 3000 | 182.244 | 741.740 | 582.373 | 478.102 | −924.168 | 386.791 | −6.735 |
| 3100 | 182.287 | 747.716 | 587.610 | 496.328 | −921.319 | 430 443 | −7.253 |
| 3200 | 182.325 | 753.504 | 592.705 | 514.559 | −918.347 | 474.001 | −7.737 |
| 3300 | 182.360 | 759.115 | 597.663 | 532.793 | −915.245 | 517.465 | −8 191 |
| 3400 | 182.393 | 764.560 | 602.492 | 551.031 | −912.005 | 560.832 | −8.616 |
| 3500 | 182.422 | 769.847 | 607.198 | 569.272 | −908.621 | 604.102 | −9.016 |
| 3600 | 182.449 | 774.987 | 611.788 | 587.515 | −905.091 | 647.273 | −9.392 |
| 3700 | 182.474 | 779 986 | 616.267 | 605.761 | −901 412 | 690.344 | −9.746 |
| 3800 | 182.497 | 784.853 | 620.639 | 624.010 | −897.581 | 733.313 | −10.080 |
| 3900 | 182.518 | 789.593 | 624.911 | 642.261 | −893.599 | 776.180 | −10.396 |
| 4000 | 182.538 | 794.214 | 629.086 | 660.514 | −889.465 | 818.943 | −10.694 |
| 4100 | 182.556 | 798.722 | 633.169 | 678 768 | −885.181 | 861.599 | −10.977 |
| 4200 | 182.573 | 803.121 | 637.163 | 697.025 | −880.749 | 904.151 | −11.245 |
| 4300 | 182.589 | 807.418 | 641.073 | 715.283 | −876.170 | 946.594 | −11.499 |
| 4400 | 182.603 | 811.615 | 644.901 | 733.542 | −871.446 | 988.930 | −11.740 |
| 4500 | 182.617 | 815.719 | 648.652 | 751.804 | −866.582 | 1031.158 | −11.969 |
| 4600 | 182.630 | 819.733 | 652.327 | 770.066 | −861.579 | 1073.274 | −12.187 |
| 4700 | 182.642 | 823.661 | 655.931 | 788.330 | −856.441 | 1115.281 | −12.395 |
| 4800 | 182.653 | 827.506 | 659.466 | 806.594 | −851.172 | 1157.178 | −12.593 |
| 4900 | 182.664 | 831.273 | 662.934 | 824.860 | −845.774 | 1198.962 | −12.781 |
| 5000 | 182.674 | 834.963 | 666.338 | 843.127 | −840.252 | 1240.635 | −12.961 |
| 5100 | 182.684 | 838.580 | 669.679 | 861.395 | −834 609 | 1282.197 | −13.132 |
| 5200 | 182.692 | 842.128 | 672.962 | 879 664 | −828.849 | 1323.648 | −13.296 |
| 5300 | 182.701 | 845.608 | 676.187 | 897 933 | −822.976 | 1364.986 | −13.453 |
| 5400 | 182.709 | 849.023 | 679.356 | 916.204 | −816.992 | 1406.212 | −13.602 |
| 5500 | 182.716 | 852.376 | 682.471 | 934.475 | −810.901 | 1447.326 | −13.746 |
| 5600 | 182.723 | 855.668 | 685.535 | 952.747 | −804.707 | 1488.330 | −13.883 |
| 5700 | 182.730 | 858.902 | 688.548 | 971.020 | −798.413 | 1529.220 | −14.014 |
| 5800 | 182.736 | 862.080 | 691.513 | 989.293 | −792.023 | 1570.000 | −14.139 |
| 5900 | 182.742 | 865.204 | 694.430 | 1007.567 | −785.539 | 1610.671 | −14.260 |
| 6000 | 182.748 | 868.276 | 697.302 | 1025.842 | −778.964 | 1651.228 | −14.375 |

PREVIOUS December 1969 (1 atm) CURRENT· December 1969 (1 bar)

$S°(298.15 K) = [531.554 \pm 16.7] J·K^{-1}·mol^{-1}$

$\Delta_f H°(0 K) = -2686.418 \pm 8.4 kJ·mol^{-1}$
$\Delta_f H°(298.15 K) = 2697.843 \pm 8.4 kJ·mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ |
|---|---|
| 759 (2) | 261 (4) |
| 738 (2) | 112 (4) |
| 683 (2) | [400](4) |
| [500](2) | [90](3) |
| 713 (4) | [60](3) |

Ground State Quantum Weight: [3] $\sigma = [4]$
Point Group. $[D_{2h}]$
Bond Distances Mo–F = [1.78] Å; $Mo–F_{bridge} = [2.06]$ Å
Bond Angles: F–Mo–F = [90° or 180°]; $F_{bridge}–Mo–F_{bridge} = [90]°$
Product of the Moments of Inertia: $I_A I_B I_C = [3.683573 \times 10^{-111}] g^3·cm^6$

## Enthalpy of Formation

We adopt $\Delta_f H°(298.15 K) = -644.8 \pm 2 kcal·mol^{-1}$ in agreement with Brewer.[1] This is derived by proceeding from $\Delta_f H°(MoF_5$, cr, 298.15 K) to $\Delta_f H°(MoF_5$, l, 298.15 K) to $\Delta_f H°$(dimer, g, 298.15 K). Brewer[1] adopted $\Delta_f H°(MoF_5$, cr, 298.15 K) = $-331.9 \pm 1$ kcal $mol^{-1}$ from the measurements of Burgess *et al.*[2] and Nuttall *et al.*[3] Krause and Douglas[4] measured $\Delta_{fus}H°(318.82 K) = 1.46 \pm 0.07 kcal·mol^{-1}$ and the $\Delta C_p°$ correction to 298.15 K is only $-4$ cal $K^{-1}$ $mol^{-1}$. The heat of vaporization to the dimer $\Delta_{vap}H°(298.15 K) = 15.99$ kcal $mol^{-1}$ was derived by Krause[5] from vapor density data.

The value of $\Delta_f H°(0 K)$ combined with JANAF data[11] for Mo(g) and F(g) gives $\Delta_{at}H°(0 K) = 1139.9 \pm 8 kcal·mol^{-1}$ and an average bond energy of $\Delta_{at}H°(0 K)/10 = 114.0 \pm 1 kcal·mol^{-1}$.

## Heat Capacity and Entropy

For $Mo_2F_{10}(g)$, the dimer of $MoF_5(g)$, Douglas,[6] Krause,[5] and Brewer[1] have used the $MoF_5(g)$ frequencies with doubled degeneracy along with estimates of two triply degenerate frequencies. The frequencies, $cm^{-1}$, and degeneracies for $MoF_5(g)$ were assigned from the spectroscopic data of Acquista and Abramowitz[7] and two fundamentals were estimated[8] — — 759(1), 738(1), 683(1), [500](1), 713(2), 261(2), 112(2), and [200](2). Douglas[6] and Krause[5] elected to use an estimate of [400](2) rather than [200](2) while, for $MoF_5$, Brewer[1] and Hildenbrand[9] retained the [200](2) estimate. The derived functions for $Mo_2F_{10}(g)$ presented here and by Brewer[1] use the [400](4) estimate. For the six remaining frequencies, Douglas[6] has chosen the estimates [121](3) and [90](3) and Krause[5] has chosen [60](6), Brewer[1] has used [90](3) and [60](3), one of the alternative estimates of Douglas,[6] in order to match the selected entropy of the liquid and the entropy of vaporization to the dimer.[5] We adopt Brewer's[1] evaluation of the vibrational assignment and the estimate of an electronic ground state quantum weight of [3].[1-6]

By analogy with the $MoF_5$(cr) structure,[10] the dimer(g) molecule was assumed to have the structure of two octahedra sharing a common edge.[5,6] The two Mo atoms at the centers of the octahedra and the two bridging F atoms at the ends of the common edge form Mo–F–Mo angles of 90°. The bridging Mo–F bond distance of 2.06 Å and the non bridging Mo–F distance of 1.78 Å from $MoF_3$(cr),[10] were assumed for the gaseous dimer. All adjacent F–Mo–F angles are 90°.

The principal moments of inertia are: $I_A = 73.3619 \times 10^{-39}$, $I_B = 220.8005 \times 10^{-39}$, $I_C = 227.4042 \times 10^{-39} g·cm^2$.

This table is in good agreement with the critical evaluation by Brewer[1] on which it is based.

## References

[1] L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication, (September 1978); a preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.
[2] J. Burgess, I. Haigh, and R. D. Peacock, J. Chem. Soc., Dalton Trans. 1062 (1974).
[3] R. L. Nuttall, M. V. Kilday, and K. L. Churney in Report NBSIR 73 281, (1 July 1973) (AD Report 782028, 1974), Chapter 5.
[4] R. F. Krause, Jr., and T. B. Douglas, J. Chem. Thermodyn. 9, 1149 (1977).
[5] R. F. Krause, Jr., in "Proc. Symp. on High Temperature Metal Halide Chemistry," D. L. Hildenbrand and D. D. Cubicciotti, Eds., The Electrochem. Soc Vol. 78 1, 199–209, (1978).
[6] T. B. Douglas, J. Chem. Thermodyn. 9, 1165 (1977).
[7] N. Acquista and S. Abramowitz, J. Chem. Phys. 58, 5484 (1973).
[8] T. B. Douglas, R. F. Krause, Jr., N. Acquista, and S. Abramowitz, in Report NBSIR 73 280, (1 January 1973) (AD Report 782094,1973), Chapter 3.
[9] D. L. Hildenbrand, Stanford Research Institute, personal communication to L. Brewer. Also see P. D. Kleinschmidt, K. H. Lau, and D. L. Hildenbrand, J. Chem. Thermodyn. 11, 765 (1979).
[10] A. J. Edwards, R. D. Peacock, and R. W. H. Small, J. Chem. Soc. 4486 (1962).
[11] JANAF Thermochemical Tables: Mo(g), 3–31–78, F(g), 9–30–65.

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

|  | $J·K^{-1}mol^{-1}$ |  |  | $kJ·mol^{-1}$ |  |  |  |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −41.869 | −2686.418 | −2686.418 | INFINITE |
| 100 | 121.299 | 352.980 | 693.437 | −34.046 | −2694.112 | −2642.820 | 1380.468 |
| 200 | 174.754 | 454.231 | 549.884 | −19.131 | −2697.527 | −2589.929 | 676.420 |
| 250 | 195.952 | 495.583 | 534.963 | −9.845 | −2697.989 | −2562.962 | 535.502 |
| 298.15 | 212.349 | 531.554 | 531.554 | 0. | −2697.843 | −2536.961 | 444.465 |
| 300 | 212.904 | 532.870 | 531.558 | 0.393 | −2697.828 | −2535.962 | 441.550 |
| 350 | 226.083 | 566.722 | 534.202 | 11.382 | −2697.211 | −2509.028 | 374.452 |
| 400 | 236.249 | 597.604 | 540.226 | 22.951 | −2696.277 | −2482.206 | 324.143 |
| 450 | 244.122 | 625.905 | 548.196 | 34.969 | −2695.125 | −2455.514 | 285.029 |
| 500 | 250.274 | 651.957 | 557.287 | 47.335 | −2693.820 | −2428.959 | 253.752 |
| 600 | 259 028 | 698.420 | 577.032 | 72.833 | −2690.923 | −2376.255 | 206.871 |
| 700 | 264.757 | 738.809 | 597.322 | 99.041 | −2687.818 | −2324 053 | 173.423 |
| 800 | 268.674 | 774.434 | 617.279 | 125.724 | −2684.624 | −2272.304 | 148.366 |
| 900 | 271.456 | 806.248 | 636.539 | 152 738 | −2681.414 | −2220.957 | 128.901 |
| 1000 | 273.496 | 834.960 | 654.969 | 179.991 | −2678.236 | −2169.967 | 113.347 |
| 1100 | 275.033 | 861.102 | 672.538 | 207.421 | −2675.131 | −2119.291 | 100.637 |
| 1200 | 276.218 | 885.086 | 689.265 | 234.986 | −2672.133 | −2068.893 | 90.057 |
| 1300 | 277.150 | 907.234 | 705.191 | 262.656 | −2669.271 | −2018.740 | 81.114 |
| 1400 | 277.895 | 927.801 | 720.366 | 290.409 | −2666.570 | −1968.802 | 73.457 |
| 1500 | 278.501 | 946.995 | 734.842 | 318.230 | −2664.052 | −1919.050 | 66.827 |
| 1600 | 278.999 | 964.986 | 748.669 | 346.106 | −2661.735 | −1869.460 | 61.032 |
| 1700 | 279.414 | 981.913 | 761.897 | 374.027 | −2659.631 | −1820.008 | 55.922 |
| 1800 | 279.763 | 997.894 | 774.568 | 401.987 | −2657.753 | −1770.673 | 51.384 |
| 1900 | 280.059 | 1013.028 | 786.724 | 429.978 | −2656.110 | −1721.438 | 47.326 |
| 2000 | 280.313 | 1027.400 | 798.401 | 457.997 | −2654.709 | −1672.281 | 43.676 |
| 2100 | 280.531 | 1041.082 | 809.634 | 486.040 | −2653.555 | −1623 190 | 40.375 |
| 2200 | 280.721 | 1054.136 | 820.453 | 514.102 | −2652.651 | −1574.147 | 37.375 |
| 2300 | 280.887 | 1066.619 | 830.887 | 542.183 | −2652.001 | −1525 139 | 34.637 |
| 2400 | 281 033 | 1078.576 | 840.960 | 570.279 | −2651.608 | −1476.155 | 32.128 |
| 2500 | 281.162 | 1090.051 | 850.696 | 598.389 | −2651.478 | −1427.181 | 29.819 |
| 2600 | 281.277 | 1101.081 | 860.115 | 626.511 | −2651.638 | −1378.207 | 27.689 |
| 2700 | 281.379 | 1111.698 | 869.238 | 654.644 | −2652.152 | −1329.220 | 25.715 |
| 2800 | 281.470 | 1121.933 | 878.081 | 682.787 | −2653.129 | −1280.207 | 23.883 |
| 2900 | 281.553 | 1131.812 | 886.661 | 710.938 | −2726.487 | −1231.049 | 22.174 |
| 3000 | 281.627 | 1141.358 | 894.992 | 739.097 | −2724.766 | −1179.511 | 20.537 |
| 3100 | 281.694 | 1150.594 | 903.090 | 767.263 | −2722.904 | −1128.034 | 19.007 |
| 3200 | 281.755 | 1159.538 | 910.965 | 795.435 | −2720.893 | −1076.618 | 17.574 |
| 3300 | 281.810 | 1168.209 | 918.629 | 823.614 | −2718 724 | −1025.267 | 16.229 |
| 3400 | 281.861 | 1176.623 | 926.094 | 851.797 | −2716.393 | −973.985 | 14.963 |
| 3500 | 281.908 | 1184 794 | 933.369 | 879.986 | −2713.895 | −922.773 | 13.772 |
| 3600 | 281.950 | 1192.736 | 940.464 | 908.179 | −2711.226 | −871.635 | 12.647 |
| 3700 | 281 990 | 1200.462 | 947.387 | 936.376 | −2708.383 | −820.574 | 11.584 |
| 3800 | 282.026 | 1207.982 | 954.146 | 964.577 | −2705.367 | −769.594 | 10.579 |
| 3900 | 282.059 | 1215.309 | 960 749 | 992.781 | −2702.176 | −718.692 | 9.626 |
| 4000 | 282.091 | 1222.450 | 967.203 | 1020.988 | −2698.811 | −667.876 | 8.722 |
| 4100 | 282.119 | 1229.416 | 973.514 | 1049.199 | −2695.273 | −617.147 | 7.863 |
| 4200 | 282.146 | 1236.215 | 979.688 | 1077.412 | −2691.564 | −566.505 | 7 046 |
| 4300 | 282.171 | 1242.854 | 985.731 | 1105.628 | −2687.687 | −515.955 | 6.268 |
| 4400 | 282.194 | 1249.341 | 991.649 | 1133.846 | −2683.643 | −465.495 | 5.526 |
| 4500 | 282.216 | 1255.683 | 997.446 | 1162.067 | −2679.437 | −415.129 | 4.819 |
| 4600 | 282.236 | 1261.886 | 1003.128 | 1190.290 | −2675.071 | −364.860 | 4.143 |
| 4700 | 282.255 | 1267.956 | 1008.698 | 1218.514 | −2670.549 | −314.686 | 3.497 |
| 4800 | 282.273 | 1273.899 | 1014.161 | 1246.741 | −2665.874 | −264.610 | 2.880 |
| 4900 | 282.290 | 1279.719 | 1019.522 | 1274.969 | −2661.051 | −214.633 | 2.288 |
| 5000 | 282.306 | 1285.423 | 1024.783 | 1303.199 | −3838.853 | −153.294 | 1.601 |
| 5100 | 282.321 | 1291.013 | 1029.948 | 1331.430 | −3837.103 | −79.601 | 0.815 |
| 5200 | 282.335 | 1296.495 | 1035.022 | 1359.663 | −3835.509 | −5.939 | 0.060 |
| 5300 | 282.348 | 1301.873 | 1040.006 | 1387.897 | −3834.068 | 67.692 | −0.667 |
| 5400 | 282.361 | 1307.151 | 1044.905 | 1416 132 | −3832.786 | 141.298 | −1.367 |
| 5500 | 282.372 | 1312.332 | 1049.720 | 1444.369 | −3831.657 | 214 880 | −2.041 |
| 5600 | 282.384 | 1317.421 | 1054.455 | 1472.607 | −3830.683 | 288 446 | −2.691 |
| 5700 | 282.394 | 1322 419 | 1059.112 | 1500.846 | −3829 859 | 361.992 | −3.317 |
| 5800 | 282.404 | 1327.330 | 1063.695 | 1529.086 | −3829.186 | 435.526 | −3.922 |
| 5900 | 282.414 | 1332.158 | 1068.204 | 1557.327 | −3828.658 | 509.053 | −4.507 |
| 6000 | 282.423 | 1336.904 | 1072.643 | 1585.568 | −3828.279 | 582.568 | −5.072 |

PREVIOUS March 1979 (1 atm) CURRENT: March 1979 (1 bar)

## Sulfur Fluoride ($S_2F_{10}$) IDEAL GAS $M_r = 254.104030$ Sulfur Fluoride ($S_2F_{10}$) $F_{10}S_2(g)$

$S^\circ(298.15\ K) = [396.943 \pm 8.4]\ kJ{\cdot}mol^{-1}$

$\Delta_f H^\circ(0\ K) = -2040.744 \pm 29.3\ kJ{\cdot}mol^{-1}$
$\Delta_f H^\circ(298.15\ K) = -2064.386 \pm 29.3\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|---|---|
| 913 (1) | 938 (1) | 410 (2) | 860 (2) |
| 690 (1) | 684 (1) | [150](2) | 634 (2) |
| [642](1) | 571 (1) | 728 (2) | 425 (2) |
| 247 (1) | 826 (2) | 624 (2) | 188 (2) |
| Torsion | 544 (2) | 509 (2) | |

Ground State Quantum Weight: [1] $\sigma = 8$
Point Group: [$D_{4h}$]
Bond Distances: S–F = 1.56 ± 0.02 Å; S–S = 2.21 ± 0.03 Å
Bond Angles: F*–S–F* = 90°; F*–S–S = 90°
F**–S–S* = 180°; (*–equatorial **–axial)
Product of the Moments of Inertia: $I_A I_B I_C = 8.747547 \times 10^{-112}\ g^3{\cdot}cm^6$
Reduced Moment of Inertia: $I_{red} = 1.5354 \times 10^{-38}\ g{\cdot}cm^2$
Barrier to Internal Rotation: V = [8.0] $kcal{\cdot}mol^{-1}$

### Enthalpy of Formation

The kinetics of the decomposition of gaseous $S_2F_{10}$ have been studied by Trost and McIntosh[1] from 434 455 K. Benson and Bott[2] have reevaluated these kinetic data and have reported two values for the equilibrium constant of the dissociation process $S_2F_{10}(g) = SF_4(g) + SF_6(g)$. Both values refer to a temperature of 444 K. We analyze these two $K_p$ values by the 3rd law method, and we obtain the result $\Delta_r H^\circ(298.15\ K) = 19.26 \pm 1.4\ kcal{\cdot}mol^{-1}$. The adopted value of $\Delta_f H^\circ(S_2F_{10}, g, 298.15\ K) = -493.4 \pm 7\ kcal{\cdot}mol^{-1}$ is obtained by combining the value of $\Delta_r H^\circ$ with JANAF enthalpies of formation[3] for $SF_4$ and $SF_6$.

The heat of atomization, $\Delta_a H^\circ(0\ K)$, and bond dissocation energy $D_0^\circ(F_5S{-}SF_5)$ are calculated to be $802.8 \pm 11.0\ kcal{\cdot}mol^{-1}$ and $58.4 \pm 14.0\ kcal{\cdot}mol^{-1}$, respectively. The latter value agrees with an upper limit value of 62.6 kcal mol$^{-1}$ for the bond energy of a covalent S–S linkage established from thermochemical data[3] for the $S_8$ ring.

### Heat Capacity and Entropy

The results of electron diffraction experiments[4] show that the $S_2F_{10}$ molecule consists of two $SF_5$ octahedral groups sharing a common S–S bond. The adopted bond lengths and angles are taken from this study.[4] The relative orientation of the two $SF_5$ groups has not been experimentally established,[5–7] but the staggered configuration of $D_{4d}$ symmetry has been predicted to be more stable[8] than the eclipsed form ($D_{4h}$ symmetry). We assume that the point group is $D_{4d}$. The principal moments of inertia are: $I_A = 61.4204 \times 10^{-39}$ and $I_B = I_C = 119.3402 \times 10^{-39}\ g{\cdot}cm^2$.

The vibrational spectra of $S_2F_{10}$ have been studied in detail in three independent investigations.[5–7] The reported fundamental frequencies show reasonable agreement but the assignments of the observed fundamentals made by Wilmshurst and Bernstein[5] differ somewhat from those made by Dodd *et al.*[6] The adopted frequencies and assignments except for the torsion ($\nu_5$) and $SF_5$ rocking frequency ($\nu_{12}$) are taken from Dodd *et al.*[6] We estimate the unobserved $\nu_{12}$ fundamental at 150 cm$^{-1}$. Other estimated values that have been reported include 200 cm$^{-1}$ [2] and 37 cm$^{-1}$.[5] The inactive torsional frequency is treated as a hindered internal rotation. We use an estimated potential barrier of 8.0 $kcal{\cdot}mol^{-1}$ [5] to calculate heat capacity contributions for hindered rotation from the table of Pitzer and Brewer.[9] Contributions below 201 K could not be obtained by this procedure since the values of the ratio V/RT were outside the range of the table. $C_p^\circ$ value between 150 200 K are estimated by graphical interpolation of the hindered rotor $C_p^\circ$ data above 210 K and the corresponding data for a harmonic oscillator ($\nu_5 = 89$ cm$^{-1}$)[5] below 150 K. This treatment assumes that the internal rotation approaches harmonic oscillation as V/RT >> 1 The uncertainty (±2 cal $K^{-1}{\cdot}mol^{-1}$) in the value of $S^\circ(298.15\ K)$ includes the possibility that the potential barrier is as low as 4.0 $kcal{\cdot}mol^{-1}$ [8] and contains a contribution from the uncertainty due to the two estimated vibrational frequencies.

Previously published thermodynamic functions[10, 11] for $S_2F_{10}$ are based on the assumption that free internal rotation exists in the molecule and on different estimates[5] for the $SF_5$ rocking fundamentals. Benson and Bott[2] have shown that these earlier frequencies[5] give values for $S^\circ(S_2F_{10}, g)$ which are too high by several units. Our treatment of internal rotation is consistent with the interpretation of electron diffraction data[4] which indicates that the rotation is not completely restricted. It should also be noted that the $C_p^\circ$ data reported by Pass[11] are erroneous above 400 K.

### References

[1] W. R. Trost and R. L. McIntosh, Can J Chem. 29, 508 (1951).
[2] S W. Benson and J. Bott, Int. J Chem. Kinet. 1, 451 (1969).

Continued on page 1217

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p^\circ$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log K$_f$ |
| 0 | 0. | 0. | INFINITE | −29.307 | −2040.744 | −2040 744 | INFINITE |
| 100 | 69.170 | 271.813 | 518.037 | −24.622 | −2051.974 | −1991.466 | 1040.235 |
| 200 | 124.892 | 336.657 | 411.591 | −14.987 | −2060.267 | −1927.492 | 503.409 |
| 298.15 | 176.682 | 396.943 | 396.943 | 0. | −2064.386 | −1861.311 | 326.094 |
| 300 | 177.473 | 398.038 | 396.946 | 0.328 | −2064.432 | −1860.051 | 323.864 |
| 400 | 211.418 | 454.110 | 404.360 | 19.900 | −2070.149 | −1791.494 | 233.945 |
| 500 | 232.735 | 503.752 | 419.380 | 42.186 | −2072.548 | −1721.547 | 179.849 |
| 600 | 246.438 | 547.482 | 437.162 | 66.192 | −2073.079 | −1651.270 | 143 756 |
| 700 | 255.525 | 586.198 | 455.742 | 91.319 | −2072.404 | −1581.009 | 117.976 |
| 800 | 261.768 | 620.750 | 474.248 | 117.202 | −2070.991 | −1510.899 | 98.652 |
| 900 | 266.123 | 651.847 | 492.282 | 143.608 | −2175.369 | −1438.835 | 83.508 |
| 1000 | 269.228 | 680.054 | 509.671 | 170.383 | −2170.756 | −1357.244 | 70.895 |
| 1100 | 271.377 | 705.819 | 526.349 | 197.417 | −2166.065 | −1276.120 | 60.598 |
| 1200 | 273.094 | 729.508 | 542.305 | 224.644 | −2161.341 | −1195 424 | 52.035 |
| 1300 | 274.275 | 751.416 | 557.558 | 252.014 | −2156.622 | −1115.122 | 44.806 |
| 1400 | 275.232 | 771.778 | 572.141 | 279.492 | −2151.934 | −1035.184 | 38.623 |
| 1500 | 275.907 | 790.791 | 586.091 | 307.049 | −2147.295 | −955.578 | 33.276 |
| 1600 | 276.470 | 808.616 | 599.448 | 334.669 | −2142.716 | −876.279 | 28.608 |
| 1700 | 276.813 | 825.387 | 612.250 | 362.334 | −2138.203 | −797.265 | 24.497 |
| 1800 | 277.117 | 841.218 | 624.535 | 390.030 | −2133.759 | −718.515 | 20.851 |
| 1900 | 277.384 | 856.208 | 636.337 | 417.756 | −2129.371 | −640.011 | 17.595 |
| 2000 | 277.613 | 870.442 | 647.689 | 445.506 | −2125.029 | −561.735 | 14.671 |
| 2100 | 277.754 | 883.991 | 658.622 | 473.274 | −2120.721 | −483.678 | 12.031 |
| 2200 | 277.883 | 896.915 | 669.162 | 501.056 | −2116.432 | −405.824 | 9.635 |
| 2300 | 277.997 | 909.270 | 679.335 | 528.851 | −2112.143 | −328.164 | 7.453 |
| 2400 | 278.098 | 921.103 | 689.164 | 556.655 | −2107.836 | −250.692 | 5.456 |
| 2500 | 278.186 | 932.458 | 698.670 | 584.470 | −2103.492 | −173 400 | 3.623 |
| 2600 | 278.245 | 943.370 | 707.873 | 612.291 | −2099.093 | −96.283 | 1.934 |
| 2700 | 278.298 | 953.872 | 716.791 | 640.119 | −2094.622 | −19.337 | 0.374 |
| 2800 | 278.345 | 963.994 | 725.440 | 667.951 | −2090.064 | 57.443 | −1.072 |
| 2900 | 278.386 | 973.762 | 733.835 | 695.787 | −2085.402 | 134.057 | −2.415 |
| 3000 | 278.420 | 983.200 | 741.991 | 723.628 | −2080.626 | 210.509 | −3.665 |
| 3100 | 278.441 | 992.330 | 749.920 | 751.471 | −2075.722 | 286.799 | −4.833 |
| 3200 | 278.459 | 1001.170 | 757.634 | 779.316 | −2070.683 | 362.930 | −5.924 |
| 3300 | 278.475 | 1009.739 | 765.144 | 807.162 | −2065.499 | 438.901 | −6.947 |
| 3400 | 278.488 | 1018.053 | 772.461 | 835.011 | −2060.164 | 514.712 | −7.908 |
| 3500 | 278.500 | 1026.125 | 779.594 | 862.860 | −2054.674 | 590.364 | −8.811 |
| 3600 | 278.504 | 1033.971 | 786.552 | 890.710 | −2049.026 | 665.858 | −9.661 |
| 3700 | 278.508 | 1041.602 | 793.342 | 918.561 | −2043.216 | 741.191 | −10.464 |
| 3800 | 278.512 | 1049.029 | 799.973 | 946.412 | −2037.243 | 816.365 | −11.222 |
| 3900 | 278.516 | 1056.264 | 806.453 | 974.263 | −2031.108 | 891.381 | −11.939 |
| 4000 | 278.521 | 1063.315 | 812.786 | 1002.115 | −2024.811 | 966.238 | −12.618 |
| 4100 | 278.526 | 1070 193 | 818.981 | 1029.967 | −2018.353 | 1040.933 | −13.262 |
| 4200 | 278.531 | 1076.905 | 825.043 | 1057.820 | −2011.736 | 1115.471 | −13.873 |
| 4300 | 278.535 | 1083.459 | 830.976 | 1085.674 | −2004.963 | 1189.847 | −14.454 |
| 4400 | 278.539 | 1089.862 | 836.788 | 1113.527 | −1998.036 | 1264 066 | −15.006 |
| 4500 | 278.541 | 1096.122 | 842.481 | 1141.381 | −1990.959 | 1338.126 | −15.533 |
| 4600 | 278.542 | 1102.244 | 848.062 | 1169.235 | −1983.735 | 1412.025 | −16.034 |
| 4700 | 278.543 | 1108.234 | 853.534 | 1197.090 | −1976.370 | 1485.768 | −16.512 |
| 4800 | 278.543 | 1114.098 | 858.902 | 1224.944 | −1968.866 | 1559.351 | −16.969 |
| 4900 | 278.544 | 1119.842 | 864.169 | 1252.798 | −1961.228 | 1632.777 | −17.406 |
| 5000 | 278.546 | 1125.469 | 869.338 | 1280.653 | −1953.459 | 1706.045 | −17.823 |
| 5100 | 278.548 | 1130.985 | 874.415 | 1308.507 | −1945.565 | 1779.157 | −18.222 |
| 5200 | 278.549 | 1136.394 | 879.401 | 1336.362 | −1937.548 | 1852.114 | −18.605 |
| 5300 | 278.551 | 1141.700 | 884.300 | 1364.217 | −1929 414 | 1924.914 | −18.971 |
| 5400 | 278.553 | 1146.906 | 889.115 | 1392.073 | −1921.166 | 1997.560 | −19.323 |
| 5500 | 278.554 | 1152.018 | 893.849 | 1419.928 | −1912.809 | 2070.051 | −19.660 |
| 5600 | 278.555 | 1157.037 | 898.504 | 1447.783 | −1904.345 | 2142.392 | −19.983 |
| 5700 | 278.556 | 1161.967 | 903.083 | 1475.639 | −1895.780 | 2214.577 | −20.294 |
| 5800 | 278.557 | 1166.812 | 907.589 | 1503 495 | −1887.117 | 2286.613 | −20.593 |
| 5900 | 278.558 | 1171.574 | 912.023 | 1531.350 | −1878.359 | 2358.501 | −20.881 |
| 6000 | 278.558 | 1176.255 | 916.388 | 1559.206 | −1869.510 | 2430.236 | −21.157 |

PREVIOUS: CURRENT December 1977

Sulfur Fluoride ($S_2F_{10}$) $F_{10}S_2(g)$

## Molybdenum Fluoride ($(MoF_5)_3$) IDEAL GAS $M_r = 572.796045$ Molybdenum Fluoride ($(MoF_5)_3$) $F_{15}Mo_3(g)$

$S°(298.15\ K) = [706.844 \pm 29.3]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -4049.417 \pm 20.9\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -4065.593 \pm 20.9\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies

| $\nu$, cm$^{-1}$ | $\nu$, cm$^{-1}$ |
|---|---|
| 759 (3) | 261 (6) |
| 738 (3) | 112 (6) |
| 683 (3) | [400](6) |
| [500](3) | [106](6) |
| 713 (6) | [53](6) |

Ground State Quantum Weight: [4] $\sigma = [6]$
Point Group: [$D_{3h}$]
Bond Distances: Mo–F = [1.78] Å; Mo–$F_{bridge}$ = [2.06] Å
Bond Angles: F–Mo–F = [90° or 180°], $F_{bridge}$–Mo–$F_{bridge}$ = [90°]
Product of the Moments of Inertia: $I_A I_B I_C = [9.5696 \times 10^{-110}]\ g^3{\cdot}cm^6$

### Enthalpy of Formation

We adopt $\Delta_f H°(Mo_3F_{15}$, g, 298.15 K) = −971.7 ± 5 kcal·mol$^{-1}$ to agree with Brewer.[1] This is based on 1) the $\Delta_f H°(MoF_5$, cr, 298.15 K) = −331.9 ± 1 kcal·mol$^{-1}$ adopted by Brewer from the measurements of Burgess *et al.*[2] and Nuttall *et al.*[3] 2) the heat of fusion $\Delta_{fus}H°$(318.82 K) = 1.46 ± 0.07 kcal·mol$^{-1}$ measured by Krause and Douglas,[4] and 3) a heat of vaporization to the trimer $\Delta_{vap}H°$(298.15 K) = 18.9 kcal·mol$^{-1}$. This heat of vaporization was derived by Brewer[1] from a re–evaluation of the vapor density data of Douglas[5] — the proportion of $Mo_3F_{15}(g)$ in the saturated vapor was reduced to be consistent with no appreciable monomer and a vapor density corresponding to $Mo_2F_{10}(g)$. Douglas[5] had chosen $\Delta_{vap}H°$(298.15 K) of $MoF_5(l)$ to $Mo_3F_{15}(g)$ equal to 17.7 kcal·mol$^{-1}$ from a possible range of 16 to 21 kcal·mol$^{-1}$. The value of $\Delta_f H°$(0 K) combined with JANAF data[6] for Mo(g) and F(g) gives $\Delta_{at}H°$(0 K) = 1714.5 ± 14 kcal·mol$^{-1}$ and an average Mo–F bond energy of $\Delta_{at}H°$(0 K)/15 = 114.3 ± 1 kcal·mol$^{-1}$.

### Heat Capacity and Entropy

Brewer[1] has followed Douglas's[5] choice of [4] for the electronic ground state quantum weight, 2) of vibrational frequencies and 3) of molecular configuration.

The $MoF_5(g)$ monomer vibrational frequencies were used, with triple the degeneracy, for the trimer, $Mo_3F_{15}$, and the 12 remaining frequencies were estimated as [106](6) and [53](6).[5] The vibrational frequencies for $MoF_5(g)$ had been assigned from the spectroscopic data of Aquista and Abramowitz[7] and two fundamentals had been estimated,[8] these frequencies, cm$^{-1}$, and degeneracies are 759(1), 738(1), 683(1), [500](1), 713(2), 261(2), and [200](2). Douglas[5] used [400](2) rather than [200](2).

The structure assumed by Douglas[5] consists of three tetragonal bipyramids joined by three bridging F atoms such that the three Mo atoms and the three bridging F atoms form a planar, irregular hexagon. The $F_{bridge}$–Mo–$F_{bridge}$ angles are 90°, the Mo– $F_{bridge}$–Mo angles are 150°; the remaining F–Mo–F angles are either 90° or 180°. The Mo–$F_{bridge}$ bond distance, 2 06 Å, and the Mo–F bond distance, 1.78 Å, are taken from the x–ray study of $MoF_5$(cr) by Edwards *et al.*[9]

The principal moments of inertia are $I_A = I_B = 3.8417 \times 10^{-37}$, $I_C = 6.4840 \times 10^{-37}\ g{\cdot}cm^2$.

This table is in good agreement with the critical evaluation of Brewer[1] on which it is based.

### References

[1] L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication, (September 1978); a preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.
[2] J. Burgess, I. Haigh, and R. D. Peacock, J. Chem. Soc., Dalton Trans. 1062 (1974).
[3] R. E. Nuttall, M. V. Kilday, and K. L. Churney in NBSIR 73–281, (AD Report 782028, 1974), Chap. 5., 1 (July 1973).
[4] R. F. Krause, Jr., and T. B. Douglas, J. Chem. Thermodyn. 9, 1149 (1977).
[5] T. B. Douglas, J. Chem. Thermodyn. 9, 1165 (1977).
[6] JANAF Thermochemical Tables: Mo(g), 3–31–78; F(g), 9–30–65.
[7] N. Aquista and S. Abramowitz, J. Chem. Phys. 58, 5484 (1973).
[8] T. B. Douglas, R. F. Krause, Jr., N. Aquista, and S. Abramowitz in NBSIR 73–380 (AD Report 782094, Chap. 3) (January 1, 1973).
[9] A. J. Edwards, R. D. Peacock, and R. W. H. Small, J. Chem. Soc. 4486 (1962).

Enthalpy Reference Temperature = $T_r$ = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

| | J·K$^{-1}$mol$^{-1}$ | | | kJ·mol$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| T/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
| 0 | 0. | 0. | INFINITE | −63.765 | −4049.417 | −4049 417 | INFINITE |
| 100 | 186.331 | 431.758 | 956.105 | −52.435 | −4061.363 | −3974.653 | 2076.146 |
| 200 | 269.353 | 587.843 | 735.038 | −29.439 | −4065.861 | −3885.765 | 1014.858 |
| 250 | 301.534 | 651.527 | 712.085 | −15.139 | −4066.184 | −3840.681 | 802.466 |
| 298.15 | 326.335 | 706.844 | 706.844 | 0. | −4065.593 | −3797.290 | 665.269 |
| 300 | 327.175 | 708.865 | 706.850 | 0.604 | −4065.556 | −3795.625 | 660.877 |
| 350 | 347.072 | 760.860 | 710.911 | 17.482 | −4064.236 | −3750.733 | 559.766 |
| 400 | 362.408 | 808.250 | 720.161 | 35.236 | −4062.436 | −3706 066 | 483.963 |
| 450 | 374.275 | 851.650 | 732.394 | 53.665 | −4060.304 | −3661.644 | 425.033 |
| 500 | 383.545 | 891.583 | 746.343 | 72.620 | −4057.940 | −3617.474 | 377.915 |
| 600 | 396.731 | 962.767 | 776.629 | 111.683 | −4052.778 | −3529.858 | 307.301 |
| 700 | 405.357 | 1024.615 | 807 735 | 151.816 | −4047.300 | −3443.135 | 256.930 |
| 800 | 411.255 | 1079.152 | 838.321 | 192.664 | −4041.687 | −3357.208 | 219.203 |
| 900 | 415.443 | 1127.846 | 867.834 | 234 010 | −4036.046 | −3271.987 | 189.901 |
| 1000 | 418.513 | 1171.784 | 896.068 | 275.716 | −4030.453 | −3187.392 | 166.492 |
| 1100 | 420.826 | 1211.786 | 922.979 | 317.688 | −4024.968 | −3103.353 | 147.366 |
| 1200 | 422.610 | 1248.482 | 948.596 | 359.863 | −4019.642 | −3019.805 | 131.449 |
| 1300 | 424 012 | 1282.366 | 972.984 | 402.197 | −4014.521 | −2936.695 | 117.998 |
| 1400 | 425.134 | 1313.832 | 996.220 | 444.656 | −4009.641 | −2853 971 | 106.483 |
| 1500 | 426.046 | 1343.195 | 1018.384 | 487.217 | −4005.035 | −2771.585 | 96.515 |
| 1600 | 426.795 | 1370.716 | 1039.553 | 529.860 | −4000.729 | −2689.497 | 87.803 |
| 1700 | 427.420 | 1396.610 | 1059.803 | 572.572 | −3996.743 | −2607.668 | 80 124 |
| 1800 | 427.945 | 1421.056 | 1079.200 | 615.341 | −3993.097 | −2526.064 | 73.304 |
| 1900 | 428.391 | 1444.206 | 1097.807 | 658.158 | −3989.802 | −2444.656 | 67.208 |
| 2000 | 428.772 | 1466 189 | 1115.681 | 701 017 | −3986.871 | −2363 408 | 61.726 |
| 2100 | 429.101 | 1487.117 | 1132.874 | 743.911 | −3984.309 | −2282.301 | 56.769 |
| 2200 | 429.387 | 1507.086 | 1149.433 | 786.836 | −3982.123 | −2201.306 | 52.266 |
| 2300 | 429.637 | 1526.178 | 1165.401 | 829.787 | −3980.317 | −2120.400 | 48.156 |
| 2400 | 429.857 | 1544.468 | 1180.817 | 872.762 | −3978.897 | −2039.566 | 44.390 |
| 2500 | 430.051 | 1562 020 | 1195.717 | 915.758 | −3977.871 | −1958.783 | 40.927 |
| 2600 | 430 223 | 1578.890 | 1210.132 | 958.771 | −3977.280 | −1878 033 | 37.730 |
| 2700 | 430.376 | 1595.130 | 1224.092 | 1001.802 | −3977.221 | −1797.296 | 34 771 |
| 2800 | 430.514 | 1610.784 | 1237.625 | 1044.846 | −3977.856 | −1716.549 | 32.023 |
| 2900 | 430.638 | 1625.894 | 1250 754 | 1087.904 | −4087.062 | −1635.615 | 29 461 |
| 3000 | 430.749 | 1640.495 | 1263.504 | 1130.973 | −4083.649 | −1551 140 | 27.008 |
| 3100 | 430.850 | 1654.621 | 1275.894 | 1174.053 | −4080.025 | −1466.784 | 24.715 |
| 3200 | 430.942 | 1668.301 | 1287.944 | 1217.143 | −4076.177 | −1382.546 | 22.568 |
| 3300 | 431.026 | 1681.563 | 1299.672 | 1260.242 | −4072.094 | −1298.432 | 20.552 |
| 3400 | 431.102 | 1694 432 | 1311.094 | 1303.348 | −4067.766 | −1214.446 | 18 658 |
| 3500 | 431.172 | 1706.929 | 1322.226 | 1346 462 | −4063.187 | −1130.591 | 16.873 |
| 3600 | 431.237 | 1719.077 | 1333.082 | 1389.582 | −4058.352 | −1046.869 | 15.190 |
| 3700 | 431.296 | 1730.893 | 1343.674 | 1432.709 | −4053.258 | −963.286 | 13.599 |
| 3800 | 431.350 | 1742.396 | 1354.016 | 1475.841 | −4047.902 | −879.847 | 12.094 |
| 3900 | 431.401 | 1753.601 | 1364.119 | 1518.979 | −4042.284 | −796.548 | 10.669 |
| 4000 | 431.447 | 1764.524 | 1373.993 | 1562.121 | −4036.406 | −713.397 | 9.316 |
| 4100 | 431.491 | 1775 178 | 1383.649 | 1605.268 | −4030.268 | −630.399 | 8.031 |
| 4200 | 431.531 | 1785.576 | 1393.095 | 1648.419 | −4023.873 | −547.551 | 6.810 |
| 4300 | 431.569 | 1795.731 | 1402.341 | 1691.574 | −4017.226 | −464.862 | 5.647 |
| 4400 | 431.604 | 1805.653 | 1411.395 | 1734.733 | −4010.330 | −382.327 | 4.539 |
| 4500 | 431.636 | 1815.352 | 1420.265 | 1777.895 | −4003.189 | −299.951 | 3.482 |
| 4600 | 431 667 | 1824.840 | 1428.957 | 1821.060 | −3995.808 | −217 739 | 2 473 |
| 4700 | 431.696 | 1834.123 | 1437.479 | 1864.228 | −3988 194 | −135.688 | 1.508 |
| 4800 | 431.722 | 1843.212 | 1445.838 | 1907.399 | −3980.351 | −53.801 | 0.585 |
| 4900 | 431 748 | 1852.114 | 1454.038 | 1950.573 | −3972.285 | 27 918 | −0.298 |
| 5000 | 431.771 | 1860.837 | 1462.087 | 1993.749 | −5738.157 | 126.664 | −1.323 |
| 5100 | 431.794 | 1869.388 | 1469.990 | 2036.927 | −5734.700 | 243 926 | −2.498 |
| 5200 | 431.815 | 1877.772 | 1477.752 | 2080.108 | −5731.478 | 361.124 | −3.628 |
| 5300 | 431.835 | 1885.998 | 1485.377 | 2123.290 | −5728.486 | 478.260 | −4.714 |
| 5400 | 431.854 | 1894.070 | 1492.871 | 2166.474 | −5725.731 | 595.341 | −5 759 |
| 5500 | 431.872 | 1901.994 | 1500.238 | 2209.661 | −5723.206 | 712.373 | −6.766 |
| 5600 | 431.888 | 1909 776 | 1507.482 | 2252.849 | −5720.914 | 829 365 | −7.736 |
| 5700 | 431.905 | 1917 421 | 1514.607 | 2296.038 | −5718.847 | 946.312 | −8 672 |
| 5800 | 431.920 | 1924.932 | 1521.617 | 2339.230 | −5717.007 | 1063.227 | −9.575 |
| 5900 | 431.934 | 1932.316 | 1528.515 | 2382.422 | −5715.382 | 1180.116 | −10.448 |
| 6000 | 431.948 | 1939.576 | 1535.306 | 2425.616 | −5713.982 | 1296.974 | −11.291 |

PREVIOUS. March 1979 (1 atm) CURRENT. March 1979 (1 bar)

## Continued from page 1064

[6] A. C. P. Pugh and R. F. Barrow, Trans. Faraday Soc. **54**, 671 (1958).
[7] F. M. Page and T. M Sugden, Nature **183**, 1672 (1959)
[8] E. M. Bulewicz, L. F. Phillips, and T. M. Sugden, Trans. Faraday Soc. **57**, 921 (1961).
[9] R. F Barrow and A. D. Caunt, Proc. Roy. Soc. (London) **A219**, 120 (1953).
[10] A. G Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall Ltd., London, (1968).
[11] L. Grabner and V. Hughes, Phys. Rev. **79**, 819 (1950).
[12] R. K. Ritchie and H. Lew, Can. J. Phys. **42**, 43 (1964).
[13] V. I. Baikov and K. P. Vasilevskii, Opt. Spektrosk. **22**, 198 (1967).
[14] G. W Green and H. Lew, Can. J. Phys. **38**, 482 (1960).
[15] S. E. Veazey and W. Gordy, Phys. Rev. **138**, A1303 (1965).

## Continued from page 1068

[8] P. A. Akishin, L. N. Gorokhov and L. N Sidorov, Russ. J. Phys Chem. **33**, 648 (1959).
[9] M. Eisenstadt, G. M. Rothberg, and P. Kusch, J. Chem. Phys. **29**, 797 (1958).
[10] G. M. Rothberg, M. Eisenstadt, and P. Kusch, J. Chem. Phys **30**, 517 (1959).
[11] K. A. Sense and R. W. Stone, J. Phys. Chem. **62**, 1411 (1958).
[12] A Buchler and J. L. Stauffer, "Thermodynamics," Vol I, International Atomic Energy Agency, Vienna, p. 271, (1966).
[13] A. M. Evseev, G. V. Pozharskaya, A. N. Nesmeyanov, and Y. I Gerasimov, Russ. J. Inorg. Chem. **4**, 997 (1959).
[14] G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York, (1950).
[15] A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, (1968).
[16] F. M. Page and T. M. Sugden, Nature, **183**, 1672 (1959).
[17] E. M. Bulewicz, L. F. Phillips, and T. M. Sugden, Trans. Faraday Soc **57**, 921 (1961)
[18] S. E Veazey and W. Gordy, Phys. Rev **138**, A1303 (1965).
[19] G. L. Vidale, J. Phys. Chem. **64**, 314 (1960).
[20] K. P. Vasilevskii and V. I. Baikov, Opt. Spectry. (USSR) **11**, 21 (1961).
[21] L. Wharten, W. Klemperer, L. P. Gold, R. Strauch, J. J. Gallagher, and V E. Derr, J Chem Phys. **38**, 1203 (1963).
[22] R Braunstein and J. W. Trischka, Phys. Rev. **98**, 1092 (1955).

## Continued from page 1070

However, thermodynamic functions calculated with the alternate set of vibrational constants are not significantly different from those adopted here. The uncertainty in the $\omega_e x_e$ values is large, probably near ±1 $cm^{-1}$. The partition function $Q = Q_n \Sigma Q_r^i Q_v^i g_i \exp(-C_2\epsilon_i/T)$ is used to calculate the thermodynamic functions with first–order anharmonic corrections included for $Q_r$ and $Q_v$.

### References

[1] E. Murad, D. L. Hildenbrand, and R. P. Main, J. Chem Phys 45, 263 (1966).
[2] D L. Hildenbrand, J. Chem. Phys. 48, 3657 (1968).
[3] T. C. Ehlert, Ph.D Thesis, University of Wisconsin, (1963).
[4] T. C. Ehlert, G. D Blue, J. W. Green and J. L. Margrave, J Chem. Phys. **41**, 2250 (1964).
[5] B. Rosen, ed., "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, (1970).
[6] R. Hultgren *et al.*, "Selected Values of the Thermodynamic Properties of the Elements," Am. Soc for Metals, Ohio, (1973).
[7] U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).
[8] JANAF Thermochemical Tables· Mg(g), 9–30–62, $MgF_2$(cr, g), 6–30–75, $AlF_3$(g), 6–30–70; AlF(g), 12–31–75; $F^-$(g), 12–31–75.
[9] K S. Krasnov and N. V. Karaseva, Optics and Spectroscopy **19**, 14 (1963).
[10] L B. Knight, Jr., W. C. Easley, and W. Weltner, Jr., J. Chem. Phys. **54**, 322 (1971).
[11] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall Ltd., London, (1968).
[12] G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed., D. Van Nostrand Company, Inc., New York, (1950).
[13] O. N Singh, B. P. Asthana, and O. N. Singh, Spectrosc. Lett. **7**, 175 (1974).
[14] R. F. Barrow and J. R. Beale, Proc. Phys. Soc **91**, 483 (1967).
[15] M. M Novikov and L. V. Gurvich, Zh. Prikl. Spectrosk. **14**, 820 (1971).

## Continued from page 1071

### References

[1] J. W Green, G. D. Blue, T. C Ehlert and J. L. Margrave, J Chem. Phys. **41**, 2245 (1964).
[2] T C Ehlert, G. D. Blue, J W. Green and J. L. Margrave, J. Chem. Phys. **41**, 2250 (1964).
[3] D. L. Hildenbrand, J. Chem. Phys 48, 3657 (1968).
[4] J Berkowitz and J. R. Marquart, J Chem. Phys 37, 1853 (1962).
[5] E. Murad, D. L Hildenbrand and R. P. Main, J Chem. Phys **45**, 263 (1966).
[6] D L. Hildenbrand, J. Chem. Phys. 48, 2458 (1968).
[7] R. F. Barrow and J R. Beale, Proc. Phys. Soc. **91**, 483 (1967).
[8] JANAF Thermochemical Tables. MgF(g), 12–31–75, NaF(g), 12–31–68, MgO(g), 12–31–74.
[9] R M. Badger, J. Chem. Phys. **2**, 128 (1934).
[10] R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London) **219A**, 120 (1953).
[11] M M. Novikov and L. V. Gurvich, Zh. Prikl. Spectrosk. **14**, 820 (1971).
[12] F. A. Jenkins and R. Grinfeld, Phys. Rev. **45**, 229 (1934).
[13] C. A. Fowler, Jr., Phys. Rev. **59**, 645 (1941).
[14] R. F Barrow, ed., "Diatomic Molecules, A Critical Bibliography of Spectroscopic Data," Centre National de la Recherche Scientifique, Paris, (1973).
[15] G A. Capelle, H P. Broida, and R. W. Field, J. Chem. Phys. **62**, 3131 (1975).

## Continued from page 1077

[10] J. P Harrison, G. Lombardo, and P. P. Peressini, J. Phys. Chem. Solids **29**, 557 (1968).
[11] E. G. King, J. Amer Chem. Soc. **79**, 2056 (1957)
[12] C. J. O'Brien and K.K. Kelley, J. Amer. Chem. Soc. **79**, 5616 (1957).
[13] W. B. Frank, J. Phys. Chem. **65**, 2081 (1961).
[14] T B. Douglas and D. A. Ditmars, U. S. Nat. Bur Stand. Rept. 9389, (1966).
[15] F. Koref, Ann. Physik (4) **36**, 49 (1911).
[16] A. N Krestovnikov and G A. Karetnikov, Legkie Metal. **3**, 29 (1934).
[17] V S Lyashenko, Metallurg (USSR) **10**, 85 (1935).

## Continued from page 1080

[8] P. Entner and A. Neckel, Monatsh. Chem. **98**, 1083 (1967).
[9] R C. Miller and P. Kusch, J. Chem. Phys. **25**, 860 (1956).
[10] M Eisenstadt, G. M Rothberg and P. Kusch, J Chem. Phys. **29**, 797 (1958).
[11] A G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, (1968).
[12] G Herzberg, "Spectra of Diatomic Molecules," D. van Nostrand Company, Inc., New York, (1950)
[13] E. M. Bulewicz, L. F Phillips, and T M. Sugden, Trans. Faraday Soc. **57**, 921 (1961).
[14] F M. Page and T M Sugden, Nature **183**, 1672 (1959).
[15] S. E. Veazey and W Gordy, Phys. Rev. **138**, A 1303 (1965).
[16] R K. Bauer and H. Lew, Can. J Phys. **41**, 1461 (1963).
[17] A. Snelson and K. S. Pitzer, J. Phys. Chem. **67**, 882 (1963).
[18] R K. Ritchie and H. Lew, Can. J. Phys. **42**, 43 (1964).
[19] C D. Hollowell, A J. Hebert and K Street, Jr., J Chem. Phys. **41**, 3540 (1964).
[20] V. I. Baikov and K. P. Vasilevskii, Opt. Spectry **22**, 198 (1967).

## Continued from page 1084

[16] M.E Jacox, J Mol. Spectrosc. **84**, 74 (1980).
[17] K C. Kim and G.M. Campbell, Chem. Phys. Lett. **116**, 236 (1985).
[18] M.E Jacox, J Phys. Chem Ref. Data, Monograph No. 3 (1994).
[19] A. Glissman and H.J. Schumacher, Z. physik. Chem **B24**, 328 (1934).
[20] M.M. Matchuk, V I. Tupikov, A.I. Malkova and S.Ya. Pshezhetskii, Opt. i. Spektrosk. **40**, 14 (1976).
[21] P.P. Chegodaev and V.I. Tupikov, Dokl. Akad. Nauk SSSR **210** (3), 647 (1973).
[22] R.W Fessenden and R H Schuler, J Chem. Phys. **44**, 434 (1966).

## Continued from page 1117

[10] W. Klemperer and W. G. Norris, J. Chem. Phys. **34**, 1071 (1961).
[11] M. J. Linevsky, J. Chem. Phys. **34**, 587 (1961), **38**, 658 (1963).
[12] A. Buchler, J L. Stauffer, and W. Klemperer, J. Amer. Chem. Soc. **86**, 4544 (1964).
[13] A. Snelson and K. S. Pitzer, J. Phys. Chem. **67**, 882 (1963).
[14] S. Schlick and O. Schnepp, J. Chem. Phys. **41**, 463 (1964).
[15] A Snelson, Illinois Institute of Technology Research Institute, IITRI–U6001–13, 14 May 1963 – 12 (August 1966).
[16] J. Berkowitz, J. Chem. Phys. **32**, 1519 (1960).

## Continued from page 1118

### References

[1] E. Rudzitis, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. **68**, 2978 (1964).
[2] D R. Torgeson and Th. G. Sahama, J. Amer. Chem. Soc. **70**, 2156 (1948).
[3] H v. Wartenberg, Z. Anorg. Allg. Chem. **249**, 100 (1942).
[4] L. Domange, Ann. Chim. Phys. **7**, 225 (1937).
[5] T. N. Rezukhina, T. F. Sisoeva, L. I. Halokhonova, and E. G. Ippolitor, J. Chem. Thermodyn **6**, 883 (1974).
[6] W. H Skelton and J. W. Patterson, J Less Common Metals **31**, 47 (1973).
[7] JANAF Thermochemical Tables: Mg(OH)$_2$(cr), 3–31–67; H$_2$O(g), 3–31–61; HF(g), 12–31–68; AlF$_3$(cr), 6–30–70; MgO(cr), 12–31–74.
[8] U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).
[9] V. B. Parker, NSRDS–NBS (April 2, 1965).
[10] S. S. Todd, J. Amer. Chem. Soc. **71**, 4115 (1949).
[11] B. F. Taylor, J. Amer. Chem. Soc. **67**, 150 (1945).
[12] A. N. Krestovnikov and G. A. Karetnikov, Legkie Metal. **3**, 29 (1934).
[13] H. Kojima, S. G. Whiteway, and C R. Masson, Can. J Chem. **46**, 2968 (1968).
[14] G Petit and F. Delbove, Compt. rend. **254**, 1388 (1962).
[15] A Duncanson and R. W. H. Stevenson, Proc. Phys Soc. **72**, 1001 (1958).

## Continued from page 1121

is 158°. An energy minimum has been reported at 140° with a CNDO approximation.[19] Unfortunately, the vapor pressure data are not sufficiently precise to be of use in the selection of a structure. The entropies of these two forms differ by only about 1.5 cal $K^{-1}\cdot mol^{-1}$ at temperatures in the range of the vapor pressure data. We tentatively adopt a bond angle of 158° but assign an alternate uncertainty ($\pm 3$ cal $K^{-1}\cdot mol^{-1}$) to $S°(298.15\ K)$ to include the possibility that the angle is 180°. The Mg–F bond length is taken from the electron diffraction studies of Akishin *et al.*[11] The individual moments of inertia are: $I_A = 0.2808 \times 10^{-39}$, $I_B = 19.0477 \times 10^{-39}$, and $I_C = 9.3285\ 10^{-39}\ g\cdot cm^2$.

The symmetric stretching frequency is a compromise between the Krypton matrix infrared ($\nu_1 = 478\ cm^{-1}$)[17] and Raman ($\nu_1 = 545\ cm^{-1}$)[23] values. Also, an intermediate value ($\nu_2 = 215\ cm^{-1}$) is selected for the bending frequency from the estimated gas–phase value (270 $cm^{-1}$) of Snelson[13] and that (165 $cm^{-1}$) which was observed in the high temperature (~2000 K) infrared spectrum[20] of the vapor. $\nu_3$ is the gas phase value that was estimated by Snelson[13] from frequencies measured in three matrices. The Krypton frequencies for $\nu_2$ and $\nu_3$ reported by Mann *et al.*[17] and Lesiecki and Nibler[23] agree quite well with those of Snelson.[13] Also, the results of Hauge *et al.*[22] provide further support for the adopted $\nu_3$ value. If $MgF_2$ is assumed to be linear and $\nu_2$ is reduced to 165 $cm^{-1}$, then our free energy functions are decreased by 2.1 cal $K^{-1}\cdot mol^{-1}$ at 298.15 K, 1.6 cal $K^{-1}\cdot mol^{-1}$ at 1000 K and 1.0 cal $K^{-1}\cdot mol^{-1}$ at 2000 K These alternate functions are also reasonably consistent with the reported vapor pressure data. Previously published free energy functions[21] for $MgF_2$(g) which were based on a linear structure are several units (2 5 cal $K^{-1}\cdot mol^{-1}$) too low due to the use of an incorrect bending frequency (470 $cm^{-1}$).

### References

[1] O. Ruff and L. LeBoucher, Z. anorg. allg. Chem. **219**, 376 (1934).
[2] K. G. Gunther, Glastech. Ber. **31**, 9 (1958).
[3] J. Berkowitz and J. R. Marquart, J. Chem. Phys. **37**, 1853 (1962).
[4] G. Layne, Dow Chemical Co., personal communication, (May, 1975).
[5] R. R. Hammer, Ph.D. Thesis, University of California, (1961).
[6] R R. Hammer and J. A. Pask, J. Amer. Ceram. Soc. **47**, 264 (1964).
[7] M. A. Greenbaum, H. C.Ko, M. Wong, and M. Farber, J. Phys. Chem. **68**, 965 (1964).
[8] D. L. Hildenbrand, Standard Research Institute, personal communication, (September 1975).
[9] J. W. Green, G. D Blue, T. C. Ehlert and J. L. Margrave, J. Chem. Phys. **41**, 2245 (1964).
[10] JANAF Thermochemical Tables. BeF$_2$(g), 6–30–70.
[11] P. A. Akishin, V. P. Spiridonov, G. A. Sobolev, and V. A. Naumov, Zhur. Fiz. Khim. **31**, 461 (1957).
[12] A. Buchler, J. L. Stauffer, and W. Klemperer, J. Amer. Chem. Soc. **86**, 4544 (1964).
[13] A. Snelson, J. Phys. Chem. **70**, 3208 (1966).
[14] M. Astier and P. Millie, J. Organometal. Chem. **31**, 139 (1971).
[15] M. Astier, G. Berthier, and P. Millie, J. Chem. Phys. **57**, 5008 (1972).
[16] J L. Gole, A.K. Q. Siu and E. F. Hayes, J. Chem. Phys. **58**, 857 (1973).
[17] D. E. Mann, G. V Calder, K. S. Seshadri, D. White and M. J. Linevsky, J. Chem. Phys. **46**, 1138 (1967).
[18] V. Calder, D. E. Mann, K. S. Seshadri, M. Allaveua and D. White, J. Chem. Phys. **51**, 2093 (1969).
[19] J. F. Labarre and C. Leibovici, J. Chim. Phys. Physiochim. Biol. **69**, 541 (1972).
[20] V. I Baikov, Optics and Spectroscopy **25**, 194 (1968).
[21] L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. **63**, 111 (1963).
[22] R H. Hauge, J. L. Margrave, and A. S Kana'an, J Chem. Soc., Faraday Transaction II **71**, 1082 (1975).
[23] M. L. Lesiecki and J. W. Nibler, J. Chem. Phys. **64**, 871 (1976).
[24] A. Allavena and S. Besnainov, J. Mol. Struct. **11**, 439 (1975).

## Continued from page 1136

[6] H. M. Rosenstock, K. Draxl, B. W. Steiner, and J T. Herron, J. Phys. Chem. Ref. Data, **6**, Suppl. 1 (1977).
[7] M. S Wei, J. H. Current and J. Gendell, J Chem. Phys. **52**, 1592 (1970)
[8] W Nelson, G Jackel and W. Gordy, J. Chem. Phys. **52**, 1592 (1970)
[9] D. Kilcast and C Thomson, J. Chem Soc., Faraday Trans II. **68**, 435 (1972).
[10] A Hudson and J. T. Wiffen, Chem. Phys. Lett. **29**, 113 (1974).
[11] JANAF Thermochemical Tables: PF$_2$(g), 6–30–77; SiF$_2$(g), 6–30–76.

## Continued from page 1143

### References

[1] D. L. Hildenbrand, J. Phys. Chem. **77**, 897 (1973).
[2] JANAF Thermochemical Tables. S(g), 6–30–71, SF$_6$(g), SF$_4$(g), SF$_3$(g), and SF(g), 6–30–76, F(g), 9–30–65; SO$_2$(g), 6–30–6.
[3] A. L. Companion, Theoret. Chim. Acta, **25**, 268 (1972)
[4] J. F. Bott, J. Chem. Phys. **54**, 181 (1971).
[5] G. Di Lonardo and A. Trombetti, Trans. Faraday Soc. **66**, 2694 (1970).
[6] W. H. Kirchhoff, D. R. Johnson, and F. X. Powell, J. Mol. Spectro. **48**, 157 (1973).
[7] D. R. Johnson and F. X. Powell, Science, **164**, 950 (1969).
[8] F. Seel, in "Advances in Inorganic Chemistry and Radiochemistry", H. J Emeleus and A. G. Sharpe, eds., Vol. 16, Academic Press, New York, (1974).
[9] C. Bliefert and K. P. Wanczek, Z. Naturforsch. **259**, 1770 (1970).
[10] R. L. Wilkins, Aerospace Corporation, Report No TR–0158 (3240–20)–19, (July 1968).
[11] P. A. G. O'Hare, Argonne National Laboratory, ANL–7315, (July 1968).

## Continued from page 1144

[3] B Solouki, P. Rosmus, and H. Bock, Chem. Phys. Letters, **26**, 20 (1974).
[4] N. P. C. Westwood, Chem. Phys. Letters, **25**, 558 (1974).
[5] U.S. Nat. Bur Stand. NSRDS–NBS (June 26, 1969).
[6] A. L. Companion, Theoret. Chim. Acta (Berl.) **25**, 268 (1972)
[7] V. H. Dibeler and F. L. Mohler, J. Res. Nat. Bur. Stand. **40**, 25 (1948).
[8] Glemser, A. Muller, D. Bohler, and B Krebs, Z. anorg allg. Chem. **357**, 184 (1968).
[9] P. W. Harland, D. W. H. Rankin, and J. C. J. Thynne, Int. J. Spec. Ion Phys **13**, 395 (1974).
[10] A. D. Walsh, J. Chem. Soc. **1953**, 2266 (1953).
[11] R. J. Buenker and S. D. Peyerimhoff, J. Chem. Phys. **45**, 3682 (1966).
[12] A. B Cornford, D. C. Frost, F. G. Herring, and C. A. McDowell, J. Chem. Phys. **55**, 2820 (1971).
[13] J K. Burdett, L. Hodges, V. Dunning, and J. H. Current, J. Phys. Chem. **74**, 4053 (1970).

## Continued from page 1149

[3] U. S. Nat. Bur. Stand. Tech. Note 270–6, (1971).
[4] JANAF Thermochemical Tables: Consistent with HF(g), 12–31–68; SrO(cr) and $BaCl_2$(cr), 12–31–72, $CaF_2$, 12–31–68.
[5] E. Petersen, Z. Physik. Chem. 4, 384 (1889).
[6] U. S. Nat. Bur. Stand. Tech. Note 270–4, (1969).
[7] H. Stephen and T. Stephen, "Solubilities of Inorganic and Organic Compounds," Vol. I, The Pergamon Press, Ltd., London, (1963).
[8] R. Barany, E. G. King, and S. S. Todd, J. Amer. Chem. Soc. 79, 3639 (1957).
[9] A. Finch, P. J. Gardner, and C. J Steadman, Can. J. Chem. 46, 3447 (1968).
[10] D. F. Smith, T. E. Gardner, B. B. Letson, and A. R. Taylor, U. S. Bur. Mines RI–6316, (1963).
[11] R. I. Efremova and E. V. Matizen, Izv. Sib. Akad. Nauk SSSR, Ser. Khim. Nauk, (1), 3 (1970).
[12] A. S. Dworkina and M. A. Bredig, J. Chem. Eng. Data, 8, 416 (1963).

## Continued from page 1164

[10] P. N. Schatz and I. W. Levin, J Chem. Phys. 29, 475 (1958).
[11] E. L. Pace and L. Pierce, J. Chem. Phys. 23, 1248 (1955).
[12] M. K. Wilson and S. R. Polo, J. Chem. Phys. 20, 1716 (1952).
[13] Yu. I. Kotov and W. N. Tatevskii, Opt. Spectry 14, 160, Supplement 2 Mol. Spectrosc (1963).
[14] J. Sheridan and W. Gordy, Phys. Rev. 79, 513 (1950).
[15] V. Schomaker and C. Lu, J. Amer. Chem. Soc. 72, 1182 (1950).
[16] L. Pierce and E. L. Pace, J. Chem. Phys. 23, 551 (1955).
[17] S. Abramowitz *et al.*, U. S. Nat. Bur. Stand. Report 10904, 239, (1972).
[18] CODATA Task Group on Fundamental Constants, CODATA Bulletin 11, (December 1973).
[19] IUPAC Commission on Atomic Weights, Pure Appl Chem. 47, 75 (1976).

## Continued from page 1169

[6] P. W. Harland and J. C. J. Thynne, J. Phys. Chem. 75, 3517 (1971).
[7] V. H. Dibeler and F. L. Mohler, J. Res. Nat. Bur. Stand. 40, 25 (1948).
[8] J. Delwiche, Dynamic Mass Spectrom. 1, 71 (1971).
[9] A. J. Colussi, J. R Morton, K. F. Preston, and R. W. Fessenden, J Chem. Phys. 61, 1247 (1974).
[10] R. A. Frey, R. L. Redington, and A. L. K. Aljbury, J. Chem. Phys. 54, 344 (1971).
[11] I. W. Levin, J. Chem. Phys. 55, 5393 (1971).
[12] R. L. Wilkins, Aerospace Corporation, Report No. TR–0158 (3240–20)–19, (July 1968).

## Continued from page 1170

[5] D. F. Torgerson and J. B. Westmore, Can J. Chem. 53, 933 (1975).
[6] G. S. Paulett and M. Lustig, J. Amer. Chem. Soc. 87, 1020 (1965).
[7] D. D. Gibler, C. J. Adams, M. Fischer, A. Zalkin, and N. Bartlett, Inorg. Chem. 11, 2325 (1972).
[8] M. Azeem, M. Brownstein, and R. J. Gillespie, Can J. Chem. 47, 4159 (1969).
[9] R. A. Frey, R. L Redington, and A. L. K. Aljibury, J. Chem. Phys. 54, 344 (1971).
[10] J. Delwiche, Dynamic Mass Spectrom. I, 71 (1970).

## Continued from page 1187

[3] J. D. Vaugh and E. L. Muetterties, J. Phys. Chem. 64, 1787 (1960).
[4] M. J. Nichols, Ph.D Thesis, University of Durham, England, (1958).
[5] D. L. Hildenbrand, J. Phys. Chem. 77, 897 (1973).
[6] V. H. Dibeler and F. L. Mohler, J. Res. Nat. Bur. Stand. 40, 25 (1948).
[7] J. Delwiche, Dynamic Mass Spectrom. 1, 71 (1970).
[8] O. Glemser, A. Muller, D. Bohler, and B. Krebs, Z. anorg. allgem. Chem. 357, 184 (1968).
[9] J. Kay and F. M. Page, Trans Faraday Soc. 60, 1042 (1964).
[10] C E. Vanderzee and W. Wm. Rodenburg, J. Chem. Thermodyn. 2, 461 (1970).
[11] P. A. G. O'Hare, Argonne National Laboratory, ANL 7315, (July 1968).
[12] U. S. Nat. Bur. Stand. Tech. Note 270 3, (1968).

[13] V. B. Parker, D. D. Wagman, and D. Garvin., NBSIR 75 968, (January 1976).
[14] K. Kimura and S. H. Bauer, J. Chem. Phys. 39, 3172 (1963).
[15] W. M. Tolles and W. D. Gwinn, J. Chem. Phys. 36, 1119 (1962).
[16] F. A. Cotton, J. W. George, and J. S. Waugh, J. Chem. Phys. 28, 944 (1958).
[17] J Bacon, R. J Gillespie, and J. W. Quail, Can. J. Chem. 41, 1016 (1963).
[18] R. W. Shaw, Jr., T. X. Carroll, and T. D. Thomas, J. Amer. Chem. Soc. 95, 2033 (1973).
[19] R W. Shaw, Jr., T. X. Carroll, and T. D. Thomas, J. Amer. Chem. Soc. 95, 5870 (1973).
[20] I. W Levin, J. Chem. Phys. 55, 5393 (1971).
[21] R. E. Dodd, L. A. Woodward, and H. L. Roberts, Trans. Faraday Soc. 52, 1052 (1956).
[22] K. O. Christe and W Sawodny, J. Chem. Phys. 52, 6320 (1970).
[23] I. W. Levin and C. V Berney, J. Chem. Phys. 44, 2557 (1966).
[24] R. L. Redington and C. V. Berney, J. Chem. Phys. 43, 2020 (1965).
[25] R. D Brown and J. B. Peel, Aust. J. Chem. 21, 2617 (1968).
[26] M. Radhakrishnan, Z. Naturforsch. 18a, 103 (1963).
[27] R. L. Wilkins, Aerospace Corporation, Report No. TR 0158 (3240 20) 19, (July 1968).

## Continued from page 1188

[3] JANAF Thermochemical Tables: $SF_4$(g), 6–30–76; $SF_4^-$(g) and $SF_3^+$(g), 12–31–76.
[4] R. L. Dekock, B. R. Higginson, D R. Lloyd, A. Breeze, D. W. J. Cruickshank, and D. R. Armstrong, Mol. Phys. 24, 1059 (1972).
[5] R. A. Frey, R. L. Redington, and A. L. K. Aljibury, J Chem. Phys. 54, 344 (1971).
[6] F. C. Fehsenfeld, J. Chem. Phys. 54, 438 (1971).
[7] A. L. Companion, Theoret. Chim. Acta (Berl.) 25, 268 (1972).
[8] J. Delwiche, dynamic Mass Spectron. 1, 71 (1970).
[9] V. H. Dibeler and F. L. Molhler, J. Res Nat. Bur Stand. 40, 25 (1948).
[10] P Harland and J. C. J. Thynne, J. Phys. Chem. 73, 4031 (1969).
[11] R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 45, 1845 (1966).
[12] J. R. Morton and K. F. Preston, Chem. Phys. Letters, 18, 98 (1973).
[13] A. R. Gregory, Chem. Phys Letters, 28, 552 (1974).
[14] J Higuchi, J. Chem. Phys 50, 1001 (1969).
[15] A. J. Colussi, J. R. Morton, and K. F. Preston, J. Phys. Chem 79, 651 (1975).

## Continued from page 1189

[5] J. R. Morton and K. F. Preston, J. Chem. Phys. 58, 3112 (1973).
[6] A. R. Gregory, J. Chem. Phys. 60, 3713 (1974).
[7] S. R. Ungemach and H. F Schaefer, J. Amer. Chem. Soc. 98, 1958 (1976).
[8] K. O. Christe and W Sawodny, Z. anorg. allg. Chem. 374, 306 (1970).
[9] D. L. Hildenbrand, Stanford Research Institute, personal communication, (March 1977).
[10] R. J. Donovan, P. W. Harland, J. H. Knox, J. A. Makowski, and J. C. J Thynne, Int. J. Mass Spectrom. Ion Phys. 13, 464 (1974).

## Continued from page 1194

[5] D. L. Hildenbrand and L. P. Theard, Aeronutronic, U–1187, Ford Motor Company, 15 (March 1961).
[6] D. L. Hildenbrand and L P. Thread, Aeronutronic, U–1274, Ford Motor Company, 15 (June 1961).
[7] N. P. Galkin, Y. N. Tumanov, V. I. Tarasov and Y. D. Shishhov, Russ. J. Inorg. Chem. 8, 1054 (1963).
[8] P. A. Akishin, V. I. Belousov and L. N. Sidorov, Russ. J. Inorg. Chem. 8, 1520 (1963).
[9] W. Fischer, T. Petzel and S. Lauter, Z. Anorg. Allg. Chem. 333, 226 (1964).
[10] L. N. Sirorov, P. A. Akishim, V. B. Shil'ts and Y. M. Korenev, Russ J. Phys. Chem. 39, 1146 (1965).
[11] V P. Spiridonov, Vestn. Mosk. Univ. Ser. II, Khim. 23, 113 (1968).
[12] I. N Godnev, A M. Aleksandrovskaia and I. V. Rigina, Opt. Spectry, USSR 7, 172 (1959).
[13] A. Buchler, J. B. Berkowitz-Mattuck and D. H. Dugre, J. Chem. Phys. 34, 2202 (1961).
[14] M. Blander and H. W. Morgan, presented at the 138th Meeting, American Chemical Society, New York, (September 1960).
[15] R. H. Hauge, J L. Margrave and J W Hastie, High Temp. Sci. 5, 89 (1973).
[16] G Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, p. 182, (1945).
[17] I. N. Godnev, A M Aleksandrooskaya and A. S. Sverdlin, Opt. Spektrosk. 29, 676 (1970).

## Continuation of discussions of selected F species

### Continued from page 1199

[5] A. P. Modica, J. Phys. Chem. 77, 2713 (1973).
[6] J. F. Bott and T. A. Jacobs, J. Chem. Phys. 50, 3850 (1969).
[7] J. L. Lyman, J. Chem. Phys. 67, 1868 (1977).
[8] J. R. Morton and K. F. Preston, Chem. Phys. Lett. 18, 98 (1973).
[9] A. R. Gregory, Chem. Phys. Lett. 28, 552 (1974).
[10] H. A. Edwards and M. A. Mouty, J. Chem. Soc. 1969, 703 (1969).
[11] R. R. Smardzewski and W. B. Fox, J. Chem. Phys. 67, 2309 (1977).
[12] K. O. Christe, Spectrochim. Acta. 27A, 631 (1971).
[13] J. Delwiche, Dynamic Mass Spectrom. 1, 71 (1971).
[14] P. A. O'Hare, Argonne National Laboratory, ANL–7315, (July 1968).
[15] R. L. Wilkins, Aerospace Corporation, Report No. TR–0158 (3240–20)–(July 19, 1968).

### Continued from page 1200

**References**

[1] V. H. Dibeler and J. A. Walker, J. Chem. Phys. 44, 4405 (1966).
[2] V. H. Dibeler and F. L. Mohler, J. Res. Nat. Bur. Stand. 40, 25 (1948).
[3] R. E. Fox and R. K. Curran, J. Chem. Phys. 34, 1595 (1961).
[4] J. Delwiche, Dynamic Mass Spectrom. 1, 71 (1970).
[5] D. L. Hildenbrand, J. Phys. Chem. 77, 897 (1973).
[6] D. C. Frost, C. A. McDowell, J. S. Sandhu, and D. A. Vroom, Advan. Mass Spectrom 4, 781 (1968).
[7] A. W. Potts, H. J. Lempka, D. G. Streets, and W. C. Price, Phil. Trans. Roy Soc Lond. A 268, 59 (1970).
[8] B. P. Pullen, Ph.D. Thesis, University of Tennessee, (1970).
[9] P. Harland and J. C. J Thynne, J. Phys. Chem. 73, 4031 (1969).
[10] JANAF Thermochemical Tables: $SF_6$(g), 6–30–76; F(g), 9–30–65, Cl(g), 6–30–72; $SF_3^-$(g), $SF_3^+$(g) and $SF_4^+$(g), 12–31–76; $SF_5$(g) and $SF_5^-$(g), 12–31–77; $Cl_5$(g), 6–30–66[11] U. S. Nat. Bur Stand. Tech. Note 270–3, (1968).
[12] D. F. Torgerson and J. B. Westmore, Can. J Chem. 53, 933 (1975).
[13] F. C. Fehsenfeld, J. Chem. Phys. 54, 438 (1971).
[14] J. R. Morton and K. F. Preston, Chem. Phys. Lett. 18, 98 (1973).
[15] A. R. Gregory, Chem. Phys. Lett. 28, 552 (1974).
[16] L. F. Drullinger and J. E. Griffiths, Spectrochim. Acta. 27, 1793 (1971).
[17] H. A. Edwards and M. A. Mouty, J. Chem. Soc. 1969, 703 (1969).
[18] K. O. Christe, Spectrochim. Acta, 27A, 631 (1971).

### Continued from page 1201

**References**

[1] P. Harland and J. C. J. Thynne, J. Phys. Chem. 73, 4031 (1969).
[2] W. M. Hickman and D. Berg, Advan. Mass. Spec. 1958, 458 (1958).
[3] C. Lifshitz, A. M. Peers, R. Grajower, and M. Weiss, J. Chem. Phys 53, 4605 (1970).
[4] C. L. Chen and P. J. Chantry, Bull. Amer. Phys. Soc. 15, 418 (1970).
[5] C. Lifshitz, T. O. Tiernan, and B. M. Hughes, J. Chem. Phys. 59, 3182 (1973).
[6] R. N. Compton and C. D. Cooper, J. Chem. Phys. 59, 4140 (1973).
[7] JANAF Thermochemical Tables: $SF_6$(g), 6–30–76; F(g), 9–30–65, Cl(g), 6–30–72; $SF_3^-$(g) and $SF_4^-$(g), 12–31–76; $ClF_5$(g), 6–30–66; $SF_5$(g) and $SF_5^+$(g), 12–31–77.
[8] U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).
[9] F. C. Fehsenfeld, J. Chem. Phys. 54, 438 (1971).
[10] J. Kay and F. M. Page, Trans. Faraday Soc. 60, 1042 (1964).
[11] L. F. Drullinger and J E. Griffiths, Spectrochim. Acta. 27A, 1793 (1971).
[12] K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, Inorg. Chem. 11, 1679 (1972).
[13] H. A. Edwards and M. A. Mouty, J. Chem. Soc. 1969, 703 (1969).
[14] R. R. Smardzewski and W. B. Fox, J. Chem. Phys. 67, 2309 (1977).

### Continued from page 1203

[4] A. P. Brady, O. E. Myers, and J. K. Clauss, J. Phys. Chem. 64, 558 (1960).
[5] D. W. Osborne, F. Schreiner, J. G. Malm, H Selig, and L. Rochester, J Chem. Phys. 44, 2802 (1966).
[6] O. Ruff and E. Ascher, Z. Anorg. Allg. Chem. 196, 413 (1931).
[7] G. H. Cady and G. B. Hargreaves, J. Chem. Soc. 1563 (1961).
[8] D. Meixner, A. Heintz, and R. N. Lichtenthaler, Ber. Bunsenges, Phys. Chem. 82, 220 (1978).
[9] L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication, (September 1978), of preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.

### Continued from page 1205

[11] L. O. Brockway and L. Pauling, Proc. Natl. Acad. Sci. 19, 68 (1933).
[12] H. Braune and S. Knobe, Z. Physik. Chem. 21, 297 (1933).
[13] H. H. Claassen, G. L. Goodman, J. H. Holloway and H. Selig, J. Chem. Phys. 53, 341 (1970).
[14] W. Holzer and R. Ouillon, Chem. Phys. Letters, 24, 589 (1974).
[15] J. S. Shirk and H. H. Claassen, J. Chem. Phys. 54, 3237 (1971).
[16] S. Abramowitz and I. W. Levin, J. Chem. Phys. 44, 3353 (1966).
[17] H. Brunet and M. Perez, J. Mol. Spectrosc. 29, 472 (1969).
[18] V D. Klimov and E. A. Lobikov, Opt. Spektrosk. 30, 25 (1971).
[19] B. Weinstock and G L. Goodman, in "Advances in Chemical Physics," Vol. 9, Ed. by I Prigogine, Interscience, (1965).
[20] A. Rosenberg and G. Birnbaum, J. Chem. Phys. 52, 683 (1970).
[21] E L. Rozenberg and M. E Dyatkina, Zhur. Strukt. Khim. 11, 299 (1970).
[22] R. E. LaVilla, J. Chem. Phys. 57, 899 (1972).
[23] J. L. Dehmer, J. Chem. Phys. 56, 4496 (1972).
[24] K. K. Kelley and E. G. King, U S. Bur. Mines Bull. 592, (1961).
[25] A. Eucken and E. Schroder, Z. Physik. Chem. 41B, 307 (1938).
[26] G. Nagarajin and D. C. Brinkley, Z. Naturforsch. 26a, 1658 (1971).
[27] R. L. Wilkins, Aerospace Corporation, Report No. TR–0158(3240–20)–19, (July 1968).
[28] F. A. Gianturco, Chem. Phys. Letters 17, 127 (1972).

### Continued from page 1206

[7] E. Chen, R. D George and W. E. Wentworth, J. Chem. Phys. 49, 1973 (1968).
[8] F. C. Fehsenfeld, J. Chem. Phys. 54, 438 (1971).
[9] P. R Hammond, J. Chem. Phys. 55, 3468 (1971).
[10] A. L. Companion, Theoret. Chem. Acta (Berl.) 25, 268 (1972).
[11] J R. Morton, K. F Preston and J. C Tait, J. Chem. Phys. 62, 2029 (1975).
[12] L. S. Bartell and R. M. Gavin, J. Chem. Phys. 48, 2460 (1968).
[13] J E. Barefield and W. A. Guillory, J. Phys. Chem. 81, 634 (1977).
[14] C. Lifshitz, T. O. Tiernan and B. M. Hughes, J Chem. Phys. 59, 3182 (1973).
[15] F C. Fehsenfeld, J. Chem Phys. 53, 2000 (1970).

### Continued from page 1212

[3] JANAF Thermochemical Tables: $SF_4$(g) and $SF_6$(g), 6–30–76; $S_8$(g), 6–30–64.
[4] R. B Harvey and S. H. Bauer, J. Amer Chem. Soc 75, 2840 (1953).
[5] J. K. Wilmshurst and H. J. Berstein, Can. J. Chem. 35, 191 (1957).
[6] R. E. Dodd, L. A. Woodward, and H. L. Roberts, Trans. Faraday Soc. 53, 1545 (1957).
[7] R. R. Smardzewski, R. E. Noftle and W B. Fox, J Mol. Spectrosc. 62, 449 (1976).
[8] F. Crasnier, J. F. Labarre, and C. Leibovici, J. Fluorine Chem. 3, 307 (1973).
[9] K. S. Pitzer and L. Brewer, "Thermodynamics," 2nd ed., McGraw Hill Book Company, New York, (1961).
[10] P. A. G. O'Hare, Argonne National Laboratory, ANL 7315, (July 1968).
[11] G. Pass, J. Appl. Chem. (London), 19, 77 (1969).