| | | | |
|---|---|---|---|
| 0 | to | 716 | K crystal, alpha |
| 716 | to | 1115 | K crystal, beta |
| 1115 | to | 1773.658 | K liquid |
| above | | 1773.658 | K ideal monatomic gas |

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 | −5.736 | 0. | 0. | 0. |
| 100 | 19.504 | 15.967 | 63.525 | −4.756 | 0. | 0. | 0. |
| 200 | 24.542 | 31.489 | 43.924 | −2.487 | 0. | 0. | 0. |
| 298.15 | 25.929 | 41.588 | 41.588 | 0. | 0. | 0. | 0. |
| 300 | 25.946 | 41.749 | 41.589 | 0.048 | 0. | 0. | 0. |
| 400 | 26.868 | 49.322 | 42.615 | 2.683 | 0. | 0. | 0. |
| 500 | 28.487 | 55.487 | 44.590 | 5.448 | 0. | 0. | 0. |
| 600 | 30.382 | 60.846 | 46.861 | 8.391 | 0. | 0. | 0. |
| 700 | 32.406 | 65.680 | 49.210 | 11.529 | 0. | 0. | 0. |
| 716.000 | 32.737 | 66.416 | 49.586 | 12.051 | ALPHA <--> BETA | | |
| 716.000 | 31.503 | 67.715 | 49.586 | 12.981 | TRANSITION | | |
| 800 | 33.818 | 71.335 | 51.681 | 15.723 | 0. | 0. | 0. |
| 900 | 36.713 | 75.484 | 54.097 | 19.249 | 0. | 0. | 0. |
| 1000 | 39.706 | 79.507 | 56.437 | 23.069 | 0. | 0. | 0. |
| 1100 | 42.763 | 83.434 | 58.714 | 27.192 | 0. | 0. | 0. |
| 1115.000 | 43.226 | 84.017 | 59.050 | 27.837 | BETA <--> LIQUID | | |
| 1115.000 | 35.000 | 91.676 | 59.050 | 36.377 | TRANSITION | | |
| 1200 | 35.000 | 94.247 | 61.453 | 39.352 | 0. | 0. | 0. |
| 1300 | 35.000 | 97.049 | 64.085 | 42.852 | 0. | 0. | 0. |
| 1400 | 35.000 | 99.642 | 66.533 | 46.352 | 0. | 0. | 0. |
| 1500 | 35.000 | 102.057 | 68.822 | 49.852 | 0. | 0. | 0. |
| 1600 | 35.000 | 104.316 | 70.971 | 53.352 | 0. | 0. | 0. |
| 1700 | 35.000 | 106.438 | 72.995 | 56.852 | 0. | 0. | 0. |
| 1773.658 | 35.000 | 107.922 | 74.415 | 59.430 | LIQUID <--> IDEAL GAS | | |
| 1773.658 | 20.837 | 191.956 | 74.415 | 208.477 | FUGACITY = 1 bar | | |
| 1800 | 20.845 | 192.263 | 76.138 | 209.026 | 0. | 0. | 0. |
| 1900 | 20.888 | 193.391 | 82.279 | 211.112 | 0. | 0. | 0. |
| 2000 | 20.953 | 194.464 | 87.862 | 213.204 | 0. | 0. | 0. |
| 2100 | 21.046 | 195.489 | 92.963 | 215.304 | 0. | 0. | 0. |
| 2200 | 21.173 | 196.470 | 97.646 | 217.415 | 0. | 0. | 0. |
| 2300 | 21.343 | 197.415 | 101.963 | 219.540 | 0. | 0. | 0. |
| 2400 | 21.561 | 198.328 | 105.959 | 221.685 | 0. | 0. | 0. |
| 2500 | 21.836 | 199.214 | 109.672 | 223.854 | 0. | 0. | 0. |
| 2600 | 22.173 | 200.076 | 113.132 | 226.054 | 0. | 0. | 0. |
| 2700 | 22.578 | 200.921 | 116.368 | 228.291 | 0. | 0. | 0. |
| 2800 | 23.057 | 201.750 | 119.403 | 230.572 | 0. | 0. | 0. |
| 2900 | 23.614 | 202.569 | 122.257 | 232.905 | 0. | 0. | 0. |
| 3000 | 24.251 | 203.380 | 124.947 | 235.298 | 0. | 0. | 0. |
| 3100 | 24.970 | 204.186 | 127.490 | 237.758 | 0. | 0. | 0. |
| 3200 | 25.772 | 204.992 | 129.900 | 240.295 | 0. | 0. | 0. |
| 3300 | 26.655 | 205.798 | 132.187 | 242.915 | 0. | 0. | 0. |
| 3400 | 27.618 | 206.608 | 134.364 | 245.628 | 0. | 0. | 0. |
| 3500 | 28.657 | 207.423 | 136.440 | 248.441 | 0. | 0. | 0. |
| 3600 | 29.767 | 208.246 | 138.423 | 251.362 | 0. | 0. | 0. |
| 3700 | 30.944 | 209.077 | 140.321 | 254.397 | 0. | 0. | 0. |
| 3800 | 32.180 | 209.919 | 142.142 | 257.553 | 0. | 0. | 0. |
| 3900 | 33.469 | 210.771 | 143.891 | 260.835 | 0. | 0. | 0. |
| 4000 | 34.801 | 211.635 | 145.573 | 264.248 | 0. | 0. | 0. |
| 4100 | 36.169 | 212.511 | 147.195 | 267.796 | 0. | 0. | 0. |
| 4200 | 37.564 | 213.400 | 148.761 | 271.482 | 0. | 0. | 0. |
| 4300 | 38.977 | 214.300 | 150.275 | 275.309 | 0. | 0. | 0. |
| 4400 | 40.389 | 215.212 | 151.740 | 279.275 | 0. | 0. | 0. |
| 4500 | 41.755 | 216.131 | 153.161 | 283.367 | 0. | 0. | 0. |
| 4600 | 43.135 | 217.063 | 154.540 | 287.607 | 0. | 0. | 0. |
| 4700 | 44.507 | 218.005 | 155.880 | 291.990 | 0. | 0. | 0. |
| 4800 | 45.851 | 218.956 | 157.184 | 296.508 | 0. | 0. | 0. |
| 4900 | 47.160 | 219.915 | 158.454 | 301.159 | 0. | 0. | 0. |
| 5000 | 48.426 | 220.881 | 159.693 | 305.938 | 0. | 0. | 0. |
| 5200 | 50.805 | 222.827 | 162.084 | 315.861 | 0. | 0. | 0. |
| 5400 | 52.964 | 224.785 | 164.370 | 326.242 | 0. | 0. | 0. |
| 5600 | 54.857 | 226.745 | 166.562 | 337.021 | 0. | 0. | 0. |
| 5800 | 56.500 | 228.699 | 168.671 | 348.161 | 0. | 0. | 0. |
| 6000 | 57.878 | 230.639 | 170.705 | 359.603 | 0. | 0. | 0. |

PREVIOUS: December 1968 (1 atm)  CURRENT: September 1983 (1 bar)

Pearson Notation: cF4
$S°(298\ 15\ K) = 41.588\ J·K^{-1}·mol^{-1}$
$T_{tr}$ (α → β) = 716 ± 3 K

$\Delta_f H°(0\ K) = 0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ·mol^{-1}$
$\Delta_{tr} H° = 0.930 \pm 0.08\ kJ·mol^{-1}$

### Enthalpy of Formation

Zero by definition.

### Heat Capacity and Entropy

The thermal functions given here are those recommended by CODATA.[1] The low temperature heat capacity of α–CA(cr) has been measured many times: Griffil *et al.* (1.8–4.2 K),[2] Agarwal and Betterton (1.1–4.2 K),[3] Roberts (1.5–20 K),[4] Clusius and Vaughen (10–200 K),[5] Gunther (22–62 K),[6] and Eastman and Rodebush (67–293 K).[7] The adopted heat capacity values are derived assuming that the heat capacity curve should lie below and be similar to the shape of the α–Sr(cr) curve, but remain higher than the Mg curve. The experimental data would imply a crossing of the curves below 300 K which does not appear reasonable. The adopted curve is in reasonable agreement with Griffil *et al.*,[2] Roberts,[4] and Clusius and Vaughen.[5]

The high temperature heat capacities for the α and β phasis are estimates based on the experimental enthalpy studies in Zalensinskii and Zulinski,[8] Jauch,[9] and Eastman *et al.*[10] with the two constraints that the values mesh smoothly with the low temperature results and show a similarity with the Mg and Sr results.

### Transition Data

Refer to Ca(β, cr) tables for details.

### Sublimation Data

Refer to the ideal gas table for details.

### References


[1]H. J. White, Jr. Chairman, CODATA Thermodynamic Tables, Hemisphere Publishing Corp., NY, 356 pp. (1987).
[2]M. Griffil, R. W. Vest, and J. F. Smith, J. Chem. Phys. **27**, 1267 (1957).
[3]K. L. Agarwal and J. O. Betterton, J. Low Temp. Phys. **17**, 509 (1974).
[4]L. M. Roberts, Proc. Phys. soc. (London) **70B**, 738 (1957).
[5]K. Clusius and J. V. Vaughen, J. Am. Chem. Soc. **52**, 4686 (1930).
[6]P. Gunther, Ann. Physik. **51**, 828 (1916).
[7]E. D. Eastman and W. H. Rodebush, J Am. Chem. Soc. **40**, 489 (1918).
[8]E. Zalensinskii and R. Zulinskii, Bull. Intern. Acad. Polon. **1928A**, 479 (1928).
[9]R. Jauch, Diplomarbeit, Techn. Hochschule, Stuttgart, (1946).
[10]E. D. Eastman, A, M. Williams and T. F. Young, J. Am. Chem. Soc. **46**, 1178 (1924).


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 | −5.736 | 0. | 0. | 0. |
| 100 | 19.504 | 15.967 | 63.525 | −4.756 | 0. | 0. | 0. |
| 200 | 24.542 | 31.489 | 43.924 | −2.487 | 0. | 0. | 0. |
| 250 | 25.411 | 37.065 | 42.012 | −1.237 | 0. | 0. | 0. |
| 298.15 | 25.929 | 41.588 | 41.588 | 0. | 0. | 0. | 0. |
| 300 | 25.946 | 41.749 | 41.589 | 0.048 | 0. | 0. | 0. |
| 350 | 26.320 | 45.774 | 41.906 | 1.354 | 0. | 0. | 0. |
| 400 | 26.868 | 49.322 | 42.615 | 2.683 | 0. | 0. | 0. |
| 450 | 27.643 | 52.531 | 43.541 | 4.045 | 0. | 0. | 0. |
| 500 | 28.487 | 55.487 | 44.590 | 5.448 | 0. | 0. | 0. |
| 600 | 30.382 | 60.846 | 46.861 | 8.391 | 0. | 0. | 0. |
| 700 | 32.406 | 65.680 | 49.210 | 11.529 | 0. | 0. | 0. |
| 716.000 | 32.737 | 66.416 | 49.586 | 12.051 | ---- ALPHA <--> BETA ---- | | |
| 800 | 34.613 | 70.150 | 51.551 | 14.879 | −0.844 | 0.104 | −0.007 |
| 900 | 36.819 | 74.354 | 53.853 | 18.451 | −0.798 | 0.219 | −0.013 |
| 1000 | 39.026 | 78.348 | 56.105 | 22.243 | −0.826 | 0.333 | −0.017 |
| 1100 | 41.232 | 82.171 | 58.302 | 26.256 | −0.936 | 0.453 | −0.022 |

PREVIOUS: December 1968  CURRENT: September 1983

Pearson Notation: cI4
$S°(298.15\ K)$ = [43.070] $J·K^{-1}·mol^{-1}$
$T_{trs}$ ($\alpha \rightarrow \beta$) = 716 ± 3 K
$T_{fus}$($\beta \rightarrow$l) = 1115 ± 2 K

$\Delta_f H(298.15\ K)$ = [1.056] $kJ·mol^{-1}$
$\Delta_{trs}H°$ = 0.930 ± $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 8.540 ± 0.10 $kJ·mol^{-1}$

## Enthalpy of Formation

The enthalpy of formation of Ca(β, cr) is calculated from that of the Ca(α, cr) by adding the enthalpy of transition and the difference in enthalpy, $H°(716\ K)–H°(298.15\ K)$, between Ca(α, cr) and Ca(β, cr).

## Heat Capacity and Entropy

The high temperatures heat capacities for the α and β phases are estimates based on the experimental enthalpy studies in Zalinsinski andAulinski.[1] Jauch,[2] and Eastman *et al.*[3] with the two constraints that the values mesh smoothly with the low temperature results and show a similarity with the Mg and Sr results.

## Transition and Fusion Data

According to Pearson,[4] calcium exists in two crystalline modifications. The low temperature phase (α) has a face – centered – cubic (cF4) structure, as does α–Sr(cr). The high temperature phase (β) has a body – centered – cubic (cI2) structure, as does β–Sr(cr). In comparison, magnesium has a hexagonal – close – packed structure. The β–Ca(cr) region of stability is 716 ± 3 K to 1115 ± 2 K.[5]

The enthalpies of transition and fusion are the values determined by Chiotti *et al.*[6] using an adiabatic calorimeter.

## Sublimation Data

Refer to the ideal gas table for details.

## References

[1]E. Zalensinskii and R. Zulinskii, Bull. Intern. Acad. Polon. **1928** A 479 (1928).
[2]R. Jauch, Diplomarbeit, Techn. Hochochule, Stuttgart, (1946).
[3]E. D Eastman, A. M. Williams and T. F. Young, J. Am. Chem. Soc. **46**, 1178 (1924).
[4]W. B. Pearson, "A Handbook of Lattice Spacings and Structures of Metals and Alloys," Pergamon Press, London, (1967).
[5]F. X. Kayser and S. D. Soderquest, J. Phys. Chem. Solids **28**, 2343 (1967).
[6]P. Chiotti, G J Gartner, *et al.*, J. Chem. Eng. Data **11**, 571 (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 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 250 | | | | | | | |
| 298.15 | 25.951 | 43.070 | 43.070 | 0. | 1.056 | 0.614 | −0.108 |
| 300 | 25.971 | 43.231 | 43.071 | 0.048 | 1.056 | 0.611 | −0.106 |
| 350 | 26.345 | 47.260 | 43.388 | 1.355 | 1.057 | 0.537 | −0.080 |
| 400 | 26.894 | 50.812 | 44.098 | 2.685 | 1.058 | 0.463 | −0.060 |
| 450 | 27.708 | 54.026 | 45.025 | 4.051 | 1.061 | 0.388 | −0.045 |
| 500 | 28.514 | 56.988 | 46.075 | 5.456 | 1.064 | 0.313 | −0.033 |
| 600 | 30.099 | 62.336 | 48.349 | 8.392 | 1.057 | 0.163 | −0.014 |
| 700 | 31.062 | 67.008 | 50.688 | 11.424 | 0.951 | 0.021 | −0.002 |
| 716.000 | 31.503 | 67.715 | 51.061 | 11.925 | ---- ALPHA <--> BETA ---- | | |
| 800 | 33.818 | 71.335 | 53.001 | 14.668 | 0. | 0. | 0. |
| 900 | 36.713 | 75.484 | 55.270 | 18.193 | 0. | 0. | 0. |
| 1000 | 39.706 | 79.507 | 57.493 | 22.014 | 0. | 0. | 0. |
| 1100 | 42.763 | 83.434 | 59.674 | 26.137 | 0. | 0. | 0. |
| 1115.000 | 43.226 | 84.017 | 59.997 | 26.782 | ---- BETA <--> LIQUID ---- | | |
| 1200 | 45.850 | 87.287 | 61.815 | 30.567 | −7.729 | 0.622 | −0.027 |
| 1300 | 48.949 | 91.080 | 63.920 | 35.307 | −6.489 | 1.270 | −0.051 |
| 1400 | 52.048 | 94.818 | 65.994 | 40.354 | −4.943 | 1.811 | −0.068 |
| 1500 | 55.566 | 98.527 | 68.039 | 45.731 | −3.066 | 2.230 | −0.078 |

PREVIOUS: December 1968 CURRENT: September 1983

## Calcium (Ca) LIQUID $A_r = 40.08$

$S°(298.15\ K) = [45.510]\ J·K^{-1}·mol^{-1}$
$T_{fus}(\beta \rightarrow l) = 1115 \pm 2\ K$

$\Delta_f H°(298.15\ K) = [7.788]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 8.540 \pm 0.10\ kJ·mol^{-1}$

### Enthalpy of Formation

The enthalpy of formation of the liquid is calculated from that of Ca(β, cr) by adding the enthalpy of fusion and the difference in enthalpy, $H°(1115\ K)–H°(298.15\ K)$, between Ca(β, cr) and the liquid.

### Heat Capacity and Entropy

The heat capacity of the liquid is chosen to be a value intermediate between the adopted values for Mg(l) and Sr(l).

### Fusion Data

Refer to the β–Ca(cr) table for details.

### Vaporization Data

$T_{vap}$ (1 bar) is calculated as the temperature at which $\Delta_r G° = 0$ for the process Ca(l) = Ca(g). $\Delta_{vap}H°$ is calculated as the difference in the enthalpies of formation between the ideal gas and liquid at $T_{vap}$.

Refer to the ideal gas table for details.

## Calcium (Ca) $Ca_1(l)$

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 | | | | | | | |
| 250 | | | | | | | |
| 298.15 | 35.000 | 45.510 | 45.510 | 0. | 7.788 | 6.618 | −1.159 |
| 300 | 35.000 | 45.727 | 45.511 | 0.065 | 7.804 | 6.611 | −1.151 |
| 350 | 35.000 | 51.122 | 45.937 | 1.815 | 8.248 | 6.377 | −0.952 |
| 400 | 35.000 | 55.796 | 46.884 | 3.565 | 8.670 | 6.080 | −0.794 |
| 450 | 35.000 | 59.918 | 48.107 | 5.315 | 9.057 | 5.733 | −0.665 |
| 500 | 35.000 | 63.606 | 49.476 | 7.065 | 9.404 | 5.345 | −0.558 |
| 600 | 35.000 | 69.987 | 52.379 | 10.565 | 9.962 | 4.477 | −0.390 |
| 700 | 35.000 | 75.382 | 55.290 | 14.065 | 10.323 | 3.532 | −0.264 |
| 800 | 35.000 | 80.056 | 58.100 | 17.565 | 9.629 | 2.652 | −0.173 |
| 900 | 35.000 | 84.178 | 60.773 | 21.065 | 9.603 | 1.779 | −0.103 |
| 1000 | 35.000 | 87.866 | 63.301 | 24.565 | 9.283 | 0.924 | −0.048 |
| 1100 | 35.000 | 91.202 | 65.688 | 28.065 | 8.660 | 0.116 | −0.005 |
| 1115.000 | 35.000 | 91.676 | 66.035 | 28.590 | ---- BETA <--> LIQUID ---- | | |
| 1200 | 35.000 | 94.247 | 67.943 | 31.565 | 0. | 0. | 0. |
| 1300 | 35.000 | 97.049 | 70.076 | 35.065 | 0. | 0. | 0. |
| 1400 | 35.000 | 99.642 | 72.096 | 38.565 | 0. | 0. | 0. |
| 1500 | 35.000 | 102.057 | 74.014 | 42.065 | 0. | 0. | 0. |
| 1600 | 35.000 | 104.316 | 75.838 | 45.565 | 0. | 0. | 0. |
| 1700 | 35.000 | 106.438 | 77.576 | 49.065 | 0. | 0. | 0. |
| 1773.658 | 35.000 | 107.922 | 78.806 | 51.643 | ----- FUGACITY = 1 bar ----- | | |
| 1800 | 35.000 | 108.438 | 79.236 | 52.565 | −148.674 | 2.211 | −0.064 |
| 1900 | 35.000 | 110.331 | 80.823 | 56.065 | −147.260 | 10.555 | −0.290 |
| 2000 | 35.000 | 112.126 | 82.344 | 59.565 | −145.852 | 18.824 | −0.492 |
| 2100 | 35.000 | 113.834 | 83.803 | 63.065 | −144.452 | 27.024 | −0.672 |
| 2200 | 35.000 | 115.462 | 85.205 | 66.565 | −143.062 | 35.157 | −0.835 |
| 2300 | 35.000 | 117.018 | 86.555 | 70.065 | −141.688 | 43.227 | −0.982 |
| 2400 | 35.000 | 118.507 | 87.855 | 73.565 | −140.333 | 51.237 | −1.115 |
| 2500 | 35.000 | 119.936 | 89.110 | 77.065 | −139.002 | 59.192 | −1.237 |

PREVIOUS: December 1968  CURRENT September 1983

0 to 716 K alpha
716 to 1115 K beta
above 1115 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 | $C_p^\circ$ | $S^\circ$ | $-[G^\circ-H^\circ(T_r)]/T$ | $H^\circ-H^\circ(T_r)$ | $\Delta_f H^\circ$ | $\Delta_f G^\circ$ | log $K_f$ |
|---|---|---|---|---|---|---|---|
| | J·K⁻¹mol⁻¹ | | | kJ·mol⁻¹ | | | |
| 0 | 0. | 0. | INFINITE | −5.736 | 0. | 0. | 0. |
| 100 | 19.504 | 15.967 | 63.525 | −4.756 | 0. | 0. | 0. |
| 200 | 24.542 | 31.489 | 43.924 | −2.487 | 0. | 0. | 0. |
| 250 | 25.411 | 37.065 | 42.012 | −1.237 | 0. | 0. | 0. |
| 298.15 | 25.929 | 41.588 | 41.588 | 0. | 0. | 0. | 0. |
| 300 | 25.946 | 41.749 | 41.589 | 0.048 | 0. | 0. | 0. |
| 350 | 26.320 | 45.774 | 41.906 | 1.354 | 0. | 0. | 0. |
| 400 | 26.868 | 49.322 | 42.615 | 2.683 | 0. | 0. | 0. |
| 450 | 27.643 | 52.531 | 43.541 | 4.045 | 0. | 0. | 0. |
| 500 | 28.487 | 55.487 | 44.590 | 5.448 | 0. | 0. | 0. |
| 600 | 30.382 | 60.846 | 46.861 | 8.391 | 0. | 0. | 0. |
| 700 | 32.406 | 65.680 | 49.210 | 11.529 | 0. | 0. | 0. |
| 716.000 | 32.737 | 66.416 | 49.586 | 12.051 | ALPHA <--> BETA TRANSITION | | |
| 716.000 | 31.503 | 67.715 | 49.586 | 12.981 | | | |
| 800 | 33.818 | 71.335 | 51.681 | 15.723 | 0. | 0. | 0. |
| 900 | 36.713 | 75.484 | 54.097 | 19.249 | 0. | 0. | 0. |
| 1000 | 39.706 | 79.507 | 56.437 | 23.069 | 0. | 0. | 0. |
| 1100 | 42.763 | 83.434 | 58.714 | 27.192 | 0. | 0. | 0. |
| 1115.000 | 43.226 | 84.017 | 59.050 | 27.837 | BETA <--> LIQUID TRANSITION | | |
| 1115.000 | 35.000 | 91.676 | 59.050 | 36.377 | | | |
| 1200 | 35.000 | 94.247 | 61.453 | 39.352 | 0. | 0. | 0. |
| 1300 | 35.000 | 97.049 | 64.085 | 42.852 | 0. | 0. | 0. |
| 1400 | 35.000 | 99.642 | 66.533 | 46.352 | 0. | 0. | 0. |
| 1500 | 35.000 | 102.057 | 68.822 | 49.852 | 0. | 0. | 0. |
| 1600 | 35.000 | 104.316 | 70.971 | 53.352 | 0. | 0. | 0. |
| 1700 | 35.000 | 106.438 | 72.995 | 56.852 | 0. | 0. | 0. |
| 1773.658 | 35.000 | 107.922 | 74.415 | 59.430 | ----- FUGACITY = 1 bar ----- | | |
| 1800 | 35.000 | 108.438 | 74.909 | 60.352 | −148.674 | 2.211 | −0.064 |
| 1900 | 35.000 | 110.331 | 76.724 | 63.852 | −147.260 | 10.555 | −0.290 |
| 2000 | 35.000 | 112.126 | 78.450 | 67.352 | −145.852 | 18.824 | −0.492 |
| 2100 | 35.000 | 113.834 | 80.094 | 70.852 | −144.452 | 27.024 | −0.672 |
| 2200 | 35.000 | 115.462 | 81.665 | 74.352 | −143.062 | 35.157 | −0.835 |
| 2300 | 35.000 | 117.018 | 83.169 | 77.852 | −141.688 | 43.227 | −0.982 |
| 2400 | 35.000 | 118.507 | 84.610 | 81.352 | −140.332 | 51.237 | −1.115 |
| 2500 | 35.000 | 119.936 | 85.995 | 84.852 | −139.002 | 59.192 | −1.237 |

PREVIOUS:  CURRENT: September 1983

IP (Ca, g) = 49305.96 ± 0.08 $cm^{-1}$
$S°$(298.15 K) = 154.886 ± 0.020 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 177.3 ± 0.8 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = 177.8 ± 0.8 $kJ·mol^{-1}$

| Electronic Level and Quantum Weight | | |
|---|---|---|
| State | $\epsilon_i$, $cm^{-1}$ | $g_i$ |
| $^1S_0$ | 0.00 | 1 |
| $^3P_0$ | 15157.901 | 1 |
| $^3P_1$ | 15210.063 | 3 |
| $^3P_2$ | 15315.943 | 5 |

### Enthalpy of Formation

The adopted enthalpy of formation value for Ca(g), $\Delta_f H°$(298.15 K) = 177.8 ± 0.8 $kJ·mol^{-1}$, is that recommended by CODATA.[1] This value was calculated, according to CODATA, from the vapor pressure measurements by Bogoslovskii *et al.* (773–1023 K),[2] Smith (844–965 K),[3] Bohdansky and Schins (1313–2060 K),[4] Schins *et al* (1558–2115 K,[5]. The study by DeMaria and Piacente (1126–1300 K),[6] and others cited in Hultgren *et al.*[7] were also considered.

### Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Sugar and Corliss,[8] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels (for $n < 80$) and cutting off the summation in the partition function[9] has no effect on the thermodynamic functions to 4000 K. This is a result of the high energy of all levels other than the ground state and the levels listed above; the next excited state is approximately 20335 $cm^{-1}$ above the ground state. Although we list only a few levels, all levels listed by Sugar and Corliss[8] and the estimated levels (for $n < 80$) are considered in the calculation. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative atomic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of additional excited states and use of different fill and cutoff procedures.[9]

The thermal functions at 298.15 K differ from the CODATA recommendations[1] for two reasons. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a reference pressure of 1 bar, whereas CODATA recommendations are based on 1 atm. Second, small changes, −0.002 $J·K^{-1}·mol^{-1}$, arise due to the use of slightly different values for the fundamental constants.

### References


[1] J. D. Cox, Chairman, CODATA Task Force on Key Values for Thermodynamics, J. Chem. Thermodyn. **10**, 903 (1978); CODATA Bulletin No. 22, (1977).
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[9] J. R. Downey, Jr., The Dow Chemical Company, Report 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 | −6.197 | 177.339 | 177.339 | INFINITE |
| 100 | 20.786 | 132.179 | 173.366 | −4.119 | 178.437 | 166.816 | −87.136 |
| 200 | 20.786 | 146.586 | 156.787 | −2.040 | 178.247 | 155.227 | −40.541 |
| 250 | 20.786 | 151.225 | 155.228 | −1.001 | 178.036 | 149.496 | −31.236 |
| 298.15 | 20.786 | 154.886 | 154.886 | 0. | 177.800 | 144.020 | −25.232 |
| 300 | 20.786 | 155.014 | 154.886 | 0.038 | 177.790 | 143.811 | −25.040 |
| 350 | 20.786 | 158.219 | 155.139 | 1.078 | 177.524 | 138.168 | −20.620 |
| 400 | 20.786 | 160.994 | 155.701 | 2.117 | 177.234 | 132.565 | −17.311 |
| 450 | 20.786 | 163.442 | 156.428 | 3.156 | 176.911 | 127.001 | −14.742 |
| 500 | 20.786 | 165.632 | 157.241 | 4.196 | 176.547 | 121.474 | −12.690 |
| 600 | 20.786 | 169.422 | 158.965 | 6.274 | 175.684 | 110.538 | −9.623 |
| 700 | 20.786 | 172.626 | 160.694 | 8.353 | 174.623 | 99.761 | −7.444 |
| 800 | 20.786 | 175.402 | 162.363 | 10.431 | 172.508 | 89.255 | −5.828 |
| 900 | 20.786 | 177.850 | 163.950 | 12.510 | 171.061 | 78.932 | −4.581 |
| 1000 | 20.786 | 180.040 | 165.452 | 14.589 | 169.319 | 68.786 | −3.593 |
| 1100 | 20.786 | 182.021 | 166.869 | 16.667 | 167.275 | 58.829 | −2.794 |
| 1200 | 20.786 | 183.830 | 168.208 | 18.746 | 157.193 | 49.694 | −2.163 |
| 1300 | 20.787 | 185.494 | 169.475 | 20.825 | 155.772 | 40.793 | −1.639 |
| 1400 | 20.789 | 187.034 | 170.675 | 22.903 | 154.351 | 32.002 | −1.194 |
| 1500 | 20.793 | 188.469 | 171.814 | 24.982 | 152.930 | 23.313 | −0.812 |
| 1600 | 20.802 | 189.811 | 172.897 | 27.062 | 151.510 | 14.718 | −0.480 |
| 1700 | 20.818 | 191.072 | 173.929 | 29.143 | 150.091 | 6.212 | −0.191 |
| 1773.658 | 20.837 | 191.956 | 174.660 | 30.677 | ----- FUGACITY = 1 bar ----- | | |
| 1800 | 20.845 | 192.263 | 174.915 | 31.226 | 0. | 0. | 0. |
| 1900 | 20.888 | 193.391 | 175.858 | 33.313 | 0. | 0. | 0. |
| 2000 | 20.953 | 194.464 | 176.762 | 35.405 | 0. | 0. | 0. |
| 2100 | 21.046 | 195.489 | 177.629 | 37.504 | 0. | 0. | 0. |
| 2200 | 21.173 | 196.470 | 178.464 | 39.615 | 0. | 0. | 0. |
| 2300 | 21.343 | 197.415 | 179.267 | 41.740 | 0. | 0. | 0. |
| 2400 | 21.561 | 198.328 | 180.043 | 43.885 | 0. | 0. | 0. |
| 2500 | 21.836 | 199.214 | 180.792 | 46.054 | 0. | 0. | 0. |
| 2600 | 22.173 | 200.076 | 181.517 | 48.254 | 0. | 0. | 0. |
| 2700 | 22.578 | 200.921 | 182.220 | 50.491 | 0. | 0. | 0. |
| 2800 | 23.057 | 201.750 | 182.903 | 52.773 | 0. | 0. | 0. |
| 2900 | 23.614 | 202.569 | 183.567 | 55.105 | 0. | 0. | 0. |
| 3000 | 24.251 | 203.380 | 184.214 | 57.498 | 0. | 0. | 0. |
| 3100 | 24.970 | 204.186 | 184.845 | 59.958 | 0. | 0. | 0. |
| 3200 | 25.772 | 204.992 | 185.462 | 62.495 | 0. | 0 | 0. |
| 3300 | 26.655 | 205.798 | 186.066 | 65.115 | 0. | 0. | 0. |
| 3400 | 27.618 | 206.608 | 186.658 | 67.828 | 0. | 0. | 0. |
| 3500 | 28.657 | 207.423 | 187.240 | 70.641 | 0. | 0. | 0. |
| 3600 | 29.767 | 208.246 | 187.812 | 73.562 | 0. | 0. | 0. |
| 3700 | 30.944 | 209.077 | 188.375 | 76.597 | 0. | 0. | 0. |
| 3800 | 32.180 | 209.919 | 188.931 | 79.753 | 0. | 0. | 0. |
| 3900 | 33.469 | 210.771 | 189.480 | 83.035 | 0. | 0. | 0. |
| 4000 | 34.801 | 211.635 | 190.023 | 86.448 | 0. | 0. | 0. |
| 4100 | 36.169 | 212.511 | 190.561 | 89.996 | 0. | 0. | 0. |
| 4200 | 37.564 | 213.400 | 191.094 | 93.682 | 0. | 0. | 0. |
| 4300 | 38.977 | 214.300 | 191.623 | 97.509 | 0. | 0. | 0. |
| 4400 | 40.389 | 215.212 | 192.149 | 101.475 | 0. | 0. | 0. |
| 4500 | 41.755 | 216.131 | 192.672 | 105.568 | 0. | 0. | 0. |
| 4600 | 43.135 | 217.063 | 193.192 | 109.808 | 0. | 0. | 0. |
| 4700 | 44.507 | 218.005 | 193.710 | 114.190 | 0. | 0. | 0. |
| 4800 | 45.851 | 218.956 | 194.226 | 118.708 | 0. | 0. | 0. |
| 4900 | 47.160 | 219.915 | 194.740 | 123.359 | 0. | 0. | 0. |
| 5000 | 48.426 | 220.881 | 195.253 | 128.138 | 0. | 0. | 0. |
| 5100 | 49.646 | 221.852 | 195.765 | 133.042 | 0. | 0. | 0. |
| 5200 | 50.805 | 222.827 | 196.276 | 138.061 | 0. | 0. | 0. |
| 5300 | 51.914 | 223.805 | 196.786 | 143.198 | 0. | 0. | 0. |
| 5400 | 52.964 | 224.785 | 197.296 | 148.442 | 0. | 0. | 0. |
| 5500 | 53.952 | 225.766 | 197.805 | 153.789 | 0. | 0. | 0. |
| 5600 | 54.857 | 226.745 | 198.312 | 159.221 | 0. | 0. | 0. |
| 5700 | 55.712 | 227.723 | 198.820 | 164.750 | 0. | 0. | 0. |
| 5800 | 56.500 | 228.699 | 199.327 | 170.361 | 0. | 0. | 0. |
| 5900 | 57.222 | 229.671 | 199.833 | 176.047 | 0. | 0. | 0. |
| 6000 | 57.878 | 230.639 | 200.338 | 181.803 | 0. | 0. | 0. |

PREVIOUS: December 1968 (1 atm)  CURRENT September 1983 (1 bar)

$IP(Ca^+, g) = 95751.87 \pm 0.03\ cm^{-1}$
$S°(298.15\ K) = 160.649 \pm 0.02\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 767.17 \pm 0.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [773.828]\ kJ·mol^{-1}$

| Electronic Levels and Quantum Weights | | |
|---|---|---|
| State | $\epsilon_i$, $cm^{-1}$ | $g_i$ |
| $^2S_{1/2}$ | 0.0 | 2 |
| $^2D_{3/2}$ | 13650.1 | 4 |
| $^2D_{5/2}$ | 13710.8 | 6 |
| $^2P_{1/2}$ | 25191.5 | 2 |
| $^2P_{3/2}$ | 25414.40 | 4 |

## Enthalpy of Formation

$\Delta_f H°(Ca^+, g, 0\ K)$ is calculated from $\Delta_f H°(Ca, g, 0\ K)$[1] using the spectroscopic value of IP(Ca) = 49305.96 ± 0.08 $cm^{-1}$(589.830 ± 0.001 $kJ·mol^{-1}$) from Sugar and Corliss.[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 and appearance potential data.

$\Delta_f H°(Ca^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(Ca, g, 0\ K)$ by using IP(Ca) with JANAF[1] enthalpies, $H°(0\ K)-H°(298\ 15\ K)$, for Ca(g), $Ca^+(g)$, and $e^-$(ref). $\Delta_r H°(Ca \rightarrow Ca^+ + e^-, 298.15\ K)$ 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 Sugar and Corliss,[2] 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[6] 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 first four excited states, the next excited state is approximately 52167 $cm^{-1}$ above the ground state. Since inclusion of these higher excited states has little effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first four excited states. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[6]

## References

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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 | −6.197 | 767.169 | | |
| 100 | 20.786 | 137.942 | 179.129 | −4.119 | | | |
| 200 | 20.786 | 152.349 | 162.550 | −2.040 | | | |
| 250 | 20.786 | 156.988 | 160.991 | −1.001 | | | |
| 298.15 | 20.786 | 160.649 | 160.649 | 0. | 773.828 | 732.075 | −128.257 |
| 300 | 20.786 | 160.777 | 160.649 | 0.038 | 773.857 | 731.816 | −127.420 |
| 350 | 20.786 | 163.981 | 160.902 | 1.078 | 774.629 | 724.748 | −108.163 |
| 400 | 20.786 | 166.757 | 161.464 | 2.117 | 775.379 | 717.570 | −93.705 |
| 450 | 20.786 | 169.205 | 162.191 | 3.156 | 776.095 | 710.301 | −82.450 |
| 500 | 20.786 | 171.395 | 163.004 | 4.196 | 776.771 | 702.954 | −73.437 |
| 600 | 20.786 | 175.185 | 164.728 | 6.274 | 777.986 | 688.073 | −59.902 |
| 700 | 20.786 | 178.389 | 166.457 | 8.353 | 779.004 | 673.004 | −50.220 |
| 800 | 20.786 | 181.165 | 168.126 | 10.431 | 778.967 | 657.908 | −42.957 |
| 900 | 20.786 | 183.613 | 169.713 | 12.510 | 779.599 | 642.734 | −37.303 |
| 1000 | 20.786 | 185.803 | 171.214 | 14.589 | 779.936 | 627.506 | −32.778 |
| 1100 | 20.786 | 187.784 | 172.632 | 16.667 | 779.970 | 612.259 | −29.074 |
| 1200 | 20 787 | 189.593 | 173.971 | 18.746 | 771.967 | 597.645 | −26.015 |
| 1300 | 20 789 | 191.257 | 175.238 | 20.825 | 772.625 | 583.091 | −23.429 |
| 1400 | 20.792 | 192.798 | 176.438 | 22.904 | 773.282 | 568.487 | −21.211 |
| 1500 | 20.800 | 194.232 | 177.577 | 24.983 | 773.940 | 553.836 | −19.286 |
| 1600 | 20.814 | 195.575 | 178.660 | 27.064 | 774.600 | 539.141 | −17.601 |
| 1700 | 20.838 | 196.838 | 179.693 | 29.147 | 775.261 | 524.405 | −16.113 |
| 1800 | 20.874 | 198.030 | 180.679 | 31.232 | 627.251 | 511.840 | −14.853 |
| 1900 | 20.927 | 199.160 | 181.622 | 33.322 | 629.333 | 505.372 | −13.894 |
| 2000 | 20.999 | 200.235 | 182.526 | 35.418 | 631.416 | 498.793 | −13.027 |
| 2100 | 21.095 | 201.262 | 183.394 | 37.523 | 633.500 | 492.111 | −12.241 |
| 2200 | 21.218 | 202.246 | 184.228 | 39.638 | 635.583 | 485.329 | −11.523 |
| 2300 | 21.369 | 203.192 | 185.032 | 41.767 | 637.665 | 478.453 | −10.866 |
| 2400 | 21.550 | 204.105 | 185.808 | 43.913 | 639.745 | 471.486 | −10.262 |
| 2500 | 21.764 | 204.989 | 186.558 | 46.078 | 641.819 | 464.433 | −9.704 |
| 2600 | 22.009 | 205.847 | 187.283 | 48.267 | 643.886 | 457.297 | −9.187 |
| 2700 | 22.286 | 206.683 | 187.986 | 50.481 | 645.943 | 450.081 | −8.707 |
| 2800 | 22.594 | 207.499 | 188.669 | 52.725 | 647.984 | 442.789 | −8.260 |
| 2900 | 22.931 | 208.298 | 189.332 | 55.001 | 650.005 | 435.425 | −7.843 |
| 3000 | 23.296 | 209.081 | 189.977 | 57.312 | 652.003 | 427.992 | −7.452 |
| 3100 | 23.686 | 209.851 | 190.606 | 59.661 | 653.970 | 420.492 | −7.085 |
| 3200 | 24.098 | 210.610 | 191.219 | 62.050 | 655.901 | 412.930 | −6.740 |
| 3300 | 24.529 | 211.358 | 191.818 | 64.481 | 657.790 | 405.308 | −6.415 |
| 3400 | 24.977 | 212.097 | 192.404 | 66.956 | 659.631 | 397.629 | −6.109 |
| 3500 | 25.438 | 212.827 | 192.977 | 69.477 | 661.417 | 389.897 | −5.819 |
| 3600 | 25.908 | 213.551 | 193.538 | 72.044 | 663.142 | 382.115 | −5.544 |
| 3700 | 26.385 | 214.267 | 194.089 | 74.659 | 664.800 | 374.285 | −5.284 |
| 3800 | 26.865 | 214.977 | 194.629 | 77.321 | 666.386 | 366.412 | −5.037 |
| 3900 | 27.345 | 215.681 | 195.160 | 80.031 | 667.893 | 358.498 | −4.802 |
| 4000 | 27.822 | 216.379 | 195.682 | 82.790 | 669.317 | 350.547 | −4.578 |
| 4100 | 28.294 | 217.072 | 196.195 | 85.596 | 670.653 | 342.561 | −4.364 |
| 4200 | 28.757 | 217.759 | 196.700 | 88.448 | 671.898 | 334.543 | −4.161 |
| 4300 | 29.210 | 218.441 | 197.198 | 91.347 | 673.048 | 326.497 | −3.966 |
| 4400 | 29.651 | 219.118 | 197.689 | 94.290 | 674.104 | 318.425 | −3.780 |
| 4500 | 30.077 | 219.789 | 198.172 | 97.276 | 675.077 | 310.330 | −3.602 |
| 4600 | 30.487 | 220.455 | 198.649 | 100.305 | 675.943 | 302.214 | −3.432 |
| 4700 | 30.880 | 221.115 | 199.120 | 103.373 | 676.708 | 294.081 | −3.268 |
| 4800 | 31.254 | 221.769 | 199.585 | 106.480 | 677.376 | 285.933 | −3.112 |
| 4900 | 31.608 | 222.417 | 200.045 | 109.623 | 677.946 | 277.772 | −2.961 |
| 5000 | 31.942 | 223.059 | 200.499 | 112.801 | 678.424 | 269.600 | −2.816 |
| 5100 | 32.255 | 223.694 | 200.947 | 116.011 | 678.808 | 261.419 | −2.677 |
| 5200 | 32.546 | 224.324 | 201.391 | 119.251 | 679.108 | 253.232 | −2.544 |
| 5300 | 32.817 | 224.946 | 201.829 | 122.520 | 679.318 | 245.040 | −2.415 |
| 5400 | 33.066 | 225.562 | 202.263 | 125.814 | 679.447 | 236.845 | −2.291 |
| 5500 | 33.293 | 226.171 | 202.692 | 129.132 | 679.497 | 228.648 | −2.172 |
| 5600 | 33.500 | 226.773 | 203.117 | 132.472 | 679.483 | 220.450 | −2.056 |
| 5700 | 33.685 | 227.367 | 203.537 | 135.831 | 679.392 | 212.253 | −1.945 |
| 5800 | 33.851 | 227.954 | 203.953 | 139.208 | 679.237 | 204.059 | −1.838 |
| 5900 | 33.997 | 228.534 | 204.365 | 142.601 | 679.021 | 195.868 | −1.734 |
| 6000 | 34.124 | 229.107 | 204.772 | 146.007 | 678.751 | 187.681 | −1.634 |

PREVIOUS: December 1970 (1 atm)  CURRENT: September 1983 (1 bar)

$S°(298\ 15\ K) = 241.56 \pm 0.8\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -103.9 \pm 13\ kJ·mol^{-1}$
$\Delta_f H°(298\ 15\ K) = -104.6 \pm 13\ kJ·mol^{-1}$

| Electronic Levels and Quantum Weights | | |
|---|---|---|
| State | $\epsilon_i$, $cm^{-1}$ | $g_i$ |
| $X^2\Sigma^+$ | 0 | 2 |
| $A^2\Pi$ | 16093.3 | 2 |
| | 16162.8 | 2 |
| $B^2\Sigma$ | 16850.6 | 2 |
| $C^2\Pi$ | 26498.9 | 2 |
| | 26574.7 | 2 |
| $D[^2\Sigma]$ | 31107.8 | 2 |
| $E[^2\Sigma]$ | 34266.4 | 2 |
| $F^2\Pi$ | 35675 | 2 |
| | 35700 | 2 |
| $G^2\Delta$ | 36705 | 2 |
| | 36710 | 2 |

$\omega_e = 369.8\ cm^{-1}$ $\omega_e x_e = 1.31\ cm^{-1}$ $\sigma = 1$
$B_e = 0.1516\ cm^{-1}$ $\alpha_e = [0.0007]\ cm^{-1}$ $r_e = 2.439$ Å

## Enthalpy of Formation

Potter[1] investigated mass spectrometrically the gaseous equilibria among Ca, CaCl, and $CaCl_2$. Ion intensities were measured 2.5 eV above the ionization threshold. Using the equilibrium constants $K = I(CaCl^+)^2/I(Ca^+)I(CaCl_2)$ which we calculate from the reported ion intensities for the reaction $Ca(g) + CaCl_2(g) \rightarrow 2\ CaCl(g)$ in the temperature range 1252–1557 K, we obtain $\Delta_f H°(298.15\ K) = 15.81$ kcal·mol$^{-1}$ by the 3rd law method. The 3rd law drift is $-2.8 \pm 3.5$ cal·K$^{-1}$·mol$^{-1}$. The enthalpy of formation is derived as $\Delta_f H°(CaCl, g, 298.15\ K) = -27\ 0$ kcal·mol$^{-1}$.

Zmbov[7] determined by mass spectrometry the enthalpy of the above reaction as $24.4 \pm 1.3$ kcal·mol$^{-1}$ with a drift of $12.5 \pm 9.4$ cal·K$^{-1}$ mol$^{-1}$. This yields the enthalpy of formation, $\Delta_f H°(CaCl, g, 298.15\ K) = -22.7$ kcal·mol$^{-1}$.

Hildenbrand[2] also determined the equilibrium constants for the reaction (a) $Ca(g) + CaCl_2(g) \rightarrow 2\ CaCl(g)$ and the reaction (b) $Ca(g) + AlCl(g) \rightarrow CaCl(g) + Al(g)$ by mass spectrometry in the temperature range 1219–1353 K. 3rd law analysis of the reported equilibrium constants gives $\Delta_r H°(298.15\ K) = 21.08$ kcal·mol$^{-1}$ and drift $= -1\ 4 \pm 1.8$ cal·K$^{-1}$·mol$^{-1}$ for reaction (a); and $\Delta_r H°(298.15\ K) = 24.20$ kcal·mol$^{-1}$ and drift $= 0.5 \pm 1.3$ cal·K$^{-1}$·mol$^{-1}$ for reaction (b). From 3rd law $\Delta_f H°(298.15\ K)$ of (a) and (b), we derived $\Delta_f H°(CaCl, g, 298.15\ K) = -24.4$ and $-23.3$ kcal·mol$^{-1}$, respectively, using all JANAF functions. Hildenbrand has also derived a corrected $D°_0(Ca–Cl) = 95.0$ kcal·mol$^{-1}$ from a linear Birge–Sponer extrapolation of the ground state vibrational levels with correction for its ionicity. This corrected $D°_0(Ca–Cl)$ yields the enthalpy of formation, $\Delta_f H°(CaCl, g, 298.15\ K) = -23.9$ kcal·mol$^{-1}$.

Ryabova and Gurvich[3] reported $D°_0(Ca–Cl) = 102 \pm 6$ kcal·mol$^{-1}$ from flame spectra studies. This leads to $\Delta_f H°(CaCl, g, 298.15\ K) = -30.9$ kcal·mol$^{-1}$.

Hildenbrand[6] determined the dissociation energy of $CaCl_2(g)$ by electron impact as $\Delta_a H°(CaCl–Cl) = 5.04 \pm 0.02$ kcal·mol$^{-1}$ which, combined with JANAF $\Delta_f H°(298.15\ K)$ of $CaCl_2(g)$ and Cl(g), gives $\Delta_f H°(CaCl, g, 298.15\ K) = -23.1$ kcal·mol$^{-1}$.

A weighted average, $\Delta_f H°(CaCl, g, 298.15\ K) = -25 \pm 3$ kcal·mol$^{-1}$ $(-104.6 \pm 13$ kJ·mol$^{-1})$ is adopted in the tabulation.

## Heat Capacity and Entropy

The vibrational constants ($\omega_e$ and $\omega_e x_e$), electronic levels and ground state configuration were taken from Herzberg.[4] Morgan and Barrow[5] made rotational analysis of the $C^2\Pi–X^2\Sigma$ system and reported $B_0 = 0.1516\ cm^{-1}$ and $r_e = 2\ 439$ Å for the ground state. The value of $\alpha_e$ is calculated from the Morse potential function. The F and G states were reported by Schutte.[8]

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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 | −9.589 | −103.862 | −103 862 | INFINITE |
| 100 | 30.307 | 205.406 | 271.974 | −6.657 | −103.367 | −112.860 | 58.952 |
| 200 | 33.959 | 227.636 | 244.777 | −3.428 | −103.925 | −122.158 | 31.905 |
| 250 | 35.001 | 235.334 | 242.143 | −1.702 | −104.259 | −126.679 | 26.468 |
| 298.15 | 35.665 | 241.559 | 241.559 | 0. | −104.600 | −130.966 | 22.945 |
| 300 | 35.685 | 241.780 | 241.560 | 0.066 | −104.613 | −131.129 | 22.832 |
| 350 | 36.151 | 247.318 | 241.996 | 1.863 | −104.982 | −135.520 | 20.225 |
| 400 | 36.481 | 252.168 | 242.971 | 3.679 | −105.370 | −139.856 | 18.263 |
| 450 | 36.724 | 256.480 | 244.237 | 5.509 | −105.791 | −144.142 | 16.732 |
| 500 | 36.910 | 260.359 | 245.658 | 7.350 | −106.250 | −148.379 | 15.501 |
| 600 | 37.174 | 267.114 | 248.688 | 11.055 | −107.303 | −156.709 | 13.643 |
| 700 | 37.356 | 272.858 | 251 741 | 14.783 | −108.551 | −164.847 | 12.301 |
| 800 | 37.493 | 277.856 | 254.699 | 18.525 | −110.852 | −172.689 | 11.275 |
| 900 | 37.602 | 282.278 | 257.523 | 22.280 | −112.483 | −180.324 | 10.466 |
| 1000 | 37.693 | 286.245 | 260.200 | 26.045 | −114.407 | −187.761 | 9.808 |
| 1100 | 37.773 | 289.841 | 262.734 | 29.818 | −116.632 | −194.992 | 9.259 |
| 1200 | 37.846 | 293.131 | 265.132 | 33.599 | −126.891 | −201.384 | 8.766 |
| 1300 | 37.913 | 296.163 | 267 404 | 37.387 | −128.489 | −207.526 | 8.339 |
| 1400 | 37.976 | 298.975 | 269.560 | 41.182 | −130.086 | −213.546 | 7.968 |
| 1500 | 38.037 | 301.597 | 271.609 | 44.983 | −131.681 | −219.452 | 7.642 |
| 1600 | 38.095 | 304.054 | 273.561 | 48.789 | −133.274 | −225.252 | 7.354 |
| 1700 | 38.154 | 306.365 | 275.423 | 52.602 | −134.866 | −230.951 | 7.096 |
| 1800 | 38.213 | 308.548 | 277.203 | 56.420 | −285.130 | −234.347 | 6.801 |
| 1900 | 38.273 | 310.616 | 278.908 | 60.244 | −285.306 | −231.521 | 6.365 |
| 2000 | 38.336 | 312.580 | 280.543 | 64.075 | −285.486 | −228.685 | 5.973 |
| 2100 | 38.404 | 314.452 | 282.113 | 67.912 | −285.673 | −225.841 | 5 617 |
| 2200 | 38.477 | 316.241 | 283.624 | 71.756 | −285.870 | −222.987 | 5.294 |
| 2300 | 38.558 | 317.953 | 285.080 | 75.607 | −286.081 | −220.124 | 4.999 |
| 2400 | 38.646 | 319.596 | 286 484 | 79.467 | −286.310 | −217.251 | 4.728 |
| 2500 | 38.745 | 321.175 | 287 840 | 83.337 | −286.562 | −214.369 | 4.479 |
| 2600 | 38.854 | 322.697 | 289.152 | 87.217 | −286.843 | −211.476 | 4.249 |
| 2700 | 38.975 | 324.165 | 290.422 | 91.108 | −287.159 | −208.571 | 4.035 |
| 2800 | 39.110 | 325.585 | 291.652 | 95.012 | −287.515 | −205.654 | 3.837 |
| 2900 | 39.257 | 326.960 | 292.846 | 98.930 | −287.919 | −202.723 | 3.651 |
| 3000 | 39.418 | 328.294 | 294.006 | 102.864 | −288.377 | −199.778 | 3.478 |
| 3100 | 39.594 | 329.589 | 295.133 | 106.815 | −288.895 | −196.816 | 3.316 |
| 3200 | 39.784 | 330.849 | 296.229 | 110.783 | −289.481 | −193.837 | 3.164 |
| 3300 | 39.988 | 332.076 | 297.297 | 114.772 | −290 140 | −190.838 | 3.021 |
| 3400 | 40.207 | 333.273 | 298.338 | 118.782 | −290.878 | −187.818 | 2.885 |
| 3500 | 40.439 | 334.442 | 299.353 | 122.814 | −291.702 | −184.775 | 2.758 |
| 3600 | 40.685 | 335.585 | 300.343 | 126.870 | −292.616 | −181.707 | 2.637 |
| 3700 | 40.944 | 336.703 | 301.311 | 130.951 | −293.625 | −178.613 | 2.522 |
| 3800 | 41.215 | 337.799 | 302.257 | 135.059 | −294.732 | −175.490 | 2.412 |
| 3900 | 41.498 | 338.873 | 303.182 | 139.195 | −295.941 | −172.336 | 2.308 |
| 4000 | 41.792 | 339.927 | 304.087 | 143.359 | −297.255 | −169.150 | 2.209 |
| 4100 | 42.096 | 340.963 | 304.974 | 147.553 | −298.674 | −165.930 | 2.114 |
| 4200 | 42.409 | 341.981 | 305.843 | 151.779 | −300.200 | −162.674 | 2.023 |
| 4300 | 42.731 | 342.983 | 306.695 | 156.035 | −301.833 | −159.381 | 1 936 |
| 4400 | 43.060 | 343.969 | 307.531 | 160.325 | −303.568 | −156.048 | 1.853 |
| 4500 | 43.396 | 344.940 | 308.352 | 164.648 | −305.394 | −152.676 | 1.772 |
| 4600 | 43.738 | 345.898 | 309.158 | 169.004 | −307.326 | −149.262 | 1.695 |
| 4700 | 44.086 | 346.842 | 309.949 | 173.396 | −309.360 | −145.804 | 1.620 |
| 4800 | 44.438 | 347.774 | 310.728 | 177.822 | −311.487 | −142.302 | 1.549 |
| 4900 | 44.793 | 348.694 | 311.493 | 182.283 | −313.703 | −138.754 | 1.479 |
| 5000 | 45.151 | 349.602 | 312.246 | 186.780 | −316.001 | −135.161 | 1.412 |
| 5100 | 45.511 | 350.500 | 312.988 | 191.314 | −318.378 | −131.520 | 1 347 |
| 5200 | 45.873 | 351.387 | 313.717 | 195.883 | −320.823 | −127.833 | 1.284 |
| 5300 | 46.235 | 352.264 | 314.436 | 200.488 | −323.336 | −124.098 | 1.223 |
| 5400 | 46.597 | 353.132 | 315.145 | 205.130 | −325.909 | −120.315 | 1.164 |
| 5500 | 46.958 | 353.990 | 315.844 | 209.807 | −328.535 | −116.483 | 1.106 |
| 5600 | 47.317 | 354.840 | 316.532 | 214.521 | −331.196 | −112.605 | 1.050 |
| 5700 | 47.675 | 355.680 | 317.212 | 219.271 | −333.905 | −108.677 | 0.996 |
| 5800 | 48.029 | 356.513 | 317.882 | 224.056 | −336 646 | −104.702 | 0.943 |
| 5900 | 48.381 | 357.337 | 318.544 | 228.877 | −339.413 | −100.679 | 0.891 |
| 6000 | 48.729 | 358.153 | 319.197 | 233.732 | −342.199 | −96.610 | 0.841 |

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = 104.6 \pm 4\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1045\ K$

$\Delta_f H°(0\ K) = -796.3 \pm 1.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -795.8 \pm 1.3\ kJ·mol^{-1}$
$\Delta_{fus} H° = 28.543 \pm 0.8\ kJ·mol^{-1}$

### Enthalpy of Formation

Parker[1] has selected the standard enthalpy of formation at 298.15 K as −190.2 kcal·mol$^{-1}$ (−795.797 kJ·mol$^{-1}$) which is adopted in the tabulation. The enthalpy of formation was derived from two independent paths. The first path involves $\Delta_f H°(Ca^{++}, aq, \infty, 298.15\ K) = -129.74$ kcal·mol$^{-1}$,[1] $\Delta_f H°(Cl^-, aq, \infty, 298.15\ K) = -39.952$ kcal·mol$^{-1}$ [2] and the enthaply of solution of $CaCl_2$(cr) in water.[3-7] The second path involves the enthalpies of reaction of Ca(cr), CaO(cr) and $CaCl_2$(cr) in aqueous HCl solution.[4,8-20]

### Heat Capacity and Entropy

Kelley and Moore[21] measured the low temperature heat capacities in the temperature range from 52.6 to 295.1 K and made an extrapolation to 0 K which yielded an entropy of 4.59 ± 0.4 cal·K$^{-1}$·mol$^{-1}$ at 50.12 K. We have adopted the measured heat capacities, but made our own extrapolation to 0 K by comparison with the measured heat capacities of $BaCl_2$(cr)[22] and $SrCl_2$(cr)[23] from 6 to 50 K. The extrapolation gives $S°(50\ K) = 2.45 \pm 1$ cal·K$^{-1}$·mol$^{-1}$, which is used in the table. Moore[24] measured high temperature enthalpy data from 403.7 to 1667 K by drop calorimetry. The low temperature heat capacities and the heat capacities from the high temperature enthalpy data are smoothly joined at 298.15 K. The deviations of the observed enthalpies from the adopted values are about 2% near 400–500 K and only a few tenths percent at higher temperatures. Dworkin and Bredig[25] determined drop–calorimetrically $H°(1045\ K) - H°(298.15\ K) = 14.3$ kcal·mol$^{-1}$, which is in very good agreement with the adopted value of 14.2 kcal·mol$^{-1}$.

### Fusion Data

The adopted melting point 1045 K was determined by Tokareva.[26] Dworkin and Bredig[25] determined the enthalpy of fusion $\Delta_{fus} H°(1045\ K) = 6.78 \pm 0.1$ kcal·mol$^{-1}$ by drop calorimetry. Chiotti *et al.*[27] also measured the enthalpy of fusion $\Delta_{fus} H°(1055\ K) = 6.79 \pm 0.2$ kcal·mol$^{-1}$ in an adiabatic calorimeter. The adopted enthalpy of fusion, 6.822 kcal mol$^{-1}$ (28.543 kJ·mol$^{-1}$), is calculated from the difference between the observed relative enthalpy of the liquid and the adopted value for the crystal at the melting point.

### Sublimation Data

The enthalpy of sublimation is calculated from the enthalpies of formation of $CaCl_2$(cr) and $CaCl_2$(g).

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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 | −15.391 | −796.270 | −796.270 | INFINITE |
| 100 | 48.812 | 35.596 | 164.875 | −12.928 | −797.700 | −780.762 | 407.828 |
| 200 | 67.357 | 76.550 | 111.119 | −6.914 | −796.992 | −764.012 | 199.539 |
| 298.15 | 72.856 | 104.602 | 104.602 | 0. | −795.797 | −748.073 | 131.059 |
| 300 | 72.927 | 105.053 | 104.603 | 0.135 | −795.773 | −747.777 | 130.200 |
| 400 | 75.647 | 126.448 | 107.502 | 7.578 | −794.434 | −731.979 | 95.587 |
| 500 | 77.153 | 143.502 | 113.054 | 15.224 | −793.125 | −716.519 | 74.854 |
| 600 | 78.199 | 157.663 | 119.342 | 22.992 | −791.931 | −701.312 | 61.055 |
| 700 | 79.370 | 169.801 | 125.704 | 30.868 | −790.866 | −686.294 | 51.212 |
| 800 | 80.919 | 180.495 | 131.897 | 38.878 | −790.750 | −671.318 | 43.833 |
| 900 | 83.094 | 190.145 | 137.841 | 47.074 | −789.800 | −656.447 | 38.099 |
| 1000 | 85.772 | 199.033 | 143.521 | 55.512 | −788.919 | −641.678 | 33.518 |
| 1045.000 | 87.090 | 202.837 | 145.994 | 59.401 | --- CRYSTAL <--> LIQUID --- | | |
| 1100 | 88.701 | 207.345 | 148.950 | 64.236 | −788.069 | −626.995 | 29.774 |
| 1200 | 91.630 | 215.189 | 154.146 | 73.252 | −794.974 | −611.767 | 26.630 |
| 1300 | 94.558 | 222.639 | 159.130 | 82.561 | −792.937 | −596.580 | 23.971 |
| 1400 | 97.487 | 229.754 | 163.922 | 92.164 | −790.616 | −581.561 | 21.698 |
| 1500 | 100.416 | 236.579 | 168.540 | 102.059 | −788.012 | −566.717 | 19.735 |
| 1600 | 103.345 | 243.154 | 172.999 | 112.247 | −785.124 | −552.057 | 18.023 |
| 1700 | 106.274 | 249.507 | 177.314 | 122.728 | −781.951 | −537.586 | 16.518 |
| 1800 | 109.202 | 255.664 | 181.497 | 133.502 | −927.169 | −521.099 | 15.122 |
| 1900 | 112.131 | 261.647 | 185.558 | 144.568 | −922.016 | −498.679 | 13.710 |
| 2000 | 115.060 | 267.473 | 189.509 | 155.928 | −916.586 | −476.537 | 12.446 |

PREVIOUS: CURRENT: June 1970

$S°(298.15\ K)$ = [123.868] $J·K^{-1}·mol^{-1}$
$T_{fus}$ = 1045 K

$\Delta_f H°(298.15\ K)$ = [−774.094] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 28.543 ± 0.8 $kJ·mol^{-1}$

## Enthalpy of Formation

The enthalpy of formation is calculated from that of the crystal by adding the enthalpy of melting and the difference in enthalpy, $H°(1045\ K)–H°(298.15\ K)$, between the crystal and the liquid.

## Heat Capacity and Entropy

The constant heat capacity above the assumed glass transition at 700 K is derived from high temperature enthalpy data in a drop calorimeter from the melting point up to 1667 K by Moore.[1] Below the glass transition point, the heat capacity is assumed to be the same as that of the crystal. Dworkin and Bredig[2] reported $C_p°(l)$ = 23.6 $cal·K^{-1}·mol^{-1}$ from enthalpy measurements in a short temperature range by drop calorimetry.

$S°(298.15\ K)$ 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

The boiling point, $T_{vap}$, is calculated as the temperature at which $\Delta_r G = 0$ for $CaCl_2(l) \rightarrow CaCl_2(g)$ at one bar. The enthalpy of vaporization is the difference in $\Delta_f H°$ at $T_{vap}$ between liquid and gas.

## References

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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 | 72.856 | 123.868 | 123.868 | 0. | −774.094 | −732.115 | 128.264 |
| 300 | 72.927 | 124.319 | 123.869 | 0.135 | −774.070 | −731.855 | 127.427 |
| 400 | 75.647 | 145.714 | 126.768 | 7.578 | −772.732 | −717.983 | 93.759 |
| 500 | 77.153 | 162.768 | 132.320 | 15.224 | −771.423 | −704.449 | 73.593 |
| 600 | 78.199 | 176.929 | 138.608 | 22.992 | −770.229 | −691.169 | 60.172 |
| 700 | 79.370 | 189.067 | 144.970 | 30.868 | −769.164 | −678.078 | 50.599 |
| 700.000 | 79.370 | 189.067 | 144.970 | 30.868 | ____ GLASS <--> LIQUID ____ | | |
| 700.000 | 102.533 | 189.067 | 144.970 | 30.868 | TRANSITION | | |
| 800 | 102.533 | 202.759 | 151.357 | 41.121 | −766.804 | −665.184 | 43.432 |
| 900 | 102.533 | 214.835 | 157.752 | 51.375 | −763.797 | −652.665 | 37.880 |
| 1000 | 102.533 | 225.638 | 164.010 | 61.628 | −761.101 | −640.465 | 33.454 |
| 1045.000 | 102.533 | 230.151 | 166.762 | 66.242 | --- CRYSTAL <--> LIQUID --- | | |
| 1100 | 102.533 | 235.411 | 170.064 | 71.881 | −758.720 | −628.519 | 29.846 |
| 1200 | 102.533 | 244.332 | 175.887 | 82.135 | −764.389 | −616.153 | 26.820 |
| 1300 | 102.533 | 252.539 | 181.472 | 92.388 | −761.408 | −603.921 | 24.266 |
| 1400 | 102.533 | 260.138 | 186.822 | 102.641 | −758.436 | −591.918 | 22.085 |
| 1500 | 102.533 | 267.212 | 191.949 | 112.895 | −755.474 | −580.128 | 20.202 |
| 1600 | 102.533 | 273.829 | 196.862 | 123.148 | −752.520 | −568.534 | 18.561 |
| 1700 | 102.533 | 280.045 | 201.574 | 133.401 | −749.576 | −557.126 | 17.118 |
| 1800 | 102.533 | 285.906 | 206.098 | 143.655 | −895.314 | −543.679 | 15.777 |
| 1900 | 102.533 | 291.449 | 210.445 | 153.908 | −890.974 | −524.262 | 14.413 |
| 2000 | 102.533 | 296.709 | 214.628 | 164.161 | −886.650 | −505.073 | 13.191 |
| 2100 | 102.533 | 301.711 | 218.657 | 174.415 | −882.345 | −486.100 | 12.091 |
| 2200 | 102.533 | 306.481 | 222.541 | 184.668 | −878.063 | −467.332 | 11.096 |
| 2300 | 102.533 | 311.039 | 226.291 | 194.921 | −873.809 | −448.758 | 10.192 |
| 2400 | 102.533 | 315.403 | 229.913 | 205.174 | −869.590 | −430.368 | 9.367 |
| 2500 | 102.533 | 319.588 | 233.417 | 215.428 | −865.410 | −412.153 | 8.611 |
| 2600 | 102.533 | 323.610 | 236.809 | 225.681 | −861.279 | −394.104 | 7.918 |
| 2700 | 102.533 | 327.479 | 240.096 | 235.934 | −857.203 | −376.214 | 7.278 |
| 2800 | 102.533 | 331.208 | 243.284 | 246.188 | −853.189 | −358.473 | 6.687 |
| 2900 | 102.533 | 334.806 | 246.378 | 256.441 | −849.247 | −340.874 | 6.140 |
| 3000 | 102.533 | 338.282 | 249.384 | 266.694 | −845.384 | −323.410 | 5.631 |

PREVIOUS: CURRENT: June 1970

0 to 1045 K crystal
above 1045 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 | −15.391 | −796.270 | −796.270 | INFINITE |
| 100 | 48.812 | 35.596 | 164.875 | −12.928 | −797.700 | −780.762 | 407.828 |
| 200 | 67.357 | 76.550 | 111.119 | −6.914 | −796.992 | −764.012 | 199.539 |
| 298.15 | 72.856 | 104.602 | 104.602 | 0. | −795.797 | −748.073 | 131.059 |
| 300 | 72.927 | 105.053 | 104.603 | 0.135 | −795.773 | −747.777 | 130.200 |
| 400 | 75.647 | 126.448 | 107.502 | 7.578 | −794.434 | −731.979 | 95.587 |
| 500 | 77.153 | 143.502 | 113.054 | 15.224 | −793.125 | −716.519 | 74.854 |
| 600 | 78.199 | 157.663 | 119.342 | 22.992 | −791.931 | −701.312 | 61.055 |
| 700 | 79.370 | 169.801 | 125.704 | 30.868 | −790.866 | −686.294 | 51.212 |
| 800 | 80.919 | 180.495 | 131.897 | 38.878 | −790.750 | −671.318 | 43.833 |
| 900 | 83.094 | 190.145 | 137.841 | 47.074 | −789.800 | −656.447 | 38.099 |
| 1000 | 85.772 | 199.033 | 143.521 | 55.512 | −788.919 | −641.678 | 33.518 |
| 1045.000 | 87.090 | 202.837 | 145.994 | 59.401 | CRYSTAL <--> LIQUID | | |
| 1045.000 | 102.533 | 230.151 | 145.994 | 87.944 | TRANSITION | | |
| 1100 | 102.533 | 235.411 | 150.335 | 93.584 | −758.720 | −628.519 | 29.846 |
| 1200 | 102.533 | 244.332 | 157.801 | 103.837 | −764.389 | −616.153 | 26.820 |
| 1300 | 102.533 | 252.539 | 164.777 | 114.090 | −761.408 | −603.921 | 24.266 |
| 1400 | 102.533 | 260.138 | 171.321 | 124.344 | −758.436 | −591.918 | 22.085 |
| 1500 | 102.533 | 267.212 | 177.480 | 134.597 | −755.474 | −580.128 | 20.202 |
| 1600 | 102.533 | 273.829 | 183.298 | 144.850 | −752.520 | −568.534 | 18.561 |
| 1700 | 102.533 | 280.045 | 188.808 | 155 104 | −749.576 | −557.126 | 17.118 |
| 1800 | 102.533 | 285.906 | 194.041 | 165.357 | −895.314 | −543.679 | 15.777 |
| 1900 | 102.533 | 291.449 | 199.023 | 175.610 | −890.974 | −524.262 | 14.413 |
| 2000 | 102.533 | 296.709 | 203.777 | 185.864 | −886.650 | −505.073 | 13.191 |
| 2100 | 102.533 | 301.711 | 208.322 | 196.117 | −882.345 | −486.100 | 12.091 |
| 2200 | 102.533 | 306.481 | 212.677 | 206.370 | −878.063 | −467.332 | 11.096 |
| 2300 | 102.533 | 311.039 | 216.855 | 216.623 | −873.809 | −448.758 | 10.192 |
| 2400 | 102.533 | 315.403 | 220.871 | 226.877 | −869.590 | −430.368 | 9.367 |
| 2500 | 102.533 | 319.588 | 224.736 | 237.130 | −865.410 | −412.153 | 8.611 |
| 2600 | 102.533 | 323.610 | 228.462 | 247.383 | −861.279 | −394.104 | 7.918 |
| 2700 | 102.533 | 327.479 | 232.058 | 257.637 | −857.202 | −376.214 | 7.278 |
| 2800 | 102.533 | 331.208 | 235.533 | 267.890 | −853.189 | −358.473 | 6.687 |
| 2900 | 102.533 | 334.806 | 238.895 | 278.143 | −849.247 | −340.874 | 6.140 |
| 3000 | 102.533 | 338.282 | 242.150 | 288.397 | −845.384 | −323.410 | 5.631 |

PREVIOUS: CURRENT. June 1970

$S°(298.15\ K) = 290.3 \pm 8\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -471.7 \pm 4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -471.5 \pm 4\ kJ·mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, $cm^{-1}$ |
|---|
| [217](1) |
| 64 (2) |
| 402 (1) |

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distance: Ca–Cl – 2.51 Å
Bond Angle: Cl–Ca–Cl = 180°
Rotational Constant: $B_0 = 0.037737\ cm^{-1}$

## Enthalpy of Formation

2nd and 3rd law analyses of vapor pressure data are given below. The selected 3rd law enthalpy of vaporization is taken from Novikov's measurement[1] as $\Delta_{vap}H°(298.15\ K) = 72.30\ kcal·mol^{-1}$ which is combined with $\Delta_f H°(298.15\ K)$ of the liquid to give $\Delta_f H°(CaCl_2, g, 298.15\ K) = -112.7 \pm 1\ kcal·mol^{-1}$ ($-471.5 \pm 4\ kJ·mol^{-1}$).

3rd law analyses indicate zero dirft for Novikov's data, positive and negative drifts for Hildenbrand's [2] and Bautista's[3] data, respectively. Their enthalpies are in good agreement within ±1 kcal. Wartenberg[4] reported there was no boiling at 1819 K at 62 mm Hg pressure, and his value, $\Delta_{vap}H°(298.15\ K) = 71.1 \pm 0.7\ kcal·mol^{-1}$, serves as a guide for the minimum enthalpy of vaporization.

| Source | Method | T/K | Data Points | $\Delta_{vap}H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law | 3rd law | Drift $cal·K^{-1}·mol^{-1}$ |
|---|---|---|---|---|---|---|
| Bautista and Margrave[3] | Langmuir | 952–993 | 7 | 75.25 (80.34)* | 73.39 (78.57)* | $-1.7 \pm 6.9$ |
| Hildenbrand and Potter[2] | Torsion Effusion 0.0096 $cm^2$ Orifice | 1142–1228 | 12 | 64.99 | 71.24 | $5.3 \pm 0.4$ |
| Hildenbrand and Potter[2] | Torsion Effusion 0.015 $cm^2$ Orifice | 1111–1281 | 17 | 68.71 | 71.24 | $2.0 \pm 0.2$ |
| Hildenbrand and Potter[2] | Torsion Effusion Combined | 1111–1281 | 29 | 68.91 | 71.24 | $2.4 \pm 0.3$ |
| Dewing[5] | Knudsen Effusion | 1069–1225 | 4 | 59.37 | 71.03 | $10.2 \pm 1.6$ |
| Wartenberg and Bosse[4] | Boiling Point | 1819 | 1 | — | >71.10 | — |
| Novikov and Gavryuchenkov[1] | Boiling Point | 1591–1701 | 5 | 72.25 | 72.30 | $0.0 \pm 1.2$ |
| Lukashenko and Reutova[10] | Langmuir | 973–1023 | 6 | 78.0 | 69.01 | −9.0 |
| | Knudsen Effusion | 1073–1273 | 6 | 61.8 | 69.78 | +8.0 |

*Value in parentheses is the enthalpy of sublimation.

## Heat Capacity and Entropy

The linear structure and vibrational frequencies were determined by White and co-workers[6] in the matrix–infrared– spectrometric studies. The linear structure is consistent with experimental error with the electric–quadrupole–deflection studies,[7] and electron–diffraction data.[8] Hayes[9] has qualitatively rationalized the linear structure through molecular orbital theory. The bond length was measured by Akishin and Spiridonov.[8]

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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 | −15.118 | −471.738 | −471.738 | INFINITE |
| 100 | 49.371 | 230.265 | 340.874 | −11.061 | −471.573 | −474.102 | 247.646 |
| 200 | 56.575 | 267.082 | 295.620 | −5.708 | −471.526 | −476.652 | 124.489 |
| 250 | 58.277 | 279.904 | 291.236 | −2.833 | −471.520 | −477.934 | 99.859 |
| 298.15 | 59.325 | 290.265 | 290.265 | 0. | −471.537 | −479.169 | 83.948 |
| 300 | 59.357 | 290.632 | 290.266 | 0.110 | −471.538 | −479.216 | 83.439 |
| 350 | 60.073 | 299.839 | 290.991 | 3.097 | −471.576 | −480.493 | 71.710 |
| 400 | 60.566 | 307.895 | 292.611 | 6.113 | −471.639 | −481.763 | 62.912 |
| 450 | 60.919 | 315.050 | 294.714 | 9.151 | −471.740 | −483.023 | 56.068 |
| 500 | 61.178 | 321.482 | 297.075 | 12.204 | −471.885 | −484.269 | 50.591 |
| 600 | 61.525 | 332.670 | 302.102 | 18.340 | −472.323 | −486.708 | 42.372 |
| 700 | 61.740 | 342.171 | 307.165 | 24.504 | −472.970 | −489.057 | 36.494 |
| 800 | 61.882 | 350.425 | 312.068 | 30.686 | −474.682 | −491.195 | 32.072 |
| 900 | 61.980 | 357.720 | 316.743 | 36.879 | −475.734 | −493.199 | 28.625 |
| 1000 | 62.051 | 364.254 | 321.173 | 43.081 | −477.090 | −495.070 | 25.860 |
| 1100 | 62.104 | 370.171 | 325.363 | 49.289 | −478.755 | −496.790 | 23.591 |
| 1200 | 62.144 | 375.577 | 329.325 | 55.502 | −488.464 | −497.722 | 21.665 |
| 1300 | 62.175 | 380.552 | 333.077 | 61.718 | −489.521 | −498.451 | 20.028 |
| 1400 | 62.200 | 385.161 | 336.635 | 67.936 | −490.584 | −499.098 | 18.622 |
| 1500 | 62.221 | 389.453 | 340.014 | 74.158 | −491.653 | −499.669 | 17.400 |
| 1600 | 62.237 | 393.469 | 343.231 | 80.380 | −492.730 | −500.168 | 16.329 |
| 1700 | 62.251 | 397.242 | 346.298 | 86.605 | −493.814 | −500.600 | 15.382 |
| 1800 | 62.262 | 400.801 | 349.228 | 92.831 | −643.580 | −498.756 | 14.474 |
| 1900 | 62.272 | 404.168 | 352.032 | 99.057 | −643.267 | −490.719 | 13.491 |
| 2000 | 62.281 | 407.362 | 354.719 | 105.285 | −642.969 | −482.698 | 12.607 |
| 2100 | 62.288 | 410.401 | 357.299 | 111.513 | −642.688 | −474.692 | 11.807 |
| 2200 | 62.294 | 413.299 | 359.779 | 117.742 | −642.431 | −466.698 | 11.081 |
| 2300 | 62.299 | 416.068 | 362.167 | 123.972 | −642.201 | −458.715 | 10.418 |
| 2400 | 62.304 | 418.719 | 364.468 | 130.202 | −642.004 | −450.742 | 9.810 |
| 2500 | 62.308 | 421.263 | 366.690 | 136.433 | −641.847 | −442.776 | 9.251 |
| 2600 | 62.312 | 423.707 | 368.836 | 142.664 | −641.738 | −434.816 | 8.736 |
| 2700 | 62.315 | 426.058 | 370.912 | 148.895 | −641.684 | −426.858 | 8.258 |
| 2800 | 62.318 | 428.325 | 372.922 | 155.127 | −641.692 | −418.902 | 7.815 |
| 2900 | 62.321 | 430.512 | 374.871 | 161.359 | −641.771 | −410.944 | 7.402 |
| 3000 | 62.324 | 432.624 | 376.761 | 167.591 | −641.929 | −402.982 | 7.017 |
| 3100 | 62.326 | 434.668 | 378.596 | 173.824 | −642.175 | −395.013 | 6.656 |
| 3200 | 62.328 | 436.647 | 380.379 | 180.056 | −642.514 | −387.035 | 6.318 |
| 3300 | 62.330 | 438.565 | 382.113 | 186.289 | −642.956 | −379.045 | 6.000 |
| 3400 | 62.331 | 440.426 | 383.801 | 192.522 | −643.506 | −371.039 | 5.700 |
| 3500 | 62.333 | 442.232 | 385.445 | 198.756 | −644.172 | −363.016 | 5.418 |
| 3600 | 62.334 | 443.988 | 387.047 | 204.989 | −644.958 | −354.972 | 5.151 |
| 3700 | 62.335 | 445.696 | 388.609 | 211.222 | −645.869 | −346.905 | 4.897 |
| 3800 | 62.337 | 447.359 | 390.133 | 217.456 | −646.910 | −338.811 | 4.657 |
| 3900 | 62.338 | 448.978 | 391.622 | 223.690 | −648.084 | −330.688 | 4.429 |
| 4000 | 62.339 | 450.556 | 393.075 | 229.923 | −649.393 | −322.534 | 4.212 |
| 4100 | 62.340 | 452.095 | 394.496 | 236.157 | −650.838 | −314.344 | 4.005 |
| 4200 | 62.340 | 453.598 | 395.885 | 242.391 | −652.420 | −306.119 | 3.807 |
| 4300 | 62.341 | 455.065 | 397.245 | 248.625 | −654.138 | −297.853 | 3.618 |
| 4400 | 62.342 | 456.498 | 398.575 | 254.860 | −655.989 | −289.547 | 3.437 |
| 4500 | 62.343 | 457.899 | 399.878 | 261.094 | −657.958 | −281.198 | 3.264 |
| 4600 | 62.343 | 459.269 | 401.154 | 267.328 | −660.063 | −272.802 | 3.098 |
| 4700 | 62.344 | 460.610 | 402.405 | 273.563 | −662.296 | −264.360 | 2.938 |
| 4800 | 62.345 | 461.922 | 403.631 | 279.797 | −664.650 | −255.868 | 2.784 |
| 4900 | 62.345 | 463.208 | 404.834 | 286.031 | −667.119 | −247.327 | 2.637 |
| 5000 | 62.346 | 464.467 | 406.014 | 292.266 | −669.696 | −238.734 | 2.494 |
| 5100 | 62.346 | 465.702 | 407.173 | 298.501 | −672.377 | −230.088 | 2.357 |
| 5200 | 62.347 | 466.913 | 408.310 | 304.735 | −675.151 | −221.389 | 2.224 |
| 5300 | 62.347 | 468.100 | 409.427 | 310.970 | −678.018 | −212.636 | 2.096 |
| 5400 | 62.347 | 469.266 | 410.524 | 317.205 | −680.968 | −203.827 | 1.972 |
| 5500 | 62.348 | 470.410 | 411.603 | 323.439 | −683.993 | −194.963 | 1.852 |
| 5600 | 62.348 | 471.533 | 412.663 | 329.674 | −687.077 | −186.045 | 1.735 |
| 5700 | 62.348 | 472.637 | 413.705 | 335.909 | −690.230 | −177.070 | 1.623 |
| 5800 | 62.349 | 473.721 | 414.731 | 342.144 | −693.437 | −168.040 | 1.513 |
| 5900 | 62.349 | 474.787 | 415.740 | 348.379 | −696.690 | −158.953 | 1.407 |
| 6000 | 62.349 | 475.835 | 416.732 | 354.614 | −699.982 | −149.812 | 1.304 |

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = 229.65 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -271 \pm 8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -272 \pm 8\ kJ \cdot mol^{-1}$

| Electronic Levels and Quantum Weights | | |
|---|---|---|
| State | $\epsilon_i$, $cm^{-1}$ | $g_i$ |
| $X^2\Sigma^+$ | 0 | 2 |
| $A^2\Pi$ | 16482 | 2 |
| | 16557 | 2 |
| $B^2\Sigma$ | 18844 | 2 |
| $C^2\Pi$ | 30256 | 2 |
| | 30285 | 2 |
| $D^2\Sigma$ | 30772 | 2 |
| $E^2\Sigma$ | 34135 | 2 |
| $F^2\Pi$ | 37548 | 4 |

$\omega_e = 587.1\ cm^{-1}$ $\omega_e x_e = 2.74\ cm^{-1}$ $\sigma = 1$
$B_e = 0.3225\ cm^{-1}$ $\alpha_e = [0.0020]\ cm^{-1}$ $r_e = 2.01$ Å

## Enthalpy of Formation

Hastie and Margrave[1] have recently reviewed the dissociation energy of CaF and conclude that it is 127.5 ± 2.5 kcal·mol$^{-1}$. The analysis below considers basically the same data except that all values are JANAF.

Hildenbrand and Murad[2] in a mass spectrometric determination of the equilibria among BF, $BF_3$, Ca, CaF and $CaF_2$ reported equilibrium constants for the reaction

(A) $Ca(g) + CaF_2(g) \rightarrow 2CaF(g)$.

Blue *et al.*[3] have also examined several equilibria mass-spectrometrically and report equilibrium constants for reaction

(B) $Ca(g) + CaF_2(cr) \rightarrow 2CaF(g)$ and reaction

(C) $Ca(g) + AlF(g) \rightarrow Al(g) + CaF(g)$.

Ryabova and Gurvich [4] give a enthalpy of dissociation from flame studies for the reaction

(D) $CaF(g) \rightarrow Ca(g) + F(g)$.

The remaining reactions considered by Hastie and Margrave[1] were not included since they involved subtracting reactions not performed simultaneously, or involve species such as $SiF_2$ whose enthalpy of formation is dependent on that of CaF and $CaF_2$.

| Source | T/K | Reaction | Data Points | $\Delta_f H°$(298.15 K), kcal·mol$^{-1}$ 2nd law | 3rd law | Drift cal·K$^{-1}$·mol$^{-1}$ | $\Delta_f H°$(298.15 K) kcal·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| Hildenbrand[2] | 1583–1734 | A | 15 | 11.5 ± 6.8 | 14.70 ± 1.27 | 2.2 ± 4.1 | −65.5 ± 1.8 |
| Blue[3] | 1271–1351 | B | 9 | 146.9 ± 8.0 | 121.08 ± 1.65 | −19.4 ± 6.2 | −64.5 ± 1.7 |
| Blue[3] | 1271–1351 | C | 10* | 34.6 ± 3.5 | 32.87 ± 0.47 | −1.4 ± 2.7 | −65.7 ± 3.2 |
| Ryobova[4] | | D | | 135 ± 7 | | | −73.3 ± 7 |
| Hildenbrand[5] | 1423–1443 | A | 2 | | 32.97 | | −65.6 ± 3.2 |

*1 point rejected due to failure of a statistical test

The auxiliary enthalpies of formation used were, in kcal·mol$^{-1}$, AlF(g) = −63.4, Al(g) = 78, $CaF_2(g)$ = −187.5, $CaF_2$(cr) = −293.0 and Ca(g) = 42.85.

We adopt a median value of $\Delta_f H°$(CaF, g, 298.15 K) = −65 ± 2 kcal·mol$^{-1}$ (−271.960 ± 8 kJ·mol$^{-1}$) which corresponds to an enthalpy of dissociation of 126.7 ± 2 kcal·mol$^{-1}$.

## Heat Capacity and Entropy

Herzberg[6] gives the vibrational constants and electronic levels. Harvey[7] has reported a value for $B_0$ which corresponds to a bond length of 2.02 Å. The Morse potential function was used to calculate $\alpha_e$.

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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 | −9.130 | −270.942 | −270.942 | INFINITE |
| 100 | 29.245 | 195.821 | 258.018 | −6.220 | −270.465 | −279.932 | 146.221 |
| 200 | 31.424 | 216.653 | 232.661 | −3.201 | −271.180 | −289.148 | 75.518 |
| 250 | 32.678 | 223.804 | 230.196 | −1.598 | −271.578 | −293.593 | 61.343 |
| 298.15 | 33.661 | 229 647 | 229.647 | 0. | −271.960 | −297.799 | 52.173 |
| 300 | 33.695 | 229.855 | 229.648 | 0.062 | −271.975 | −297.959 | 51.879 |
| 350 | 34.477 | 235.111 | 230.061 | 1.767 | −272.370 | −302.259 | 45.110 |
| 400 | 35.075 | 239.756 | 230.988 | 3.507 | −272.775 | −306.501 | 40.025 |
| 450 | 35.534 | 243.914 | 232.197 | 5.273 | −273.205 | −310.692 | 36.064 |
| 500 | 35.893 | 247.678 | 233.560 | 7.059 | −273.671 | −314.832 | 32.890 |
| 600 | 36.409 | 254.271 | 236.478 | 10.676 | −274.733 | −322.968 | 28.117 |
| 700 | 36.755 | 259.911 | 239.432 | 14.335 | −275.989 | −330.910 | 24.693 |
| 800 | 37.002 | 264.836 | 242.307 | 18.023 | −278.299 | −338.555 | 22.105 |
| 900 | 37.188 | 269.205 | 245.057 | 21.733 | −279.942 | −345.991 | 20.081 |
| 1000 | 37.335 | 273 131 | 247.672 | 25.460 | −281.881 | −353.229 | 18.451 |
| 1100 | 37.454 | 276.695 | 250.151 | 29.199 | −284.124 | −360.258 | 17.107 |
| 1200 | 37.556 | 279.959 | 252.500 | 32.950 | −294.406 | −366.446 | 15.951 |
| 1300 | 37.644 | 282.968 | 254.730 | 36.710 | −296.031 | −372.384 | 14.963 |
| 1400 | 37.722 | 285.761 | 256.848 | 40.478 | −297.658 | −378.196 | 14.111 |
| 1500 | 37.793 | 288.366 | 258.863 | 44.254 | −299.287 | −383.892 | 13.368 |
| 1600 | 37.860 | 290.807 | 260.784 | 48.037 | −300.919 | −389.479 | 12.715 |
| 1700 | 37.922 | 293.104 | 262.619 | 51.826 | −302.552 | −394.964 | 12.136 |
| 1800 | 37.983 | 295.274 | 264.373 | 55.621 | −452.861 | −398.142 | 11.554 |
| 1900 | 38.043 | 297.329 | 266.054 | 59.423 | −453.082 | −395.096 | 10.862 |
| 2000 | 38.103 | 299.282 | 267.667 | 63.230 | −453.307 | −392.038 | 10.239 |
| 2100 | 38.165 | 301.142 | 269.217 | 67.043 | −453.537 | −388.969 | 9.675 |
| 2200 | 38.230 | 302.919 | 270.709 | 70.863 | −453.772 | −385.889 | 9.162 |
| 2300 | 38.300 | 304.620 | 272.147 | 74.689 | −454.016 | −382.798 | 8.694 |
| 2400 | 38.375 | 306.252 | 273.534 | 78.523 | −454.268 | −379.697 | 8.264 |
| 2500 | 38.457 | 307.820 | 274.874 | 82.364 | −454.533 | −376.584 | 7.868 |
| 2600 | 38.548 | 309.330 | 276.170 | 86.215 | −454.814 | −373.460 | 7.503 |
| 2700 | 38.647 | 310.787 | 277.426 | 90.074 | −455.115 | −370.326 | 7.164 |
| 2800 | 38.757 | 312.194 | 278.642 | 93.944 | −455.440 | −367.180 | 6.850 |
| 2900 | 38.877 | 313.556 | 279.823 | 97.826 | −455.794 | −364.021 | 6.557 |
| 3000 | 39.009 | 314.876 | 280.970 | 101.720 | −456.183 | −360.850 | 6.283 |
| 3100 | 39.153 | 316.158 | 282.084 | 105.628 | −456.612 | −357.666 | 6.027 |
| 3200 | 39.309 | 317.403 | 283.168 | 109.551 | −457.089 | −354.466 | 5.786 |
| 3300 | 39.476 | 318.615 | 284.224 | 113.490 | −457.618 | −351.251 | 5.560 |
| 3400 | 39.657 | 319.797 | 285.253 | 117.447 | −458.207 | −348.019 | 5.347 |
| 3500 | 39.849 | 320.949 | 286.257 | 121.422 | −458.860 | −344.769 | 5.145 |
| 3600 | 40.053 | 322.074 | 287.236 | 125.417 | −459.585 | −341.499 | 4.955 |
| 3700 | 40.269 | 323.175 | 288.193 | 129.433 | −460.387 | −338.208 | 4.775 |
| 3800 | 40.496 | 324.251 | 289.127 | 133.471 | −461.269 | −334.895 | 4.603 |
| 3900 | 40.734 | 325.306 | 290.042 | 137.533 | −462.238 | −331.556 | 4.441 |
| 4000 | 40.982 | 326.341 | 290.936 | 141.619 | −463.297 | −328.192 | 4.286 |
| 4100 | 41.239 | 327.356 | 291.812 | 145.730 | −464.448 | −324.801 | 4.138 |
| 4200 | 41.506 | 328.353 | 292.670 | 149.867 | −465.695 | −321.380 | 3.997 |
| 4300 | 41.781 | 329.333 | 293.512 | 154.031 | −467.038 | −317.928 | 3.862 |
| 4400 | 42.063 | 330.296 | 294.337 | 158.223 | −468.476 | −314.444 | 3.733 |
| 4500 | 42.352 | 331.245 | 295.146 | 162.444 | −469.996 | −310.927 | 3.609 |
| 4600 | 42.648 | 332.179 | 295.941 | 166.694 | −471.619 | −307.375 | 3.490 |
| 4700 | 42.949 | 333.099 | 296.722 | 170.974 | −473.338 | −303.786 | 3.376 |
| 4800 | 43.254 | 334.007 | 297.489 | 175.284 | −475.149 | −300.160 | 3.266 |
| 4900 | 43.564 | 334.902 | 298.244 | 179.625 | −477.046 | −296.495 | 3.161 |
| 5000 | 43.878 | 335.785 | 298.986 | 183.997 | −479.026 | −292.790 | 3.059 |
| 5100 | 44.194 | 336.657 | 299.716 | 188.400 | −481.086 | −289.045 | 2.960 |
| 5200 | 44.512 | 337.518 | 300.435 | 192.835 | −483.215 | −285.259 | 2.865 |
| 5300 | 44.831 | 338.369 | 301.142 | 197.303 | −485.417 | −281.432 | 2.774 |
| 5400 | 45.152 | 339.210 | 301.840 | 201.802 | −487.682 | −277.562 | 2.685 |
| 5500 | 45.473 | 340.042 | 302.527 | 206.333 | −490.004 | −273.649 | 2.599 |
| 5600 | 45.793 | 340.864 | 303.204 | 210.896 | −492.368 | −269.695 | 2.516 |
| 5700 | 46.112 | 341.677 | 303.872 | 215.492 | −494.785 | −265.698 | 2.435 |
| 5800 | 46.430 | 342.482 | 304.531 | 220.119 | −497.242 | −261.657 | 2.356 |
| 5900 | 46.747 | 343.278 | 305.181 | 224.778 | −499.731 | −257.574 | 2.280 |
| 6000 | 47.060 | 344.067 | 305.822 | 229.468 | −502.247 | −253.448 | 2.206 |

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

$S°(298.15\ K) = 68.572 \pm 0.33\ J·K^{-1}·mol^{-1}$
$T_{trs} = 1424 \pm 20\ K\ (\alpha-\beta)$
$T_{fus} = 1691 \pm 5\ K$

$\Delta_f H°(0\ K) = -1223.0 \pm 6.3\ kJ\ mol^{-1}$
$\Delta_f H°(298.15\ K) = -1225.9 \pm 6.3\ kJ·mol^{-1}$
$\Delta_{trs} H° = 4.770 \pm 0.4\ kJ·mol^{-1}$
$\Delta_{fus} H° = 29.706 \pm 0.4\ kJ·mol^{-1}$

## Enthalpy of Formation

Torgeson and Sahama[1] measured the enthalpy of solution of CaO in aqueous 20.1% HF as $-54.96 \pm 0.02$ kcal·mol$^{-1}$. Using $\Delta_f H°$(CaO, cr, 298.15 K) = $-151.79$ kcal·mol$^{-1}$,[2] $\Delta_f H°(H_2O, l, 298.15\ K) = -68.317$ kcal·mol$^{-1}$ [3] and $\Delta_f H°$(HF4 4$H_2O$, 298.15 K) = $-76.60$ kcal·mol$^{-1}$, we obtain $\Delta_f H°(CaF_2, cr, 298.15\ K) = -291.6 \pm 0.6$ kcal·mol$^{-1}$.

Smyshlyaev and Edeleva[5] report the solubility product of $CaF_2$ as $2.7 \pm 0.27 \times 10^{-11}$ in dilute HCl, which yields $\Delta G°(298.15\ K) = 14.42$ kcal·mol$^{-1}$ for the reaction $CaF_2(cr) \rightarrow Ca^{++}(aq, \infty) + 2F^-(aq, \infty)$. Using $\Delta_f G°(Ca^{++}, aq, \infty, 298.15\ K) = -132.30$ kcal·mol$^{-1}$ [2] and $\Delta_f G°(F^-, aq, \infty, 298.15\ K) = -66.95$ kcal·mol$^{-1}$ [4] we obtain $\Delta_f G°(CaF_2, cr, 298.15\ K) = -280.64 \pm 0.6$ kcal·mol$^{-1}$, which, using the adopted functions, yields $\Delta_f H°(CaF_2, cr, 298.15\ K) = -293.1 \pm 0.6$ kcal·mol$^{-1}$.

Vecher and Vecher[17] have measured the emf of a high temperature solid state cell and report $\Delta_r G°(1200) = -17.6 \pm 0.2$ kcal·mol$^{-1}$ for the reaction $CaO(cr) + MgF_2(cr) \rightarrow CaF_2(cr) + MgO(cr)$. This reduces to $\Delta_r H°(298.15\ K) = -17.6$ kcal·mol$^{-1}$, using JANAF values for MgO and $MgF_2$ and CaO from reference 2, yields $\Delta_f H°(CaF_2, cr, 298.15\ K) = -294.4 \pm 1.3$ kcal·mol$^{-1}$.

Kohlrausch[18] reported the solubility of $CaF_2$ and fluorspar, which yield solubility products of $3.6 \times 10^{-11}$ and $2.8 \times 10^{-11}$ From these we obtain, as above, $\Delta_f H°(CaF_2, cr, 298.15\ K) = -292.9$ and $-293.1$ kcal·mol$^{-1}$.

Guntz[19] made measurements on the neutralization of $Ca(OH)_2$(aq) and HF(aq) which yield $\Delta_f H°(CaF_2, cr, 298.15\ K) = -293.1$ kcal·mol$^{-1}$, according to Parker.[2]

A median value of $\Delta_f H°(CaF_2, cr, 298.15\ K) = -293 \pm 1.5$ kcal·mol$^{-1}$ ($-1225.912 \pm 6.3$ kJ·mol$^{-1}$) is adopted.

## Heat Capacity and Entropy

Huffman and Norwood[6] have measured the low temperature heat capacity in the range 3.6 to 30 K, Eucken and Schwers[7] in the range 17 to 86 K and Todd[8] from 54 to 296.5 K. We have fitted a smooth polynomial curve through the data of references 6 and 8 and this yields $S°(298.15\ K) = 16.38 \pm 0.08$ cal·K$^{-1}$·mol$^{-1}$ based on $S°(3.6\ K) = 0.0002$ cal·K$^{-1}$·mol$^{-1}$. The values of reference 7 deviate considerably at the lowest temperatures but are in reasonable agreement at higher temperatures.

The high temperature enthalpy of calcium fluoride has been reported by Naylor[9] to 1789 K, Krestnikov and Karetnikov[10] to 1273 K, and Lyashenko[11] to 1490 K. All the data are in approximate agreement and the more extensive results of Naylor on a very pure sample are adopted. The heat capacities, below 1424 K, were derived from a polynomial fit of the enthalpy data of the form $H = aT^2 + bT + c + d/T + e/T^2$.

## Transition Data

The temperature of transition is that reported by Naylor,[9] the large uncertainty has been assigned since at 1424 K the enthalpies indicate complete conversion to β–$CaF_2$, and the next lower point is at 1402 K. Evidence in support of a transition in this region comes from Lyashenko[11] whose plot indicates a break between 1273 and 1413 K. In addition, $SrCl_2$ which has the fluorite structure has a transition near the melting point. The enthalpy of transition is that reported by Naylor.[9]

## Fusion Data

McCreary[12] reports the melting point of a 99.1% pure sample as $1687 \pm 5$ K. Porter and Brown[13] report $1675 \pm 5$ K as the melting point of 99.8% pure $CaF_2$ and Rogers *et al.*[14] obtained 1684 K as the melting point. The adopted melting point, $1691 \pm 5$ K, for a sample of natural fluorite of high purity, was reported by Naylor.[9] The enthalpy of melting, 7100 kcal·mol$^{-1}$ (29.706 kJ m\uccircol$^{-1}$), is that measured by Naylor.[9] Three determinations from high temperature phase diagrams give $7250 \pm 350$ cal·mol$^{-1}$,[15] 5500 cal·mol$^{-1}$,[16] and 9800 cal·mol$^{-1}$.[14]

## Sublimation Data

Refer to the ideal gas table for details.

## References


[1] D. R. Torgeson and T. G. Sahama, J. Amer. Chem. Soc. 70, 2156 (1948).
[2] V. B. Parker, Nat. Bur. Stand., personal communication, (January 1969).
[3] U. S. Nat. Bur. Stand. Tech. Note 270–3, 264 pp. (1968).
[4] Consistent with the JANAF HF(g) value.
[5] S. I Smyshlaev and N. P. Edeleva, Izv. Vysshykh Uchebn. Zavedenii, Khim. i Khim. Tekhol. 5, 871 (1962).
[6] D. R. Huffman and M. H. Norwood, Phys. Rev. 117, 709 (1960).
[7] A. Eucken and F. Schwers, Ber. Deut. Physik. Ges. 15, 578 (1913).
[8] S. S. Todd, J. Amer. Chem. Soc. 71, 4115 (1949).
[9] B. F. Naylor, J. Amer. Chem. Soc. 67, 150 (1945).
[10] A N. Krestnikov and G. A. Karetnikov, Legkie Metal. 3, 29 (1934) and 4, 16 (1935).
[11] V. S. Lyashenko, Metallurg. 10, 85 (1935).


Continued on page 736

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 | −11.655 | −1223.006 | −1223.006 | INFINITE |
| 100 | 28.619 | 13.347 | 120.374 | −10.703 | −1225.941 | −1208.642 | 631.330 |
| 200 | 56.769 | 43.555 | 74.450 | −6.179 | −1226.615 | −1190.898 | 311.031 |
| 298.15 | 68.588 | 68.572 | 68.572 | 0. | −1225.912 | −1173.496 | 205.592 |
| 300 | 68.772 | 68.997 | 68.574 | 0.127 | −1225.891 | −1173.171 | 204.267 |
| 400 | 73.864 | 89.630 | 71.353 | 7.311 | −1224.561 | −1155.791 | 150.931 |
| 500 | 76.220 | 106.375 | 76.736 | 14.819 | −1223.184 | −1138.759 | 118.965 |
| 600 | 78.517 | 120.471 | 82.880 | 22.554 | −1221.865 | −1121.999 | 97.679 |
| 700 | 81.090 | 132.764 | 89.146 | 30.532 | −1220.577 | −1105.456 | 82.490 |
| 800 | 83.918 | 143.774 | 95.298 | 38.781 | −1220.132 | −1088.995 | 71.104 |
| 900 | 86.952 | 153.832 | 101.251 | 47.323 | −1218.769 | −1072.684 | 62.257 |
| 1000 | 90.128 | 163.157 | 106.981 | 56.177 | −1217.427 | −1056.525 | 55.187 |
| 1100 | 93.412 | 171.901 | 112.489 | 65.353 | −1216.093 | −1040.499 | 49.409 |
| 1200 | 96.780 | 180.172 | 117.788 | 74.862 | −1222.490 | −1023.973 | 44.572 |
| 1300 | 100.207 | 188.054 | 122.892 | 84.711 | −1219.910 | −1007.532 | 40.483 |
| 1400 | 103.680 | 195.607 | 127.818 | 94.905 | −1217.007 | −991.302 | 36.986 |
| 1424.000 | 104.520 | 197.376 | 128.975 | 97.403 | ALPHA <--> BETA | | |
| 1424 000 | 122 .884 | 200.726 | 128.975 | 102.173 | TRANSITION | | |
| 1500 | 123.679 | 207.136 | 132.774 | 111.542 | −1207.680 | −975.581 | 33.973 |
| 1600 | 124.725 | 215.151 | 137.675 | 123.963 | −1202.588 | −960.273 | 31.350 |
| 1691.000 | 125.677 | 222.077 | 142.032 | 135.356 | ---- BETA <--> LIQUID ---- | | |
| 1700 | 125.771 | 222.744 | 142.457 | 136.487 | −1197.409 | −945.287 | 29.045 |
| 1800 | 126 817 | 229.962 | 147.120 | 149.117 | −1340.813 | −928.397 | 26.941 |
| 1900 | 127.863 | 236.847 | 151.663 | 161.851 | −1334.037 | −905.669 | 24.899 |
| 2000 | 128.909 | 243.432 | 156.088 | 174.689 | −1327.172 | −883.301 | 23.069 |
| 2100 | 129.955 | 249.747 | 160.398 | 187.633 | −1320.215 | −861.278 | 21.423 |
| 2200 | 131.001 | 255.817 | 164.598 | 200.680 | −1313.168 | −839.589 | 19.934 |
| 2300 | 132.047 | 261.663 | 168.692 | 213.833 | −1306.029 | −818.222 | 18.582 |
| 2400 | 133.093 | 267.305 | 172.684 | 227.090 | −1298.800 | −797.167 | 17.350 |
| 2500 | 134.139 | 272.759 | 176.579 | 240.451 | −1291.482 | −776.416 | 16.222 |
| 2600 | 135.185 | 278.041 | 180.380 | 253.918 | −1284.078 | −755.959 | 15.187 |
| 2700 | 136.231 | 283.162 | 184.092 | 267.488 | −1276.591 | −735.789 | 14.235 |

PREVIOUS: CURRENT December 1968

$S°(298.15\ K) = [92.573]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1691 \pm 5\ K$

$\Delta_f H°(298.15\ K) = [-1186.067]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 29.706 \pm 0.4\ kJ·mol^{-1}$

### Enthalpy of Formation

$\Delta_f H°(CaF_2, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and difference in enthalpy, $H°(1691\ K)-H°(298.15\ K)$, between the crystal and liquid.

### Heat Capacity and Entropy

The heat capacity is derived from the enthalpy measurements of Naylor.[1] The heat capacity is constant in the real liquid range but at 1000 K a glass transition is assumed below which it follows that of the crystal. The entropy 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

The boiling point, $T_{vap}$, is calculated as the temperature at which the fugacity of $CaF_2(g)$ is one bar for the process $CaF_2(l) = CaF_2(g)$. The enthalpy of vaporization is the difference in $\Delta_f H°$ at $T_{vap}$ between the liquid and gas.

### Reference

[1]B. F. Naylor, J. Amer. Chem. Soc. 67, 150 (1945).

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 | 68.588 | 92.573 | 92.573 | 0. | −1186.067 | −1140.806 | 199.864 |
| 300 | 68.772 | 92.998 | 92.574 | 0.127 | −1186.045 | −1140.525 | 198.583 |
| 400 | 73.864 | 113.631 | 95.353 | 7.311 | −1184.716 | −1125.546 | 146.981 |
| 500 | 76.220 | 130.375 | 100.736 | 14.819 | −1183.338 | −1110.914 | 116.056 |
| 600 | 78.517 | 144.471 | 106.881 | 22.554 | −1182.019 | −1096.553 | 95.463 |
| 700 | 81.090 | 156.764 | 113.147 | 30.532 | −1180.732 | −1082.411 | 80.771 |
| 800 | 83.918 | 167.775 | 119.298 | 38.781 | −1180.286 | −1068.349 | 69.756 |
| 900 | 86.952 | 177.833 | 125.251 | 47.323 | −1178.924 | −1054.439 | 61.198 |
| 1000 | 90.128 | 187.157 | 130.981 | 56.176 | −1177.581 | −1040.680 | 54.360 |
| 1000.000 | 90.128 | 187.157 | 130.981 | 56.176 | GLASS <--> LIQUID | | |
| 1000.000 | 99.914 | 187.157 | 130.981 | 56.176 | TRANSITION | | |
| 1100 | 99.914 | 196.680 | 136.528 | 66.168 | −1175.433 | −1027.096 | 48.773 |
| 1200 | 99.914 | 205.374 | 141.908 | 76.159 | −1181.347 | −1013.072 | 44.098 |
| 1300 | 99.914 | 213.371 | 147.101 | 86.150 | −1178.625 | −999.159 | 40.147 |
| 1400 | 99.914 | 220.775 | 152.103 | 96.142 | −1175.924 | −985.456 | 36.768 |
| 1500 | 99.914 | 227.669 | 156.913 | 106.133 | −1173.243 | −971.944 | 33.846 |
| 1600 | 99.914 | 234.117 | 161.539 | 116.125 | −1170.581 | −958.611 | 31.295 |
| 1691.000 | 99.914 | 239.644 | 165.595 | 125.217 | ---- BETA <--> LIQUID ---- | | |
| 1700 | 99.914 | 240.174 | 165.988 | 126.116 | −1167.935 | −945.444 | 29.050 |
| 1800 | 99.914 | 245.885 | 170.270 | 136.107 | −1313.977 | −930.222 | 26.994 |
| 1900 | 99.914 | 251.287 | 174.393 | 146.099 | −1309.944 | −909.012 | 24.990 |
| 2000 | 99.914 | 256.412 | 178.367 | 156.090 | −1305.925 | −888.014 | 23.193 |
| 2100 | 99.914 | 261.287 | 182.201 | 166.082 | −1301.921 | −867.217 | 21.571 |
| 2200 | 99.914 | 265.935 | 185.902 | 176.073 | −1297.929 | −846.611 | 20.101 |
| 2300 | 99.914 | 270.376 | 189.479 | 186.064 | −1293.952 | −826.185 | 18.763 |
| 2400 | 99.914 | 274.629 | 192.939 | 196.056 | −1289.988 | −805.933 | 17.541 |
| 2500 | 99.914 | 278.707 | 196.289 | 206.047 | −1286.041 | −785.845 | 16.419 |
| 2600 | 99.914 | 282.626 | 199.534 | 216.038 | −1282.112 | −765.915 | 15.387 |
| 2700 | 99.914 | 286.397 | 202.682 | 226.030 | −1278.204 | −746.135 | 14.435 |
| 2800 | 99.914 | 290.031 | 205.737 | 236.021 | −1274.321 | −726.500 | 13.553 |
| 2900 | 99.914 | 293.537 | 208.705 | 246.013 | −1270.468 | −707.003 | 12.735 |
| 3000 | 99.914 | 296.924 | 211.589 | 256.004 | −1266.651 | −687.639 | 11.973 |
| 3100 | 99.914 | 300.200 | 214.395 | 265.995 | −1262.874 | −668.401 | 11.262 |
| 3200 | 99.914 | 303.372 | 217.126 | 275.987 | −1259.145 | −649.284 | 10.598 |
| 3300 | 99.914 | 306.447 | 219.787 | 285.978 | −1255.470 | −630.282 | 9.977 |
| 3400 | 99.914 | 309.429 | 222.380 | 295.970 | −1251.856 | −611.392 | 9.393 |
| 3500 | 99.914 | 312.326 | 224.908 | 305.961 | −1248.310 | −592.606 | 8.844 |
| 3600 | 99.914 | 315.140 | 227.376 | 315.952 | −1244.837 | −573.921 | 8.327 |
| 3700 | 99.914 | 317.878 | 229.785 | 325.944 | −1241.446 | −555.331 | 7.840 |
| 3800 | 99.914 | 320.542 | 232.138 | 335.935 | −1238.141 | −536.833 | 7.379 |
| 3900 | 99.914 | 323.138 | 234.439 | 345.927 | −1234.928 | −518.419 | 6.943 |
| 4000 | 99.914 | 325.667 | 236.688 | 355.918 | −1231.812 | −500.087 | 6.530 |

PREVIOUS: CURRENT: December 1968

| | | | |
|---|---|---|---|
| 0 | to 1424 | K | crystal, alpha |
| 1424 | to 1691 | K | crystal, beta |
| above | 1691 | 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 | −11.655 | −1223.006 | −1223.006 | INFINITE |
| 100 | 28.619 | 13.347 | 120.374 | −10.703 | −1225.941 | −1208.642 | 631.330 |
| 200 | 56.769 | 43.555 | 74.450 | −6.179 | −1226.615 | −1190.898 | 311.031 |
| 298.15 | 68.588 | 68.572 | 68.572 | 0. | −1225.912 | −1173.496 | 205.592 |
| 300 | 68.772 | 68.997 | 68.574 | 0.127 | −1225.891 | −1173.171 | 204.267 |
| 400 | 73.864 | 89.630 | 71.353 | 7.311 | −1224.561 | −1155.791 | 150.931 |
| 500 | 76.220 | 106.375 | 76.736 | 14.819 | −1223.184 | −1138.759 | 118.965 |
| 600 | 78.517 | 120.471 | 82.880 | 22.554 | −1221.865 | −1121.999 | 97.679 |
| 700 | 81.090 | 132.764 | 89.146 | 30.532 | −1220.577 | −1105.456 | 82.490 |
| 800 | 83.918 | 143.774 | 95.298 | 38.781 | −1220.132 | −1088.995 | 71.104 |
| 900 | 86.952 | 153.832 | 101.251 | 47.323 | −1218.769 | −1072.684 | 62.257 |
| 1000 | 90.128 | 163.157 | 106.981 | 56.177 | −1217.427 | −1056.525 | 55.187 |
| 1100 | 93.412 | 171.901 | 112.489 | 65.353 | −1216.093 | −1040.499 | 49.409 |
| 1200 | 96.780 | 180.172 | 117.788 | 74.862 | −1222.490 | −1023.973 | 44.572 |
| 1300 | 100.207 | 188.054 | 122.892 | 84.711 | −1219.910 | −1007.532 | 40.483 |
| 1400 | 103.680 | 195.607 | 127.818 | 94.905 | −1217.007 | −991.302 | 36.986 |
| 1424.000 | 104.520 | 197.376 | 128.975 | 97.403 | ALPHA <--> BETA TRANSITION | | |
| 1424.000 | 122.884 | 200.726 | 128.975 | 102.173 | | | |
| 1500 | 123.679 | 207.136 | 132.774 | 111.542 | −1207.680 | −975.581 | 33.973 |
| 1600 | 124.725 | 215.151 | 137.675 | 123.963 | −1202.588 | −960.273 | 31.350 |
| 1691.000 | 125.677 | 222.077 | 142.032 | 135.356 | BETA <--> LIQUID TRANSITION | | |
| 1691.000 | 99.914 | 239.644 | 142.032 | 165.062 | | | |
| 1700 | 99.914 | 240.174 | 142.550 | 165.961 | −1167.935 | −945.444 | 29.050 |
| 1800 | 99.914 | 245.885 | 148.134 | 175.953 | −1313.977 | −930.222 | 26.994 |
| 1900 | 99.914 | 251.287 | 153.422 | 185.944 | −1309.944 | −909.012 | 24.990 |
| 2000 | 99.914 | 256.412 | 158.444 | 195.936 | −1305.925 | −888.014 | 23.193 |
| 2100 | 99.914 | 261.287 | 163.227 | 205.927 | −1301.921 | −867.217 | 21.571 |
| 2200 | 99.914 | 265.935 | 167.790 | 215.918 | −1297.929 | −846.611 | 20.101 |
| 2300 | 99.914 | 270.376 | 172.155 | 225.910 | −1293.952 | −826.185 | 18.763 |
| 2400 | 99.914 | 274.629 | 176.337 | 235.901 | −1289.988 | −805.933 | 17.541 |
| 2500 | 99.914 | 278.707 | 180.350 | 245.893 | −1286.041 | −785.845 | 16.419 |
| 2600 | 99.914 | 282.626 | 184.209 | 255.884 | −1282.112 | −765.915 | 15.387 |
| 2700 | 99.914 | 286.397 | 187.925 | 265.875 | −1278.204 | −746.135 | 14.435 |
| 2800 | 99.914 | 290.031 | 191.507 | 275.867 | −1274.321 | −726.500 | 13.553 |
| 2900 | 99.914 | 293.537 | 194.965 | 285.858 | −1270.468 | −707.003 | 12.735 |
| 3000 | 99.914 | 296.924 | 198.307 | 295.850 | −1266.651 | −687.639 | 11.973 |
| 3100 | 99.914 | 300.200 | 201.542 | 305.841 | −1262.874 | −668.401 | 11.262 |
| 3200 | 99.914 | 303.372 | 204.675 | 315.832 | −1259.145 | −649.284 | 10.598 |
| 3300 | 99.914 | 306.447 | 207.712 | 325.824 | −1255.470 | −630.282 | 9.977 |
| 3400 | 99.914 | 309.429 | 210.660 | 335.815 | −1251.856 | −611.392 | 9.393 |
| 3500 | 99.914 | 312.326 | 213.524 | 345.807 | −1248.310 | −592.606 | 8.844 |
| 3600 | 99.914 | 315.140 | 216.308 | 355.798 | −1244.837 | −573.921 | 8.327 |
| 3700 | 99.914 | 317.878 | 219.016 | 365.789 | −1241.446 | −555.331 | 7.840 |
| 3800 | 99.914 | 320.542 | 221.653 | 375.781 | −1238.141 | −536.833 | 7.379 |
| 3900 | 99.914 | 323.138 | 224.222 | 385.772 | −1234.928 | −518.419 | 6.943 |
| 4000 | 99.914 | 325.667 | 226.726 | 395.763 | −1231.812 | −500.087 | 6.530 |

PREVIOUS. CURRENT. December 1968

$S°(298.15\ K) = 273.80 \pm 2.1\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -782.6 \pm 8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -784.5 \pm 8\ kJ·mol^{-1}$

| Vibrational Frequencies and Degeneracies $\upsilon$, $cm^{-1}$ |
|---|
| 484 (1) |
| 163 (1) |
| 554 (1) |

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: $C_{2v}$
Bond Distance: Ca–F = 2.1 Å
Bond Angle: F–Ca–F = 135 ± 7°
Product of the Moments of Inertia. $I_A I_B I_C = 1.283897 \times 10^{-114}\ g^3\ cm^6$

## Enthalpy of Formation

The enthalpy of formation is obtained from that of the crystal by adding $\Delta_{sub}H°(298.15\ K)$. The vapor pressure data of five authors are analyzed by 2nd and 3rd law methods to give $\Delta_{sub}H°(298.15\ K)$ as listed below. Note that the drifts are small and both positive and negative confirming the correctness of the functions used.

| Reference | T/K | Data Points | $\Delta_{sub}H°(298.15\ K)$, kcal·mol$^{-1}$ 2nd law | 3rd law | Drift cal·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| Freeman[1] | 1463–1668 | 9 | 106.2 ± 3.7 | 105.66 ± 0.9 | −0.2 ± 2.3 |
| Blue *et al.*[2] | 1246–1498 | 6 | 99.6 ± 2.5 | 106.00 ± 1.0 | 4.1 ± 2.0 |
| Schulz and Searcy[3] | 1421–1689 | 34 | 102.4 ± 0.3 | 104.00 ± 0.2 | 1.0 ± 0.2 |
| Pottie[4] | 1823 | 1 | 106.4 | | |
| Ruff and LeBoucher[5] | 2086–2208 | 7 | 106.7 ± 4.8 | 105.22 ± 0.5 | −0.7 ± 2.2 |
| Blue *et al.*[2]* | 1242–1669 | 19 | 104.7 ± 0.5 | | |

*This set was not analyzed by the 3rd law since the absolute pressures were adjusted by the authors to match their weight loss values.

A median value of 105.5 ± 0.5 kcal·mol$^{-1}$ (441.412 ± 2.1 kJ·mol$^{-1}$) is adopted for the enthalpy of sublimation which yields $\Delta_f H°(CaF_2, g, 298.15\ K) = -187.5 \pm 2$ kcal·mol$^{-1}$ (−784.5 ± 8 kJ·mol$^{-1}$).

## Heat Capacity and Entropy

The bond length was measured by Aksihin and Spiridonov,[6] but the diffraction patterns were interpreted as indicating a linear molecule. The vibrational frequencies and bond angle are those reported by Calder[7] using matrix isolation spectroscopy and isotopically enriched materials.

The principal moments of inertia are: $I_A = 2.0918 \times 10^{-39}$, $I_B = 23.7505 \times 10^{-39}$, and $I_C = 25.8423 \times 10^{-39}\ g·cm^2$.

## References


[1]R. D. Freeman, Tech. Doc. Rept. ASD TDR 63–754, Part II, Oklahoma State University, (1965).
[2]G. D. Blue, J. W. Green, R. G. Bautista and J. L. Margrave, J. Phys. Chem. 67, 877 (1963).
[3]D. A. Schulz and A. W Searcy, J. Phys. Chem. 67, 103 (1963).
[4]R. W. Pottie, quoted by Freeman.[1]
[5]O. Ruff and L. LeBoucher, Z. Anorg. Chem. 219, 376 (1934).
[6]P. A. Akishin and V. P. Spiridonov, Kristallografiya, 2, 475 (1957).
[7]G. V. Calder, Nat. Bur. Stand. Rept. 9389, 253 pp. (July 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 | 0. | 0. | INFINITE | −12.658 | −782.596 | −782.596 | INFINITE |
| 100 | 39.182 | 224.769 | 315.945 | −9.118 | −782.944 | −786.787 | 410 975 |
| 200 | 46.529 | 254.242 | 278.356 | −4.823 | −783.847 | −790.267 | 206.397 |
| 250 | 49.301 | 264.937 | 274.632 | −2.424 | −784.200 | −791.830 | 165.444 |
| 298.15 | 51.267 | 273.798 | 273.798 | 0. | −784.500 | −793.272 | 138.978 |
| 300 | 51.331 | 274.115 | 273.799 | 0.095 | −784.511 | −793.326 | 138.130 |
| 350 | 52.798 | 282.144 | 274.430 | 2.700 | −784.801 | −794.772 | 118.613 |
| 400 | 53.870 | 289.268 | 275.848 | 5.368 | −785.092 | −796.177 | 103.970 |
| 450 | 54.666 | 295.661 | 277.700 | 8.082 | −785.407 | −797.544 | 92.577 |
| 500 | 55.269 | 301.454 | 279.791 | 10.832 | −785.760 | −798.874 | 83.458 |
| 600 | 56.100 | 311.610 | 284.271 | 16.403 | −786.604 | −801.421 | 69.770 |
| 700 | 56.627 | 320.300 | 288.812 | 22.042 | −787.656 | −803.811 | 59.981 |
| 800 | 56.981 | 327.886 | 293.233 | 27.723 | −789.778 | −805.930 | 52.622 |
| 900 | 57.228 | 334.613 | 297.464 | 33.434 | −791.246 | −807.864 | 46.887 |
| 1000 | 57.408 | 340.652 | 301.486 | 39.167 | −793.024 | −809.618 | 42.290 |
| 1100 | 57.543 | 346.131 | 305.299 | 44.914 | −795.119 | −811.179 | 38.520 |
| 1200 | 57.646 | 351.142 | 308.914 | 50.674 | −805.266 | −811.912 | 35.342 |
| 1300 | 57 727 | 355.759 | 312.342 | 56.443 | −806.766 | −812.405 | 32.643 |
| 1400 | 57 791 | 360.040 | 315.598 | 62.219 | −808.281 | −812.782 | 30.325 |
| 1500 | 57.843 | 364.029 | 318.695 | 68.001 | −809.809 | −813.051 | 28.313 |
| 1600 | 57.886 | 367.763 | 321.646 | 73.787 | −811.352 | −813.216 | 26.549 |
| 1700 | 57.922 | 371.274 | 324.463 | 79.578 | −812.907 | −813.285 | 24.989 |
| 1800 | 57.952 | 374.585 | 327.157 | 85.371 | −963.146 | −811.051 | 23.536 |
| 1900 | 57.977 | 377.719 | 329.736 | 91.168 | −963.308 | −802.598 | 22.065 |
| 2000 | 57.999 | 380.694 | 332.211 | 96.967 | −963.482 | −794.134 | 20.741 |
| 2100 | 58.017 | 383.524 | 334.587 | 102.768 | −963.668 | −785.663 | 19.542 |
| 2200 | 58.034 | 386.223 | 336.873 | 108.570 | −963.866 | −777.182 | 18.453 |
| 2300 | 58.048 | 388.803 | 339.076 | 114.374 | −964.075 | −768.691 | 17.458 |
| 2400 | 58.060 | 391.274 | 341.199 | 120.180 | −964.298 | −760.192 | 16.545 |
| 2500 | 58.071 | 393.645 | 343.250 | 125.986 | −964.536 | −751.682 | 15.706 |
| 2600 | 58.081 | 395.922 | 345.232 | 131.794 | −964.790 | −743.163 | 14.930 |
| 2700 | 58.090 | 398.115 | 347.151 | 137.602 | −965.065 | −734.634 | 14.212 |
| 2800 | 58.097 | 400.227 | 349.009 | 143.412 | −965.364 | −726.094 | 13.545 |
| 2900 | 58.104 | 402.266 | 350.810 | 149.222 | −965.693 | −717.543 | 12.924 |
| 3000 | 58.111 | 404.236 | 352.559 | 155.032 | −966.056 | −708.980 | 12.344 |
| 3100 | 58.116 | 406.142 | 354.256 | 160.844 | −966.459 | −700.404 | 11.802 |
| 3200 | 58.122 | 407.987 | 355.907 | 166.656 | −966.910 | −691.815 | 11.293 |
| 3300 | 58.126 | 409.775 | 357.512 | 172.468 | −967.414 | −683.210 | 10.814 |
| 3400 | 58.131 | 411.511 | 359.075 | 178.281 | −967.978 | −674.590 | 10.364 |
| 3500 | 58.135 | 413.196 | 360.597 | 184.094 | −968.610 | −665.952 | 9.939 |
| 3600 | 58.138 | 414.833 | 362.081 | 189.908 | −969.315 | −657.295 | 9.537 |
| 3700 | 58.142 | 416.426 | 363.529 | 195.722 | −970.101 | −648.617 | 9 157 |
| 3800 | 58.145 | 417.977 | 364.941 | 201.536 | −970.973 | −639.917 | 8.796 |
| 3900 | 58.147 | 419.487 | 366.321 | 207.351 | −971.937 | −631.192 | 8.454 |
| 4000 | 58.150 | 420.960 | 367.668 | 213.166 | −972.998 | −622.442 | 8.128 |
| 4100 | 58.153 | 422.396 | 368.986 | 218.981 | −974.159 | −613.664 | 7.818 |
| 4200 | 58.155 | 423.797 | 370.274 | 224.796 | −975.425 | −604.856 | 7.522 |
| 4300 | 58.157 | 425.165 | 371.535 | 230.612 | −976.797 | −596.017 | 7.240 |
| 4400 | 58.159 | 426.502 | 372.769 | 236.428 | −978.276 | −587.145 | 6.970 |
| 4500 | 58.161 | 427.809 | 373.977 | 242.243 | −979.849 | −578.239 | 6.712 |
| 4600 | 58.162 | 429.088 | 375.162 | 248.060 | −981.538 | −569.297 | 6.465 |
| 4700 | 58.164 | 430.339 | 376.322 | 253.876 | −983.338 | −560.315 | 6.227 |
| 4800 | 58.166 | 431.563 | 377.461 | 259.692 | −985.244 | −551.295 | 5.999 |
| 4900 | 58.167 | 432.762 | 378.577 | 265.509 | −987.253 | −542.234 | 5.780 |
| 5000 | 58.168 | 433.938 | 379.672 | 271.326 | −989.361 | −533.131 | 5.570 |
| 5100 | 58.170 | 435.090 | 380.748 | 277.143 | −991.567 | −523.984 | 5.367 |
| 5200 | 58.171 | 436.219 | 381.804 | 282.960 | −993.860 | −514.794 | 5.171 |
| 5300 | 58.172 | 437.327 | 382.841 | 288.777 | −996.244 | −505.558 | 4.983 |
| 5400 | 58.173 | 438.414 | 383.860 | 294.594 | −998.711 | −496.277 | 4.801 |
| 5500 | 58.174 | 439.482 | 384.862 | 300.412 | −1001.254 | −486.950 | 4.625 |
| 5600 | 58.175 | 440.530 | 385.846 | 306.229 | −1003.860 | −477.576 | 4.455 |
| 5700 | 58.176 | 441.560 | 386.815 | 312.046 | −1006.538 | −468.155 | 4.290 |
| 5800 | 58.177 | 442.572 | 387.767 | 317.864 | −1009.276 | −458.686 | 4.131 |
| 5900 | 58.177 | 443.566 | 388.705 | 323.682 | −1012.068 | −449.169 | 3.977 |
| 6000 | 58.178 | 444.544 | 389.627 | 329.500 | −1014.907 | −439.604 | 3.827 |

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

$S°(298.15\ K) = [235.47 \pm 8]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -190.0 \pm 21\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -193.9 \pm 21\ kJ·mol^{-1}$

| Electronic Levels and Quantum Weights | |
|---|---|
| $\epsilon_i$, $cm^{-1}$ | $g_i$ |
| 0 | [2] |
| [16050] | [2] |
| [16610] | [2] |
| [18050] | [2] |

| Vibrational Frequencies and Degeneracies |
|---|
| $\nu$, $cm^{-1}$ |
| [587](1) |
| [466](2) |
| [3650](1) |

Point Group: $[C_{\infty v}]$ $\sigma = 1$
Bond Distances: Ca–O = [2.03] Å; O–H = [0.96] Å
Bond Angle: Ca–O–H = [180]°
Rotational Constant: $B_0 = [0.318811]\ cm^{-1}$

## Enthalpy of Formation

The adopted $\Delta_f H°(CaOH, g, 0\ K) = -45.41 \pm 5\ kcal·mol^{-1}(-190.0 \pm 21\ kJ·mol^{-1})$ is based on an assessment of $D_0°$ values derived from flame spectra of CaOH, SrOH, and BaOH. Cotton and Jenkins[1] found both the monohydroxides and dihydroxides of the alkaline earths to be present in significant amounts in fuel–rich hydrogen–oxygen–nitrogen flames. They determined equilibrium constants for the reactions $M(g) + H_2O(g) = MOH(g) + H(g)$ and $M(g) + 2\ H_2O(g) = M(OH)_2(g) + 2\ H(g)$ and derived $D_0°$ values In earlier work, Ryabova and Gurvich[2] had considered CaOH to be the dominant compound, and Sugden and Schofield[3] had interpreted $Ca(OH)_2$ as dominant. Cotton and Jenkins[1] have recalculated the work of these last two investigations, considering both CaOH and $Ca(OH)_2$ to be present. Ryabova *et al.*[4] and Kalff and Alkemade[5] have made additional measurements.

| | $D_0°$, $kcal·mol^{-1}$ CaOH(g)=Ca(g)+OH(g) | | |
|---|---|---|---|
| Reference | As Published | As Recalculated by Cotton and Jenkins[1] | As Corrected for Current JANAF Auxiliary Data[6] |
| Ryabova and Gurvich[2] | 100 ± 8 | 99 | |
| Sugden and Schofield[3] | | 102 | |
| Cotton and Jenkins[1] | 104 ± 5 | | 105.5 |
| Ryabova *et al.*[4] | 94 ± 3 | | 97.5[a] |
| Kalff and Alkemade[5] | 102.4 | | |

[a]An approximate correction of +3.5 $kcal·mol^{-1}$ is made, 2 $kcal·mol^{-1}$ assumed from the Cotton and Jekins' type calculation for the presence of both CaOH and $Ca(OH)_2$ and 1.5 $kcal·mol^{-1}$ indicated by the recalculation of Cotton and Jenkins' work[1] using auxiliary data from the current JANAF Tables.[6]

The data analyses for BaOH(g) and $Ba(OH)_2(g)$ indicate that flame–spectral data tend to give high dissociation energies. For $Ca(OH)_2(g)$, the lowest value of $D_0°$(HO–Ca–OH) was adopted.[6] Similarly, $D_0°$(Ca–OH) = 97.5 $kcal·mol^{-1}$ is adopted.

The ratio of the dissociation energies of the alkaline earth monohalides to those of the corresponding dihalides range from 0.40 to 0.51 with the ratio for the calcium fluorides being 0.47.[6] The similarity between the halides and hydroxides has been established.[7-10] The ratio of the adopted values for the dissociation energies of CaOH(g) and $Ca(OH)_2(g)$ is 0.47 where $D_0°$ of the dihydroxide is defined by the reaction $Ca(OH)_2 = Ca(g) + 2(OH)(g)$ and is 205.6 $kcal·mol^{-1}$.

## Heat Capacity and Entropy

The analogy between gaseous monohydroxides and monohalides, particularly the monofluorides, has been recognized.[7,10] The molecular configuration is assumed to be linear in accordance with the prediction of Walsh[11] and the evidence that gaseous alkali metal hydroxides are linear.[12,14] The ground state is assumed to be $^2\Sigma^+$ by analogy with CaF and CaCl.[6] The electronic levels are estimated from the band spectra observed by James and Sugden,[15] Gaydon,[16] Zhitkevich *et al.*[17] and van der Hurk *et al.*,[18] and the comparison with CaF and CaCl.[6]

The Ca–O bond distance is estimated to be slightly larger, 0.02 Å, than the Ca–F distance[6] after noting the close similarity in bond distance of the alkali metal fluorides and hydroxides. The O–H bond distance is that in water.[6]

The Ca–O stretching frequency, 587 $cm^{-1}$, is estimated to be the same as the CaF stretching frequency.[6,10] The O–H stretching frequency, 3650 $cm^{-1}$, is estimated from the alkali hydroxide series. The bending frequency, 466 $cm^{-1}$, is estimated by assuming that the ratio of the bending force constant to the stretching force constant is 0.022, which is the average ratio found in the alkali metal monohydroxides by Acquista and Abramowitz.[10,14]

The entropy in the present table is lower by 0.20 $cal·K^{-1}·mol^{-1}$ at 298.15 K and 0.25 $cal·K^{-1}·mol^{-1}$ at 1000 K than that proposed by Jackson;[10] the data relevant to the calculations are nearly the same.

Continued on page 736

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 | −10.429 | −189.995 | −189.995 | INFINITE |
| 100 | 30.146 | 195.611 | 270.666 | −7.506 | −191.004 | −195.266 | 101.997 |
| 200 | 38.363 | 218.867 | 239.376 | −4.102 | −192.671 | −198.857 | 51.936 |
| 250 | 42.001 | 227.836 | 236.191 | −2.089 | −193.335 | −200.324 | 41.855 |
| 298.15 | 44.625 | 235.470 | 235.470 | 0. | −193.877 | −201.620 | 35.323 |
| 300 | 44.711 | 235.746 | 235.471 | 0.083 | −193.897 | −201.668 | 35.113 |
| 350 | 46.687 | 242.795 | 236.023 | 2.370 | −194.378 | −202.924 | 30.285 |
| 400 | 48.139 | 249.129 | 237.272 | 4.743 | −194.810 | −204.115 | 26.655 |
| 450 | 49.226 | 254.864 | 238.913 | 7.178 | −195.226 | −205.253 | 23.825 |
| 500 | 50.062 | 260.096 | 240.774 | 9.661 | −195.648 | −206.345 | 21.557 |
| 600 | 51.270 | 269.337 | 244.785 | 14.732 | −196.564 | −208.400 | 18.143 |
| 700 | 52.148 | 277.309 | 248.875 | 19.904 | −197.626 | −210.291 | 15.692 |
| 800 | 52.879 | 284.321 | 252.876 | 25.156 | −199.713 | −211.914 | 13.837 |
| 900 | 53.544 | 290.589 | 256.724 | 30.478 | −201.107 | −213.359 | 12.383 |
| 1000 | 54.171 | 296.263 | 260.399 | 35.864 | −202.774 | −214.633 | 11.211 |
| 1100 | 54.769 | 301.454 | 263.898 | 41.311 | −204.724 | −215.727 | 10.244 |
| 1200 | 55.336 | 306.244 | 267.230 | 46.817 | −214.692 | −216.008 | 9.403 |
| 1300 | 55.868 | 310.695 | 270.404 | 52.377 | −215.983 | −216.065 | 8.682 |
| 1400 | 56.364 | 314.853 | 273.432 | 57.989 | −217.260 | −216.024 | 8.060 |
| 1500 | 56.823 | 318.758 | 276.325 | 63.649 | −218.525 | −215.891 | 7.518 |
| 1600 | 57.244 | 322.439 | 279.093 | 69.353 | −219.781 | −215.675 | 7.041 |
| 1700 | 57.631 | 325.921 | 281.747 | 75.097 | −221.029 | −215.380 | 6.618 |
| 1800 | 57.985 | 329.225 | 284.293 | 80.878 | −370.947 | −212.801 | 6.175 |
| 1900 | 58.311 | 332.369 | 286.741 | 86.693 | −370.774 | −204.020 | 5.609 |
| 2000 | 58.610 | 335.368 | 289.098 | 92.539 | −370.606 | −195.247 | 5.099 |
| 2100 | 58.888 | 338.234 | 291.370 | 98.414 | −370.446 | −186.483 | 4 639 |
| 2200 | 59.147 | 340.980 | 293.563 | 104.316 | −370.299 | −177.727 | 4.220 |
| 2300 | 59.390 | 343.614 | 295.683 | 110.243 | −370.168 | −168.976 | 3.838 |
| 2400 | 59.622 | 346.147 | 297.733 | 116.194 | −370.059 | −160.232 | 3.487 |
| 2500 | 59.845 | 348.585 | 299.719 | 122.167 | −369.978 | −151.490 | 3.165 |
| 2600 | 60.062 | 350.937 | 301.644 | 128.162 | −369.929 | −142.752 | 2.868 |
| 2700 | 60.276 | 353.208 | 303.512 | 134.179 | −369.920 | −134.015 | 2.593 |
| 2800 | 60.488 | 355.404 | 305.326 | 140.218 | −369.956 | −125.277 | 2.337 |
| 2900 | 60.701 | 357.530 | 307.090 | 146.277 | −370.045 | −116.537 | 2.099 |
| 3000 | 60.915 | 359.591 | 308.805 | 152.358 | −370.194 | −107.793 | 1.877 |
| 3100 | 61.132 | 361.592 | 310.476 | 158.460 | −370.410 | −99.043 | 1.669 |
| 3200 | 61.354 | 363.537 | 312.104 | 164.584 | −370.700 | −90.285 | 1.474 |
| 3300 | 61.580 | 365.428 | 313.691 | 170.731 | −371.071 | −81.516 | 1.290 |
| 3400 | 61.812 | 367.270 | 315.240 | 176.901 | −371.531 | −72.735 | 1.117 |
| 3500 | 62.049 | 369.065 | 316.753 | 183.094 | −372.085 | −63.939 | 0.954 |
| 3600 | 62.291 | 370.816 | 318.230 | 189.310 | −372.741 | −55.126 | 0.800 |
| 3700 | 62.538 | 372.526 | 319.675 | 195.552 | −373.504 | −46.294 | 0.654 |
| 3800 | 62.790 | 374.197 | 321.087 | 201.818 | −374.380 | −37.438 | 0.515 |
| 3900 | 63.047 | 375.832 | 322.470 | 208.110 | −375.373 | −28.558 | 0.382 |
| 4000 | 63.307 | 377.431 | 323.824 | 214.428 | −376.487 | −19.652 | 0.257 |
| 4100 | 63.571 | 378.998 | 325.151 | 220.772 | −377.726 | −10.716 | 0.137 |
| 4200 | 63.837 | 380.533 | 326.451 | 227.142 | −379.092 | −1.748 | 0.022 |
| 4300 | 64.105 | 382.038 | 327.727 | 233.539 | −380.588 | 7.254 | −0.088 |
| 4400 | 64.375 | 383.515 | 328.978 | 239.963 | −382.210 | 16.291 | −0.193 |
| 4500 | 64.644 | 384.965 | 330.206 | 246.414 | −383.947 | 25.366 | −0.294 |
| 4600 | 64.913 | 386.388 | 331.412 | 252.892 | −385.820 | 34.482 | −0.392 |
| 4700 | 65.181 | 387.787 | 332.597 | 259.397 | −387.822 | 43.641 | −0.485 |
| 4800 | 65.446 | 389.162 | 333.761 | 265.928 | −389.948 | 52.843 | −0.575 |
| 4900 | 65.709 | 390.515 | 334.905 | 272.486 | −392.195 | 62.091 | −0.662 |
| 5000 | 65.969 | 391.845 | 336.031 | 279.070 | −394.558 | 71.386 | −0.746 |
| 5100 | 66.224 | 393.154 | 337.138 | 285.679 | −397.035 | 80.729 | −0.827 |
| 5200 | 66.475 | 394.442 | 338.228 | 292.314 | −399.616 | 90.121 | −0.905 |
| 5300 | 66.720 | 395.710 | 339.300 | 298.974 | −402.303 | 99.565 | −0.981 |
| 5400 | 66.960 | 396.960 | 340.356 | 305.658 | −405.089 | 109.060 | −1.055 |
| 5500 | 67.193 | 398.191 | 341.397 | 312.366 | −407.966 | 118.608 | −1.126 |
| 5600 | 67.419 | 399.403 | 342.422 | 319.097 | −410.921 | 128.208 | −1.196 |
| 5700 | 67.639 | 400.599 | 343.432 | 325.850 | −413.965 | 137.862 | −1.263 |
| 5800 | 67.851 | 401.777 | 344.428 | 332.624 | −417.083 | 147.571 | −1.329 |
| 5900 | 68.055 | 402.938 | 345.410 | 339.419 | −420.270 | 157.332 | −1.393 |
| 6000 | 68.251 | 404.084 | 346.378 | 346.235 | −423.521 | 167.150 | −1.455 |

PREVIOUS December 1975 (1 atm)  CURRENT. December 1975 (1 bar)

$S°(298.15\ K) = [229.90 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 366.733 \pm 63\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [369.084 \pm 63]\ kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies $\upsilon$, $cm^{-1}$ |
|---|
| [580](1) |
| [460](2) |
| [3650](1) |

Ground State Quantum Weight = [1] $\sigma = 1$
Point Group: [$C_{\infty v}$]
Bond Distances: Ca–O = [2.03] Å; O–H = [0.96] Å
Bond Angle: Ca–O–H = [180°]
Rotational Constant: $B_0$ = [0.318830] $cm^{-1}$

## Enthalpy of Formation

The ionization potential of CaOH(g) was deduced by Kelly and Padley[1] to be 5.9 ± 0.1 eV. These authors quantitatively examined the total positive ion concentrations produced from Ca aqueous salt additives in fuel rich, premixed $H_2 + O_2 + N_2$ flames. Using current JANAF auxiliary data,[2] we recalculate the ionization potential to be 5.79 eV.

Jensen[3] determined the enthalpy of reaction $\Delta_r H°(0\ K) = 35 \pm 10$ kcal·mol$^{-1}$ for $Ca(g) + OH(g) = CaOH^+(g) + e^-$ in atmospheric pressure $H_2 + O_2 + N_2$ flames using the microwave cavity resonance method. This value was calculated assuming a bent molecule for XXCaOH$^+$; the value is not significantly changed, within the uncertainty, by the change in the configuration. Using auxiliary data,[2] we derive an ionization potential of 5.75 eV, which is in good agreement with the value derived from the data of Kelly and Padley.[1]

We adopt an ionization potential of 5.77 eV (133.06 kcal·mol$^{-1}$) which is average of the above two studies.[1,3] This leads to $\Delta_f H°(0\ K) = 87.651$ kcal·mol$^{-1}$ and $\Delta_f H°(298.15\ K) = 88.213$ kcal·mol$^{-1}$ (369.08 kJ·mol$^{-1}$) for $CaOH^+(g)$. We assign an uncertainty of ±15 kcal·mol$^{-1}$.

For comparison, the appearance potential of CaF(g) has been reported as 5.8 ± 0.3 eV,[4] 5.5 ± 0.3 eV[4] and 6.0 ± 0.5 eV.[5] These values are all very similar to the ionization potential adopted here for CaOH(g). In addition, the ionization potential for Ca(g) is 6.11 eV.[2]

## Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that the gaseous alkali metal hydroxides are linear.[2,6-8] In addition, Walsh[9] had predicted that triatomic molecules (containing hydrogen) with ten or less valence electrons (CaOH$^+$ has eight valence electrons) will be linear in their ground state. The molecule CaOH$^+$ is isoelectronic with KOH.

The bond dissociation energy for $CaOH^+$ ($D_0° = 105.4$ kcal mol$^{-1}$)[2] for the process $CaOH^+(g) = Ca^+(g) + OH(g)$ is fairly close to that for CaOH ($D_0° = 97.5$ kcal·mol$^{-1}$).[2] This suggests a similar bonding in these two molecules. Thus, bond distances are assumed to be the same as those adopted for CaOH(g).[2] The ground state quantum weight is assumed to be the same as that of KOH(g).[2]

## References


[1]R. Kelly and P. J. Padley, Trans. Faraday Soc. 67, 1384 (1971).
[2]JANAF Thermochemical Tables: $e^-$, 3–31–65; $H_2(g)$ and $H_2O(g)$, 3–31–61; Ca(g), 12–31–68, OH(g) and $Ca^+(g)$, 12–31–70; H(g), 6–30–74, CaOH(g) and $Ca(OH)_2(g)$, 12–31–75.
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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 | −10.466 | 366.733 | | |
| 100 | 30.213 | 189.861 | 265.270 | −7.541 | | | |
| 200 | 38.571 | 213.223 | 233.828 | −4.121 | | | |
| 250 | 42.199 | 222.238 | 230.629 | −2.098 | | | |
| 298.15 | 44.799 | 229.905 | 229.905 | 0. | 369.084 | 356.746 | −62.501 |
| 300 | 44.884 | 230.182 | 229.906 | 0.083 | 369.104 | 356.670 | −62.102 |
| 350 | 46.834 | 237.255 | 230.460 | 2.378 | 369.670 | 354.554 | −52.914 |
| 400 | 48.263 | 243.607 | 231.713 | 4.758 | 370.284 | 352.353 | −46.013 |
| 450 | 49.331 | 249.356 | 233.359 | 7.199 | 370.913 | 350.073 | −40.635 |
| 500 | 50.151 | 254.598 | 235.225 | 9.687 | 371.535 | 347.724 | −36.327 |
| 600 | 51.336 | 263.854 | 239.245 | 14.765 | 372.705 | 342.850 | −29.848 |
| 700 | 52.198 | 271.835 | 243.344 | 19.943 | 373.727 | 337.791 | −25.206 |
| 800 | 52.919 | 278.853 | 247.353 | 25.200 | 373.724 | 332.702 | −21.723 |
| 900 | 53.576 | 285.124 | 251.207 | 30.525 | 374.412 | 327.530 | −19.009 |
| 1000 | 54.198 | 290.801 | 254.887 | 35.914 | 374.826 | 322.296 | −16.835 |
| 1100 | 54.791 | 295.995 | 258.392 | 41.364 | 374.957 | 317.034 | −15.055 |
| 1200 | 55.355 | 300.787 | 261.727 | 46.871 | 367.070 | 312.396 | −13.598 |
| 1300 | 55.884 | 305.239 | 264.905 | 52.433 | 367.859 | 307.807 | −12.368 |
| 1400 | 56.378 | 309.398 | 267.936 | 58.047 | 368.662 | 303.158 | −11.311 |
| 1500 | 56.834 | 313.304 | 270.832 | 63.708 | 369.477 | 298.451 | −10.393 |
| 1600 | 57.253 | 316.985 | 273.603 | 69.412 | 370.301 | 293.689 | −9.588 |
| 1700 | 57.637 | 320.468 | 276.258 | 75.157 | 371.132 | 288.875 | −8.876 |
| 1800 | 57.987 | 323.772 | 278.807 | 80.939 | 223.294 | 286.223 | −8.306 |
| 1900 | 58.305 | 326.916 | 281.257 | 86.753 | 225.544 | 289.658 | −7.963 |
| 2000 | 58.595 | 329.914 | 283.615 | 92.599 | 227.790 | 292.974 | −7.652 |
| 2100 | 58.859 | 332.780 | 285.889 | 98.472 | 230.026 | 296.178 | −7.367 |
| 2200 | 59.099 | 335.524 | 288.083 | 104.370 | 232.249 | 299.277 | −7.106 |
| 2300 | 59.318 | 338.156 | 290.203 | 110.291 | 234.452 | 302.274 | −6.865 |
| 2400 | 59.518 | 340.684 | 292.254 | 116.233 | 236.631 | 305.175 | −6.642 |
| 2500 | 59.700 | 343.118 | 294.240 | 122.194 | 238.779 | 307.987 | −6.435 |
| 2600 | 59.866 | 345.463 | 296.166 | 128.172 | 240.889 | 310.714 | −6.242 |
| 2700 | 60.018 | 347.725 | 298.033 | 134.166 | 242.954 | 313.360 | −6.062 |
| 2800 | 60.158 | 349.910 | 299.847 | 140.175 | 244.967 | 315.931 | −5.894 |
| 2900 | 60.286 | 352.023 | 301.610 | 146.198 | 246.919 | 318.430 | −5 736 |
| 3000 | 60.404 | 354.069 | 303.325 | 152.232 | 248.803 | 320.864 | −5.587 |
| 3100 | 60.512 | 356.052 | 304.994 | 158.278 | 250.609 | 323.236 | −5 446 |
| 3200 | 60.613 | 357.974 | 306.620 | 164.334 | 252.330 | 325.551 | −5.314 |
| 3300 | 60.705 | 359.841 | 308.204 | 170.400 | 253.956 | 327.814 | −5.189 |
| 3400 | 60.791 | 361.654 | 309.750 | 176.475 | 255.481 | 330.029 | −5.070 |
| 3500 | 60.871 | 363.418 | 311.258 | 182.558 | 256.895 | 332.201 | −4.958 |
| 3600 | 60.944 | 365.134 | 312.731 | 188.649 | 258.192 | 334.334 | −4.851 |
| 3700 | 61.013 | 366.804 | 314.170 | 194.747 | 259.364 | 336.432 | −4.750 |
| 3800 | 61.077 | 368.432 | 315.577 | 200.852 | 260.405 | 338.501 | −4.653 |
| 3900 | 61.136 | 370.020 | 316.952 | 206.962 | 261.310 | 340.544 | −4.561 |
| 4000 | 61.192 | 371.568 | 318.299 | 213.079 | 262.073 | 342.566 | −4.473 |
| 4100 | 61.244 | 373.080 | 319.616 | 219.201 | 262.690 | 344.570 | −4.390 |
| 4200 | 61.293 | 374.556 | 320.907 | 225.327 | 263.159 | 346.561 | −4.310 |
| 4300 | 61.339 | 375.999 | 322.171 | 231.459 | 263.477 | 348.543 | −4.234 |
| 4400 | 61.381 | 377.410 | 323.411 | 237.595 | 263.645 | 350.519 | −4.161 |
| 4500 | 61.422 | 378.790 | 324.626 | 243.735 | 263.676 | 352.491 | −4.092 |
| 4600 | 61.460 | 380.140 | 325.818 | 249.879 | 263.548 | 354.465 | −4.025 |
| 4700 | 61.495 | 381.462 | 326.988 | 256.027 | 263.267 | 356.445 | −3.961 |
| 4800 | 61.529 | 382.757 | 328.137 | 262.178 | 262.840 | 358.432 | −3.901 |
| 4900 | 61.561 | 384.026 | 329.264 | 268.333 | 262.268 | 360.429 | −3.842 |
| 5000 | 61.591 | 385.270 | 330.372 | 274.490 | 261.557 | 362.440 | −3.786 |
| 5100 | 61.619 | 386.490 | 331.461 | 280.651 | 260.710 | 364.465 | −3.733 |
| 5200 | 61.646 | 387.687 | 332.530 | 286.814 | 259.736 | 366.508 | −3.682 |
| 5300 | 61.671 | 388.861 | 333.582 | 292.980 | 258.633 | 368.572 | −3.633 |
| 5400 | 61.695 | 390.014 | 334.617 | 299.148 | 257.410 | 370.658 | −3.585 |
| 5500 | 61.718 | 391.147 | 335.634 | 305.319 | 256.074 | 372.767 | −3.540 |
| 5600 | 61.740 | 392.259 | 336.635 | 311.492 | 254.640 | 374.901 | −3.497 |
| 5700 | 61.761 | 393.352 | 337.621 | 317.667 | 253.098 | 377.062 | −3.455 |
| 5800 | 61.780 | 394.426 | 338.591 | 323.844 | 251.460 | 379.251 | −3.416 |
| 5900 | 61.799 | 395 482 | 339.546 | 330.023 | 249.735 | 381.468 | −3.377 |
| 6000 | 61.817 | 396.521 | 340.487 | 336.204 | 247.929 | 383 717 | −3.341 |

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

$S°(298.15\ K) = 83.387 \pm 0.4\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -977.36 \pm 1.3\ kJ\ mol^{-1}$
$\Delta_f H°(298.15\ K) = -986.09 \pm 1.3\ kJ·mol^{-1}$

## Enthalpy of Formation

Taylor and Wells[1] measured enthalpies of solution of $Ca(OH)_2$(cr) and CaO(cr) in dilute HCl and obtained $\Delta_f H°(298.15\ K) = -15.58 \pm 0.1$ kcal·mol$^{-1}$ for CaO(cr) + $H_2O$(l) = $Ca(OH)_2$(cr) which leads to $\Delta_f H°(Ca(OH)_2, cr, 298.15\ K) = -235.68 \pm 0.3$ kcal·mol$^{-1}$ using $\Delta_f H°$(CaO, cr, 298.15 K) = $-151.79 \pm 0.21$ kcal·mol$^{-1}$ [2] and $\Delta_f H°(H_2O, l, 298.15\ K) = -68.315$ kcal·mol$^{-1}$.[3] This value, $-235.68 \pm 0.3$ kcal·mol$^{-1}$ ($-986.09$ kJ·mol$^{-1}$) is adopted in the tabulation. They also measured directly the enthalpy of hydration of CaO to $Ca(OH)_2$ and found $\Delta_f H°(298.15\ K) = -15.43 \pm 0.1$ kcal·mol$^{-1}$ which leads to $\Delta_f H°(Ca(OH)_2, cr, 298.15\ K) = -235.53$ kcal·mol$^{-1}$ Both measurements are in very good agreement. Literature $\Delta_f H°$ data[4-8] determined by these two methods were within the limit of $-15.40 \pm 0.3$ kcal·mol$^{-1}$ which is in good agreement with the value adopted.

JANAF analyses of dissociation pressure data[9-11] for $Ca(OH)_2$(cr) → CaO(cr) + $H_2O$(g) are listed below. The data of Halstead and Moore[9] and of Tamaru and Shiomi[10] are in good agreement, but the pressures reported by Johnston[11] are too low due to failure to reach equilibrium. The enthalpy of formation derived from 3rd law $\Delta_r H$ of Halstead and Moore[9] or Tamaru and Shiomi[10] is in good agreement with the value adopted. However, the decomposition of $Ca(OH)_2$ may yield non-standard state CaO in the final product which was shown in a similar decomposition of $Mg(OH)_2$. See $Mg(OH)_2$ table[2] for details.

$Ca(OH)_2(cr) = CaO(cr) + H_2O(g)$

| Source | Method | T/K | Data Points | $\Delta_r H°(298.15\ K)$, kcal·mol$^{-1}$ 2nd law | 3rd law | Drift cal·K$^{-1}$·mol$^{-1}$ | $\Delta_r H°(298.15\ K)$, kcal·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| Halstead and Moore[9] | Static | 635–776.5 | 14 | 25.52 | 25.75 ± 0.15 | 0.2 ± 0.4 | −235.34 |
| Tamaru and Shiomi[10] | Static | 694–776.5 | 8 | 26.48 | 25.90 ± 0.07 | −0.8 ± 0.3 | −235.49 |
| Johnston[11] | Static | 663–804 | 7 | 26.92 | 26.76 ± 0.24 | −0.5 ± 1.0 | −236.35 |

## Heat Capacity and Entropy

The low temperature heat capacities up to 300 K are taken from the adiabatic calorimeter measurements (19–330 K) of Hatton *et al.*[12] Above 300 K, the heat capacities are based on the heat conduction calorimeter measurements (310–670 K) of Kobayashi[13] joined smoothly at 300 K with the low temperature heat capacities[12] and on a graphical comparison of the $C_p$ vs $T$ curve adopted for $Mg(OH)_2$(cr).[2] The entropy, $S°(298.15\ K) = 19.93 \pm 0.1$ cal·K$^{-1}$·mol$^{-1}$ ($83.387 \pm 0.4\ J·K^{-1}·mol^{-1}$), is derived from the adiabatic low temperature heat capacities, based on a $T^3$ extrapolation to obtain $S° = 0.070$ cal·K$^{-1}$·mol$^{-1}$ at 20 K.[12]

## Decomposition Data

$T_{dcm}$ is calculated as the temperature at which $\Delta_r G° = 0$ for the reaction $Ca(OH)_2(cr) = CaO(cr) + H_2O(g)$. Auxiliary data are from the JANAF Tables.[2]

Under a pressure of 1000 bars, Wyllie and Tuttle[14] found that $Ca(OH)_2$ melts congruently at 1108 K.

## References


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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 | −14.160 | −977.358 | −977.358 | INFINITE |
| 100 | 32.539 | 17.226 | 147.109 | −12.988 | −983.071 | −955.793 | 499.255 |
| 200 | 68.576 | 52.183 | 90.862 | −7.736 | −985.692 | −927.251 | 242.173 |
| 298.15 | 87.487 | 83.387 | 83.387 | 0. | −986.085 | −898.421 | 157.400 |
| 300 | 87.780 | 83.929 | 83.389 | 0.162 | −986.079 | −897.877 | 156.334 |
| 400 | 98.408 | 110.820 | 86.983 | 9.535 | −985.218 | −868.582 | 113.425 |
| 500 | 103.931 | 133.431 | 94.075 | 19.678 | −983.822 | −839.579 | 87.710 |
| 600 | 107.445 | 152.696 | 102.280 | 30.249 | −982.281 | −810.874 | 70.593 |
| 700 | 110.709 | 169.508 | 110.708 | 41.160 | −980.702 | −782.431 | 58.386 |
| 800 | 113.512 | 184.479 | 119.010 | 52.375 | −979.971 | −754.111 | 49.238 |
| 900 | 116.022 | 197.998 | 127.048 | 63.855 | −978.396 | −725.974 | 42.134 |
| 1000 | 117.989 | 210.328 | 134.768 | 75.560 | −976.978 | −698.005 | 36.460 |

PREVIOUS: December 1971  CURRENT: December 1975

$S°(298.15\ K) = [285.6 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -603.17 \pm 37.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -610.76 \pm 37.7\ kJ·mol^{-1}$

| Vibrational Frequencies and Degeneracies $\nu$, $cm^{-1}$ |
|---|
| [484](1) |
| [163](1) |
| [554](1) |
| [3650](2) |
| [466](4) |

Ground State Quantum Weight = [1] $\sigma = 2$
Point Group: $[C_{2v}]$
Bond Distances: Ca–O = [2.12] Å; O–H = [0.96] Å
Bond Angles: O–Ca–O = [135°], Ca–O–H = [180°]
Product of the Moments of Inertia: $I_A I_B I_C = [1261.6507 \times 10^{-117}]\ g^3·cm^6$

## Enthalpy of Formation

Dissociation energies, $D_0°$, for the reaction $Ca(OH)_2(g) = Ca(g) + 2\ OH(g)$ have been derived from flame–spectral measurements.[1–3] Ryabova and Gurvich[1] believed the dominant reaction to be $Ca(g) + H_2O(g) = CaOH(g) + H(g)$, but they also considered the possibility that $Ca(g) + 2\ H_2O(g) = Ca(OH)_2(g) + 2\ H(g)$ was the dominant reaction and derived $D_0° = 200 \pm 20\ kcal·mol^{-1}$. Sugden and Schofield[2] considered the dihydroxide to be the dominant product and derived $D_0° = 217 \pm 12\ kcal·mol^{-1}$. Cotton and Jenkins[3] found both CaOH and $Ca(OH)_2$ to be present in significant amounts in fuel–rich hydrogen–oxygen–nitrogen flames and derived $D_0° = 203.8 \pm 5\ kcal·mol^{-1}$. Cotton and Jenkins[3] recalculated the work of Ryabova and Gurvich[1] and Sugden and Schofield[2] considering both CaOH and $Ca(OH)_2$ to be present and obtained the recalculated $D_0°$ values of 199 and 201 $kcal·mol^{-1}$, respectively.

A 3rd law analysis of the experimental equilibrium constants tabulated by Cotton and Jenkins[3] using current JANAF auxiliary data[4] leads to $D_0° = 210.4\ kcal·mol^{-1}$ which is 6.6 $kcal·mol^{-1}$ higher than the 203.8 $kcal·mol^{-1}$ derived by Cotton and Jenkins.[3] Applying this difference to the data of Ryabova and Gurvich[1] and Sugden and Schofield[2] as recalculated by Cotton and Jenkins[3] gives $D_0° = 205.6$ and 207.6 $kcal·mol^{-1}$, respectively.

For $Ba(OH)_2(g)$,[4] the corrected dissociation energy of Ryabova and Gurvich,[4] $D_0° = 208.8\ kcal·mol^{-1}$, is in better agreement with the "adopted" value of 209 6 $kcal·mol^{-1}$, based on good Knudsen–cell mass–spectrometric measurements, than are the corrected dissociation energies of Sugden and Schofield or Cotton and Jenkins.[4] We adopt $D_0° = 205.6\ kcal·mol^{-1}$ for the dissociation of $Ca(OH)_2$ from which is calculated $\Delta_f H°(0\ K) = -144.16 \pm 9\ kcal·mol^{-1}$ ($-603.165 \pm 37.7\ kJ·mol^{-1}$).

The enthalpy of dissociaton listed by Jackson[5] leads to $\Delta_f H°(Ca(OH)_2, g, 298.15\ K) = -142.65\ kcal·mol^{-1}$. Another recent compilation[9] lists $\Delta_f H°(298.15\ K) = -130\ kcal·mol^{-1}$.

## Heat Capacity and Entropy

The analogy between gaseous mono– and dihydroxides and gaseous mono– and dihalides, particularly the mono– and difluorides, has been recognized.[5–8] The O–Ca–O bond angle is assumed to be the same as the F–Ca–F bond angle;[4] the Ca–O–H bond angle is considered to be linear as in CaOH.[4] The Ca–O bond distance is estimated to be slightly larger, 0.02 Å, than the Ca–F bond distance in $CaF_2$[4] after noting the close similarity in the bond distance of alkali metal fluorides and hydroxides. The O–H bond distance is taken to be the same as in water.[4]

The vibrational frequencies are estimated to be the same as in $CaF_2$[4] (O–Ca–O symmetrical and asymmetrical stretch, and bend) and as in CaOH,[4] (O–H stretch and Ca–O–H bend). The principal moments of inertia are $I_A = 2.1629 \times 10^{-39}$, $I_B = 23.0947 \times 10^{-39}$, and $I_C = 25.2576 \times 10^{-39}\ g·cm$.

Jackson[5] has used a different molecular configuration and different vibrational frequencies to estimate $S°(298.15\ K) = 68.530\ cal·K^{-1}·mol^{-1}$(1 atm). We assign an uncertainty of $\pm 2.0\ cal·K^{-1}·mol^{-1}$ to the adopted entropy.

## References


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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 | −15.288 | −603.165 | −603.165 | INFINITE |
| 100 | 41.018 | 224.358 | 341.567 | −11.721 | −606.482 | −599.918 | 313.365 |
| 200 | 60.577 | 258.745 | 291.969 | −6.645 | −609.279 | −592.151 | 154.654 |
| 250 | 68.164 | 273.122 | 286.787 | −3.416 | −610.155 | −587.762 | 122.806 |
| 298.15 | 73.450 | 285.605 | 285.605 | 0. | −610.764 | −583.390 | 102.208 |
| 300 | 73.620 | 286.060 | 285.606 | 0.136 | −610.783 | −583.221 | 101.548 |
| 350 | 77.512 | 297 717 | 286.518 | 3.920 | −611.231 | −578.589 | 86.350 |
| 400 | 80.329 | 308.261 | 288.588 | 7.869 | −611.562 | −573.903 | 74.944 |
| 450 | 82 418 | 317.849 | 291.315 | 11.941 | −611.831 | −569.179 | 66.069 |
| 500 | 84 012 | 326.619 | 294.413 | 16.103 | −612.075 | −564.426 | 58.965 |
| 600 | 86.304 | 342.152 | 301.108 | 24.626 | −612.583 | −554.850 | 48.304 |
| 700 | 87.972 | 355.587 | 307.953 | 33.343 | −613.197 | −545.181 | 40.682 |
| 800 | 89.371 | 367.427 | 314 662 | 42.212 | −614.812 | −535.310 | 34.952 |
| 900 | 90.655 | 378.028 | 321 124 | 51.214 | −615.716 | −525.321 | 30.489 |
| 1000 | 91.876 | 387.643 | 327.302 | 60.341 | −616.875 | −515.217 | 26.912 |
| 1100 | 93.045 | 396.455 | 333.194 | 69.587 | −618.300 | −504.984 | 23.980 |
| 1200 | 94.158 | 404.599 | 338.809 | 78.948 | −627.726 | −493.988 | 21.503 |
| 1300 | 95.206 | 412.178 | 344.165 | 88.417 | −628.461 | −482.813 | 19.400 |
| 1400 | 96.185 | 419.270 | 349.279 | 97.987 | −629.168 | −471.583 | 17.595 |
| 1500 | 97.090 | 425.937 | 354.169 | 107.651 | −629.853 | −460.303 | 16.029 |
| 1600 | 97.922 | 432.230 | 358.853 | 117.403 | −630.521 | −448.978 | 14.658 |
| 1700 | 98.684 | 438.190 | 363.346 | 127.233 | −631.175 | −437.611 | 13.446 |
| 1800 | 99.380 | 443.850 | 367.663 | 137.137 | −780.494 | −423.996 | 12.304 |
| 1900 | 100.014 | 449.241 | 371 816 | 147.107 | −779.723 | −404.211 | 11.113 |
| 2000 | 100.591 | 454.386 | 375.817 | 157.138 | −778.957 | −384.467 | 10.041 |
| 2100 | 101.116 | 459.306 | 379.676 | 167.224 | −778.201 | −364.761 | 9.073 |
| 2200 | 101.594 | 464.022 | 383.403 | 177.360 | −777.463 | −345.090 | 8.193 |
| 2300 | 102.030 | 468.547 | 387 008 | 187.541 | −776.749 | −325.454 | 7.391 |
| 2400 | 102.427 | 472.898 | 390.496 | 197.764 | −776.065 | −305.847 | 6.657 |
| 2500 | 102.789 | 477.087 | 393.877 | 208.025 | −775.418 | −286.268 | 5.981 |
| 2600 | 103.120 | 481.125 | 397.155 | 218.321 | −774.816 | −266.714 | 5.358 |
| 2700 | 103.424 | 485.022 | 400.338 | 228.649 | −774.267 | −247.182 | 4.782 |
| 2800 | 103.702 | 488.789 | 403.430 | 239.005 | −773.779 | −227.669 | 4.247 |
| 2900 | 103.957 | 492.432 | 406.436 | 249.388 | −773.360 | −208.174 | 3.750 |
| 3000 | 104.192 | 495.961 | 409.362 | 259.796 | −773.020 | −188.690 | 3.285 |
| 3100 | 104.408 | 499.381 | 412.211 | 270.226 | −772.765 | −169.217 | 2.851 |
| 3200 | 104.608 | 502.699 | 414 987 | 280.677 | −772.606 | −149.751 | 2.444 |
| 3300 | 104.793 | 505 921 | 417.694 | 291.147 | −772.551 | −130.288 | 2.062 |
| 3400 | 104.963 | 509.052 | 420.335 | 301.635 | −772.608 | −110.824 | 1.703 |
| 3500 | 105.122 | 512.096 | 422.914 | 312.139 | −772.786 | −91.358 | 1.363 |
| 3600 | 105.269 | 515.060 | 425.432 | 322.659 | −773.091 | −71.885 | 1.043 |
| 3700 | 105.406 | 517.946 | 427.894 | 333.193 | −773.531 | −52.402 | 0.740 |
| 3800 | 105.533 | 520.759 | 430.301 | 343.740 | −774.112 | −32.903 | 0.452 |
| 3900 | 105.652 | 523.502 | 432.656 | 354.299 | −774.840 | −13.388 | 0.179 |
| 4000 | 105 763 | 526.178 | 434.960 | 364.870 | −775.721 | 6.146 | −0.080 |
| 4100 | 105.866 | 528.791 | 437.217 | 375.451 | −776.757 | 25.706 | −0.327 |
| 4200 | 105.964 | 531.343 | 439 428 | 386.043 | −777.952 | 45.292 | −0.563 |
| 4300 | 106.055 | 533.837 | 441.595 | 396.644 | −779.309 | 64.910 | −0.788 |
| 4400 | 106.140 | 536.277 | 443.719 | 407.254 | −780.826 | 84.559 | −1.004 |
| 4500 | 106.220 | 538.663 | 445.802 | 417.872 | −782.492 | 104.244 | −1.210 |
| 4600 | 106.296 | 540.998 | 447.847 | 428.498 | −784.327 | 123.968 | −1.408 |
| 4700 | 106.367 | 543.285 | 449.853 | 439.131 | −786.326 | 143.735 | −1.597 |
| 4800 | 106.434 | 545.525 | 451.823 | 449.771 | −788.482 | 163.547 | −1.780 |
| 4900 | 106.497 | 547.720 | 453.758 | 460 417 | −790.794 | 183.405 | −1.955 |
| 5000 | 106.557 | 549.873 | 455.658 | 471.070 | −793.256 | 203.311 | −2.124 |
| 5100 | 106.614 | 551.983 | 457.527 | 481.729 | −795.867 | 223.268 | −2.287 |
| 5200 | 106.667 | 554.054 | 459.363 | 492.393 | −798.615 | 243.277 | −2.444 |
| 5300 | 106.718 | 556.086 | 461.169 | 503.062 | −801.504 | 263.341 | −2.595 |
| 5400 | 106.766 | 558.081 | 462.945 | 513.736 | −804.524 | 283.460 | −2.742 |
| 5500 | 106.811 | 560.041 | 464.693 | 524 415 | −807.669 | 303.636 | −2.884 |
| 5600 | 106.855 | 561.966 | 466.413 | 535.098 | −810.925 | 323.871 | −3.021 |
| 5700 | 106.896 | 563.858 | 468.106 | 545 786 | −814.302 | 344.165 | −3.154 |
| 5800 | 106.935 | 565.717 | 469.773 | 556 478 | −817.785 | 364.520 | −3.283 |
| 5900 | 106.972 | 567.545 | 471.414 | 567 173 | −821.368 | 384.933 | −3.408 |
| 6000 | 107.008 | 569.344 | 473.032 | 577.872 | −825.045 | 405.411 | −3.529 |

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

## Calcium Iodide (CaI)

**IDEAL GAS**

$M_r = 75.533$

## Calcium Iodide (CaI)

$CaI_1I_1(g)$

$S°(298.15\ K) = 261.31 \pm 0.2\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -2.72 \pm 84\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -5.04 \pm 84\ kJ·mol^{-1}$

| Electronic Levels and Quantum Weights | | |
|---|---|---|
| State | $\epsilon_i$, $cm^{-1}$ | $g_i$ |
| $X[^2\Sigma^+]$ | 0 | 2 |
| $A[^2\Pi]$ | 15585.1 | 2 |
| | 15645.9 | 2 |
| $B[^2\Sigma^+]$ | 15711.2 | 2 |
| $C[^2\Pi]$ | 23314.0 | 2 |
| | 23741.9 | 2 |
| $D[^2\Sigma^+]$ | 31062.0 | 2 |
| | | 2 |

$\omega_e = 238.3\ cm^{-1}$ $\quad \omega_e x_e = 0.61\ cm^{-1}$ $\quad \sigma = 1$

$B_e = [0.0667]\ cm^{-1}$ $\quad \alpha_e = [0.00023]\ cm^{-1}$ $\quad r_e = [2.88]$ Å

### Enthalpy of Formation

The adopted $\Delta_f H°(0\ K) = -0.65 \pm 20\ kcal·mol^{-1}$ is calculated from the $D_0° = 3 \pm 1$ eV($69 \pm 23\ kcal·mol^{-1}$) selected by Gaydon.[1] A linear Birge–Sponer extrapolation of $\omega_e$ and $\omega_e x_e$ data[2] with a correction for the ionic character of the molecule as described by Hildenbrand[3] gave $D_0° = 66.5\ kcal·mol^{-1}$. Other $D_0°$ values are 63.9 $kcal·mol^{-1}$ [4] as a lower bound from a consideration of ionic bonding forces and 64 $kcal·mol^{-1}$ [5] derived as a lower bound from a consideration of energy conservation and measured reaction threshold relative kinetic energy from crossed molecular beam experiments. Of the four ratios, $D_0°(CaI)/\Delta_{at}H°(CaI_2)$, $D_0°(CaI) = 69\ kcal·mol^{-1}$ gives 0.445 which is closest to 0.46 found for a series of mono- and difluorides[6] and for other alkaline earth halide systems.[8] $\Delta_f H°(298.15\ K) = -1.21 \pm 20\ kcal·mol^{-1}$ is calculated from the adopted $\Delta_f H°(0\ K) = -0.65 \pm 20\ kcal·mol^{-1}$.

### Heat Capacity and Entropy

The ground state vibrational constants are from the compilation of Rosen.[2] The value of $r_e = 2.88$ Å is assumed the same as the bond distance in $CaI_2$.[7] $B_e$ is calculated from the adopted $r_e$. $\alpha_e$ is calculted assumung a Morse potential function.

The electronic levels and their probable designation are those given by Rosen.[2]

### References


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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 | −10.010 | −2.719 | −2 719 | INFINITE |
| 100 | 32.513 | 223.091 | 293.124 | −7.003 | −2.218 | −19.881 | 10.385 |
| 200 | 35.706 | 246.842 | 264.634 | −3.558 | −3.508 | −37.083 | 9.685 |
| 250 | 36.301 | 254.880 | 261.907 | −1.757 | −4.271 | −45.390 | 9.484 |
| 298.15 | 36.646 | 261.306 | 261.306 | 0. | −5.045 | −53.240 | 9.327 |
| 300 | 36.656 | 261.532 | 261.306 | 0.068 | −5.075 | −53.538 | 9.322 |
| 350 | 36.886 | 267.201 | 261.753 | 1.907 | −5.948 | −61.548 | 9.186 |
| 400 | 37.044 | 272.138 | 262.750 | 3.755 | −14.842 | −69.156 | 9 031 |
| 450 | 37.159 | 276.508 | 264.040 | 5.610 | −16.366 | −75.854 | 8.805 |
| 500 | 37.247 | 280.428 | 265.486 | 7.471 | −37.990 | −80.481 | 8.408 |
| 600 | 37.373 | 287.230 | 268.560 | 11.202 | −39.078 | −88.880 | 7.738 |
| 700 | 37.461 | 292.998 | 271.650 | 14.944 | −40.359 | −97.081 | 7.244 |
| 800 | 37.529 | 298.005 | 274.638 | 18 694 | −42.692 | −104.982 | 6.855 |
| 900 | 37.586 | 302.429 | 277.485 | 22.449 | −44.357 | −112.671 | 6.539 |
| 1000 | 37.635 | 306.392 | 280.181 | 26.211 | −46.318 | −120.159 | 6.276 |
| 1100 | 37.679 | 309.981 | 282.729 | 29.976 | −48.583 | −127.436 | 6.051 |
| 1200 | 37.720 | 313.261 | 285.139 | 33.746 | −58.889 | −133.871 | 5.827 |
| 1300 | 37.758 | 316.282 | 287.420 | 37.520 | −60.543 | −140.052 | 5.627 |
| 1400 | 37.795 | 319.081 | 289.583 | 41.298 | −62.209 | −146.106 | 5.451 |
| 1500 | 37.832 | 321.690 | 291.637 | 45.079 | −63.891 | −152.040 | 5.294 |
| 1600 | 37.868 | 324.133 | 293.593 | 48.864 | −65.595 | −157.861 | 5.154 |
| 1700 | 37.906 | 326.430 | 295.457 | 52.653 | −67.324 | −163.575 | 5.026 |
| 1800 | 37.946 | 328.597 | 297.239 | 56.445 | −217.755 | −166.975 | 4.845 |
| 1900 | 37.989 | 330.650 | 298.944 | 60.242 | −218.130 | −164.144 | 4.513 |
| 2000 | 38.037 | 332.600 | 300.578 | 64.043 | −218.541 | −161.292 | 4.213 |
| 2100 | 38.092 | 334.457 | 302.148 | 67.850 | −218.988 | −158.419 | 3.940 |
| 2200 | 38.155 | 336.231 | 303.657 | 71.662 | −219.472 | −155.523 | 3.693 |
| 2300 | 38.227 | 337.928 | 305.110 | 75.481 | −219.991 | −152.605 | 3.466 |
| 2400 | 38.310 | 339.557 | 306.512 | 79.308 | −220.544 | −149.663 | 3.257 |
| 2500 | 38.406 | 341.123 | 307.865 | 83.143 | −221.130 | −146.698 | 3.065 |
| 2600 | 38.516 | 342.631 | 309.173 | 86.989 | −221.747 | −143.709 | 2.887 |
| 2700 | 38.640 | 344.087 | 310.440 | 90.847 | −222.395 | −140 695 | 2.722 |
| 2800 | 38 779 | 345.495 | 311.667 | 94.718 | −223.073 | −137.657 | 2.568 |
| 2900 | 38.935 | 346.858 | 312.857 | 98.603 | −223.783 | −134.594 | 2.424 |
| 3000 | 39.107 | 348.181 | 314.012 | 102.505 | −224.525 | −131.506 | 2.290 |
| 3100 | 39.295 | 349.466 | 315.135 | 106.425 | −225.302 | −128.392 | 2.163 |
| 3200 | 39.499 | 350.717 | 316.228 | 110.365 | −226.117 | −125.253 | 2.045 |
| 3300 | 39.720 | 351.936 | 317.292 | 114.326 | −226.973 | −122.088 | 1.932 |
| 3400 | 39.955 | 353.125 | 318.328 | 118.309 | −227.875 | −118.897 | 1.827 |
| 3500 | 40.206 | 354.287 | 319.339 | 122.317 | −228.827 | −115.678 | 1.726 |
| 3600 | 40.471 | 355.423 | 320.325 | 126.351 | −229.832 | −112.431 | 1.631 |
| 3700 | 40 749 | 356.536 | 321.289 | 130.412 | −230.896 | −109.155 | 1.541 |
| 3800 | 41.039 | 357.626 | 322.231 | 134.501 | −232.024 | −105.850 | 1.455 |
| 3900 | 41.341 | 358.696 | 323.152 | 138.620 | −233.218 | −102.514 | 1.373 |
| 4000 | 41.652 | 359.747 | 324.054 | 142.770 | −234.483 | −99.147 | 1.295 |
| 4100 | 41.972 | 360.779 | 324.937 | 146.951 | −235.822 | −95.747 | 1.220 |
| 4200 | 42.299 | 361.794 | 325.803 | 151.164 | −237.237 | −92.313 | 1.148 |
| 4300 | 42.633 | 362.794 | 326.652 | 155.411 | −238.731 | −88.845 | 1.079 |
| 4400 | 42.971 | 363.778 | 327.484 | 159.691 | −240.303 | −85.342 | 1.013 |
| 4500 | 43.314 | 364 747 | 328.301 | 164.005 | −241.940 | −81.803 | 0.950 |
| 4600 | 43.659 | 365.703 | 329.104 | 168.354 | −243.663 | −78.226 | 0.888 |
| 4700 | 44 005 | 366.645 | 329.893 | 172.737 | −245.468 | −74.610 | 0.829 |
| 4800 | 44.351 | 367.576 | 330.668 | 177.155 | −247.349 | −70.955 | 0.772 |
| 4900 | 44.697 | 368.494 | 331.431 | 181.607 | −249.304 | −67.260 | 0.717 |
| 5000 | 45.040 | 369.400 | 332.181 | 186.094 | −251.330 | −63.524 | 0.664 |
| 5100 | 45.381 | 370.295 | 332.920 | 190.615 | −253.424 | −59.747 | 0.612 |
| 5200 | 45.717 | 371.180 | 333.647 | 195.170 | −255.578 | −55.929 | 0.562 |
| 5300 | 46.049 | 372.054 | 334.364 | 199.759 | −257.795 | −52.069 | 0.513 |
| 5400 | 46.375 | 372.918 | 335.069 | 204.380 | −260.067 | −48.166 | 0.466 |
| 5500 | 46.694 | 373.771 | 335.765 | 209.033 | −262.390 | −44.221 | 0.420 |
| 5600 | 47.006 | 374.616 | 336.452 | 213.718 | −264.748 | −40.233 | 0.375 |
| 5700 | 47.310 | 375 450 | 337.129 | 218.434 | −267.155 | −36.203 | 0.332 |
| 5800 | 47.606 | 376.276 | 337.796 | 223.180 | −269.598 | −32.130 | 0.289 |
| 5900 | 47.894 | 377 092 | 338.456 | 227.955 | −272.070 | −28.014 | 0.248 |
| 6000 | 48.171 | 377.899 | 339.106 | 232.759 | −274.567 | −23.857 | 0.208 |

PREVIOUS: June 1974 (1 atm) — CURRENT June 1974 (1 bar)

$S°(298.15\ K) = 145.29 \pm 0.21\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1052 \pm 2\ K$

$\Delta_fH°(0\ K) = -535.8 \pm 2.1\ kJ·mol^{-1}$
$\Delta_fH°(298.15\ K) = -536.8 \pm 2.1\ kJ·mol^{-1}$
$\Delta_{fus}H° = 41.84 \pm 0.84\ kJ·mol^{-1}$

### Enthalpy of Formation

Ehrlich, Peik and Koch[1] derived $\Delta_fH°(CaI_2, cr, 298.15\ K) = -128.1 \pm 0.4\ kcal·mol^{-1}$ from enthalpy of solution measurements of Ca(cr) and $CaI_2$(cr) in 0.1 N HI. An auxiliary HI enthalpy of solution value, $-13.22\ kcal·mol^{-1}$, calculated from data in referenece[2] was used in the derivation. This auxiliary value will be changed by incorporation of the accepted CODATA value of $\Delta_fH°(I^-, aq, std.\ state, 298.15\ K) = -13.60\ kcal·mol^{-1}$ [3] in the $\Delta_fH°$(HI, aq solution, 298.15 K) table, so that the above derived enthalpy of formation of $CaI_2$(cr) will be approximately $-128.6\ kcal·mol^{-1}$.

Combining $\Delta_fH°(Ca^{+2}, aq, std.\ state, 298.15\ K) = -129.74\ kcal·mol^{-1}$, selected by Parker[4,5] with the CODATA value for $I^-$(aq, std. state)[3] gives $\Delta_fH°(CaI_2, aq, std.\ state, 298.15\ K) = -156.94\ kcal\ mol^{-1}$ Further combination with the enthalpy of solution, $-28.62\ kcal·mol^{-1}$ [5,6] gives $\Delta_fH°(CaI_2, cr, 298.15\ K) = -128.32\ kcal·mol^{-1}$. This enthalpy of solution value was based on several sets of data, one of which was that of Ehrlich, *et al.*[1,6] We adopt $-128.3 \pm 0.5\ kcal·mol^{-1}$ ($-536.807\ kJ·mol^{-1}$) because of the correlation of $\Delta_fH°(Ca^{+2}, aq, std.\ state, 298.15\ K)$ with the evaluation of data for several calcium compounds.[4]

### Heat Capacity and Entropy

Paukov, Khriplovich, and Korotkikh[7] have measured $C_p°$ (13.10–309.18 K). Our $T^3$ extrapolation is in agreement with their vluccirclalues of $S°(13\ K) = 0.516\ cal·K^{-1}·mol^{-1}$ and $H°(13\ K)–H°(0\ K) = 4.99\ cal·K^{-1}·mol^{-1}$. The low temperature heat capacity joins smoothly with a linear extrapolation from $C_p° = 18.31\ cal·K^{-1}·mol^{-1}$ at 270 K to $C_p° = 22.0\ cal·K^{-1}·mol^{-1}$ at the adopted $T_{fus} = 1052$ K. The linearly extrapolated heat capacity at 300 K is only 0.3% higher than the Paukov *et al.*[7] value and $S°(298.15\ K) = 34.72\ cal·K^{-1}·mol^{-1}$ is in agreement with Paukov *et al.*[7] Dworkin and Bredig[8] determined the heat capacity of the crystal to be $23.2\ cal·K^{-1}·mol^{-1}$ (±5%) near the melting point. By using the lower limit, $C_p° = 22.0\ cal·K^{-1}·mol^{-1}$ of Dworkin and Bredig's value,[8] $H°(1052\ K)–H°(298.15\ K)$ is bluccirclrought down to 15.24 $kcal·mol^{-1}$, about 0 7% higher than Dworkin and Bredig's drop calorimeter measurement of 15.1 (±0.2%) $kcal·mol^{-1}$.[8]

### Fusion Data

Dworkin and Bredig[8] measured $\Delta_{fus}H° = 10\ 00\ kcal·mol^{-1}$ (±2%) at $T_{fus} = 1052$ K ($S°_{fus} = 9.5\ cal·K^{-1}·mol^{-1}$) by drop calorimetry. Emons and Loeffelholz[9] determined $\Delta_{fus}H° = 6.65\ kcal·mol^{-1}$ (±5%) and $T_{fus} = 1053$ K ($\Delta_{fus}S° = 6.3\ cal·K^{-1}\ mol^{-1}$) by high temperature cryoscopy. The two pair of investigators are in much better agreement with other salts.[9] An entropy of melting criteria for choosing one of these values is not conclusive because the entropies of melting of $CdI_2$, $CdCl_2$, and $CdBr_2$which have similar layer crystal structure range from 7.5 to 9.5 $cal·K^{-1}·mol^{-1}$.[10] Hutchison[11] found $T_{fus} = 1018$ K, noting that only approximate melting points were obtained.

Because drop calorimetry is a more direct measure of the enthalpy of melting, we adopt $\Delta_{fus}H° = 10.00 \pm 0.20\ kcal·mol^{-1}$ at $T_{fus} = 1052 \pm 2$ K.

Although unconfirmed by direct experimental evidence, the discrepancy in enthalpy of melting and the adjustments required in joining low temperature and high temperature heat capacities might be explained by the existence of a solid state transition in $CaI_2$ similar to the transitions in $BaCl_2$, $SrBr_2$, or $SrCl_2$.[8]

### Sublimation Data

$\Delta_{sub}H°(298.15\ K)$ is calculated as the difference between the enthalpies of formation at 298.15 K of the ideal gas and crystal states.

### References


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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 | −17.965 | −535.838 | −535.838 | INFINITE |
| 100 | 61.840 | 67.860 | 210.957 | −14.310 | −536.213 | −535.303 | 279.614 |
| 200 | 73.304 | 115.131 | 152.260 | −7.426 | −536.530 | −534.267 | 139.536 |
| 298.15 | 77.157 | 145.287 | 145.287 | 0. | −536.807 | −533.097 | 93.396 |
| 300 | 77.195 | 145.764 | 145.288 | 0.143 | −536.813 | −533.074 | 92.816 |
| 400 | 79.161 | 168.244 | 148.340 | 7.962 | −553.267 | −531.211 | 69.369 |
| 500 | 81.170 | 186.124 | 154.168 | 15.978 | −596.213 | −521.572 | 54.488 |
| 600 | 83.136 | 201.097 | 160.775 | 24.194 | −594.694 | −506.786 | 44.120 |
| 700 | 85.103 | 214.060 | 167.481 | 32.605 | −593.188 | −492.254 | 36.732 |
| 800 | 87.069 | 225.553 | 174.035 | 41.214 | −592.553 | −477.833 | 31.199 |
| 900 | 89.036 | 235.921 | 180.344 | 50.019 | −591.064 | −463.583 | 26.906 |
| 1000 | 91.002 | 245.403 | 186.383 | 59.021 | −589.684 | −449.494 | 23.479 |
| 1052.000 | 92.048 | 250.043 | 189.416 | 63.780 | --- CRYSTAL <---> LIQUID --- | | |
| 1100 | 93.000 | 254.171 | 192.152 | 68.221 | −588.422 | −435.537 | 20.682 |
| 1200 | 94.977 | 262.348 | 197.664 | 77.620 | −595.016 | −421.067 | 18.329 |
| 1300 | 96.943 | 270.028 | 202.938 | 87.216 | −592.776 | −406.661 | 16.340 |
| 1400 | 98.910 | 277.284 | 207.992 | 97.009 | −590.370 | −392.433 | 14 642 |
| 1500 | 100.876 | 284.175 | 212.843 | 106.998 | −587.808 | −378.384 | 13.176 |

PREVIOUS: CURRENT: June 1974

## Calcium Iodide ($CaI_2$) LIQUID $M_r = 293.8890$

$S°(298.15\ K) = [178.942]\ J·K^{-1}·mol^{-1}$

$T_{fus} = 1052 \pm 2\ K$

$\Delta_f H°(298.15\ K) = [-500.170]\ kJ·mol^{-1}$

$\Delta_{fus} H° = 41.84 \pm 0.84\ kJ·mol^{-1}$

### Enthalpy of Formation

$\Delta_f H°(CaI_2, l, 298.15\ K)$ is calculated from the sum of the enthalpy of formation of the crystal, the enthalpy of melting, and the difference in enthalpy, $H°(1052\ K) - H°(298\ 15\ K)$, between the crystal and the liquid.

### Heat Capacity and Entropy

The liquid heat capacity near the melting point, 24.7 $cal·K^{-1}·mol^{-1}$, was derived by Dworkin and Bredig[1] from drop calorimetric measurements. This value is adopted and is assumed constant from 700 K to 2500 K. A glass transition is assumed at 700 K below which the heat capacity is that of the crystal.

$S°(CaI_2, l, 298.15\ K)$ is calculated from the crystal entropy in a manner similar to that used for the enthalpy of formation calculation.

### Vaporization Data

The temperature at which $\Delta_r G° = 0$ for the reaction $CaI_2(l) = CaI_2(g)$ at one bar is $T_{vap}$. Peterson and Hutchison[2] have extrapolated Knudsen effusion cell measurements in the 1076–1294 K range to obtain a normal boiling point of 1831 K (at 1 atm).

$\Delta_{vap} H°$ is the calculated difference between the enthalpies of formation of the ideal gas and the liquid at $T_{vap}$. Refer to the ideal gas table for details.

### References

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Calcium Iodide ($CaI_2$) $Ca_1I_2(l)$

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

| $T$/K | $C_p°$ | $S°$ | $-[G°-H°(T_r)]/T$ | $H°-H°(T_r)$ | $\Delta_f H°$ | $\Delta_f G°$ | log $K_f$ |
|---|---|---|---|---|---|---|---|
| | $J·K^{-1}·mol^{-1}$ | | | $kJ·mol^{-1}$ | | | |
| 0 | | | | | | | |
| 100 | | | | | | | |
| 200 | | | | | | | |
| 298.15 | 77.157 | 178.942 | 178.942 | 0. | −500.170 | −506.494 | 88.736 |
| 300 | 77.195 | 179.419 | 178.943 | 0.143 | −500.176 | −506.534 | 88.195 |
| 400 | 79.161 | 201.899 | 181.995 | 7.962 | −516.630 | −508.036 | 66.343 |
| 500 | 81.170 | 219.779 | 187.823 | 15.978 | −559.576 | −501.762 | 52.419 |
| 600 | 83.136 | 234.752 | 194.430 | 24.194 | −558.057 | −490.342 | 42.688 |
| 700 | 85.103 | 247.715 | 201.136 | 32.605 | −556.551 | −479.176 | 35.757 |
| 700.000 | 85.103 | 247.715 | 201.136 | 32.605 | GLASS <- -> LIQUID | | |
| 700.000 | 103.345 | 247.715 | 201.136 | 32.605 | TRANSITION | | |
| 800 | 103.345 | 261.515 | 207.840 | 42.940 | −554.190 | −468.240 | 30.573 |
| 900 | 103.345 | 273.687 | 214.494 | 53.274 | −551 171 | −457.680 | 26.563 |
| 1000 | 103.345 | 284.576 | 220.967 | 63.609 | −548 459 | −447.441 | 23.372 |
| 1052.000 | 103.345 | 289.815 | 224.242 | 68.983 | - - - CRYSTAL <- -> LIQUID - - - | | |
| 1100 | 103.345 | 294.426 | 227.204 | 73.943 | −546.063 | −437.458 | 20.773 |
| 1200 | 103.345 | 303.418 | 233.186 | 84.278 | −551.721 | −427.056 | 18.589 |
| 1300 | 103.345 | 311.690 | 238.911 | 94.612 | −548.742 | −416.788 | 16.747 |
| 1400 | 103.345 | 319.349 | 244.387 | 104.947 | −545.795 | −406 749 | 15.176 |
| 1500 | 103.345 | 326.479 | 249.624 | 115.281 | −542.888 | −396.919 | 13.822 |
| 1600 | 103.345 | 333.148 | 254.638 | 125.616 | −540.030 | −387.281 | 12.643 |
| 1700 | 103.345 | 339.414 | 259 443 | 135.950 | −537.232 | −377.820 | 11.609 |
| 1800 | 103.345 | 345.321 | 264 051 | 146.285 | −683.172 | −366.311 | 10.630 |
| 1900 | 103.345 | 350 908 | 268.477 | 156.619 | −679.094 | −348.819 | 9.590 |
| 2000 | 103.345 | 356.209 | 272.732 | 166.954 | −675.092 | −331.540 | 8.659 |
| 2100 | 103.345 | 361.251 | 276.828 | 177.288 | −671.165 | −314.459 | 7.822 |
| 2200 | 103.345 | 366.059 | 280.776 | 187.623 | −667.312 | −297.564 | 7.065 |
| 2300 | 103.345 | 370.653 | 284.584 | 197.957 | −663.528 | −280.842 | 6.378 |
| 2400 | 103.345 | 375.051 | 288.263 | 208.292 | −659.808 | −264.284 | 5.752 |
| 2500 | 103.345 | 379.270 | 291.819 | 218.626 | −656.147 | −247.879 | 5.179 |

PREVIOUS:  CURRENT: June 1974

Calcium Iodide ($CaI_2$) $Ca_1I_2(l)$

0 to 1052 K crystal
above 1052 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

| | $J \cdot K^{-1} \cdot mol^{-1}$ | | | $kJ \cdot mol^{-1}$ | | | |
|---|---|---|---|---|---|---|---|
| $T$/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 | −17.965 | −535.838 | −535.838 | INFINITE |
| 100 | 61.840 | 67.860 | 210.957 | −14.310 | −536.213 | −535.303 | 279.614 |
| 200 | 73.304 | 115.131 | 152.260 | −7.426 | −536.530 | −534.267 | 139.536 |
| 298.15 | 77.157 | 145.287 | 145.287 | 0. | −536.807 | −533.097 | 93.396 |
| 300 | 77.195 | 145.764 | 145.288 | 0.143 | −536.813 | −533.074 | 92.816 |
| 400 | 79.161 | 168.244 | 148.340 | 7.962 | −553.267 | −531.211 | 69.369 |
| 500 | 81.170 | 186.124 | 154.168 | 15.978 | −596.213 | −521.572 | 54.488 |
| 600 | 83.136 | 201.097 | 160.775 | 24.194 | −594.694 | −506.786 | 44.120 |
| 700 | 85.103 | 214.060 | 167.481 | 32.605 | −593.188 | −492.254 | 36.732 |
| 800 | 87.069 | 225.553 | 174.035 | 41.214 | −592.553 | −477.833 | 31.199 |
| 900 | 89.036 | 235.921 | 180.344 | 50.019 | −591.064 | −463.583 | 26.906 |
| 1000 | 91.002 | 245.403 | 186.383 | 59.021 | −589.684 | −449.494 | 23.479 |
| 1052.000 | 92.048 | 250.043 | 189.416 | 63.780 | CRYSTAL <--> LIQUID TRANSITION | | |
| 1052.000 | 103.345 | 289.815 | 189.416 | 105.620 | | | |
| 1100 | 103.345 | 294.426 | 193.898 | 110.580 | −546.063 | −437.458 | 20.773 |
| 1200 | 103.345 | 303.418 | 202.655 | 120.915 | −551.721 | −427.056 | 18.589 |
| 1300 | 103.345 | 311.690 | 210.729 | 131.249 | −548.742 | −416.788 | 16.747 |
| 1400 | 103.345 | 319.349 | 218.217 | 141.584 | −545.795 | −406.749 | 15.176 |
| 1500 | 103.345 | 326.479 | 225.200 | 151.918 | −542.888 | −396.919 | 13.822 |
| 1600 | 103.345 | 333.148 | 231.740 | 162.253 | −540.030 | −387.281 | 12.643 |
| 1700 | 103.345 | 339.414 | 237.892 | 172.587 | −537.232 | −377.820 | 11.609 |
| 1800 | 103.345 | 345.321 | 243.697 | 182.922 | −683.172 | −366.311 | 10.630 |
| 1900 | 103.345 | 350.908 | 249.194 | 193.256 | −679.094 | −348.819 | 9.590 |
| 2000 | 103.345 | 356.209 | 254.414 | 203.591 | −675.092 | −331.540 | 8.659 |
| 2100 | 103.345 | 361.251 | 259.382 | 213.925 | −671.165 | −314.459 | 7.822 |
| 2200 | 103.345 | 366.059 | 264.123 | 224.260 | −667.312 | −297.564 | 7.065 |
| 2300 | 103.345 | 370.653 | 268.655 | 234.594 | −663.528 | −280.842 | 6.378 |
| 2400 | 103.345 | 375.051 | 272.997 | 244.929 | −659.808 | −264.284 | 5.752 |
| 2500 | 103.345 | 379.270 | 277 164 | 255.263 | −656.147 | −247.879 | 5.179 |

PREVIOUS: CURRENT: June 1974

$S°(298.15\ K) = [327.57 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -255.2 \pm 17\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -258.2 \pm 17\ kJ \cdot mol^{-1}$

| Vibrational Frequencies and Degeneracies $\upsilon$, $cm^{-1}$ |
|---|
| [117](1) |
| [45](2) |
| [316](1) |

Ground State Quantum Weight = [1] $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distance. Ca–I = 2.88 ± 0.03 Å
Bond Angle: I–Ca–I = [180]°
Rotational Constant: $B_0 = 0.008008\ cm^{-1}$

## Enthalpy of Formation

Peterson and Hutchison[1] used a weight loss Knudsen effusion technique to observe vapor pressures of the liquid at 18 temperatures ranging from 1076 K to 1294 K. Our 2nd and 3rd law analyses of these data, after rejection of one point due to failure of a statistical test, yield $\Delta_{vap}H°(298.15\ K)$ (2nd law) = 60.83 ± 2.04 kcal $mol^{-1}$ and $\Delta_{vap}H°(298.15\ K)$ (3rd law) = 57.84 ± 0 98 kcal·$mol^{-1}$ with a drift of −2.6 ± 1.7 cal·$K^{-1}$·$mol^{-1}$. We adopt $\Delta_{vap}H°(298.15\ K) = 57.8 \pm 3$ kcal·$mol^{-1}$ and combine that with the adopted enthalpy of formation of the liquid to obtain $\Delta_f H°(CaI_2, g, 298.15\ K) = -61.7 \pm 4$ kcal·$mol^{-1}$(−258.153 ± 17 kJ·$mol^{-1}$).

## Heat Capacity and Entropy

The bond distance, as determined from an electron diffraction study, is taken from Akishin *et al* [3] who also judged that the bond angle was 180° ± 10–20°. We have assumed a linear structure.

To estimate the vibrational frequencies, the stretching force constants for gaseous CaF, $CaF_2$, CaCl, and $CaCl_2$ are calculated from the vibrational frequencies[4] using a valence force model The trend in the ratio of $k$(monohalide)/$k_1$(dihalide) indicates that $k(CaI)/k_1(CaI_2) = 1$ is a reasonable approximation, an approximation which has been used by Brewer *et al* [5] The stretching force constant for CaI(g) is calculated from the ground state vibrational frequency given by Rosen.[6] The bending force constant is assumed to be 0.01 times the stretching force constant.[5] The adopted vibrational frequencies are calculated from the estimated force constants. Other estimates for $\upsilon_1$, $\upsilon_2$, and $\upsilon_3$, are 121, 77, 327[7] and 118, 45, 321.[5]

We assign an uncertainty of ±2 cal·$K^{-1}$·$mol^{-1}$ to the entropy to allow for error in bond angle and vibrational frequency estimates.

## References


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[3] P. A. Akishin, V. P. Spiridonov and G A. Sobolev, Zhur. Fiz. Khim. 31, 648 (1957).
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Enthalpy Reference Temperature = $T_r$ = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

| $T$/K | $C_p°$ (J·$K^{-1}$·$mol^{-1}$) | $S°-[G°-H°(T_r)]/T$ (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 | −16.011 | −255.230 | −255.230 | INFINITE |
| 100 | 53.623 | 264.518 | 380.113 | −11.559 | −254.808 | −273.564 | 142.895 |
| 200 | 58.924 | 303.667 | 333.072 | −5.881 | −256.331 | −291.775 | 76.204 |
| 250 | 60.001 | 316.942 | 328.564 | −2.905 | −257.233 | −300.533 | 62.793 |
| 298.15 | 60.636 | 327.569 | 327.569 | 0. | −258.153 | −308.790 | 54 099 |
| 300 | 60.655 | 327.944 | 327.570 | 0.112 | −258.189 | −309.104 | 53.820 |
| 350 | 61.076 | 337.327 | 328.310 | 3.156 | −259.263 | −317.508 | 47.385 |
| 400 | 61.360 | 345.503 | 329.959 | 6.217 | −276.357 | −325.205 | 42.467 |
| 450 | 61.561 | 352.742 | 332.096 | 9.291 | −278.680 | −331.171 | 38.441 |
| 500 | 61.707 | 359.236 | 334.491 | 12.373 | −321 164 | −333.079 | 34.796 |
| 600 | 61.901 | 370.505 | 339.582 | 18.554 | −321.679 | −335.416 | 29.201 |
| 700 | 62.020 | 380.057 | 344.699 | 24.750 | −322.389 | −337.653 | 25.196 |
| 800 | 62.098 | 388.344 | 349.648 | 30.957 | −324.156 | −339.669 | 22.178 |
| 900 | 62.152 | 395.661 | 354.362 | 37.169 | −325.259 | −341.545 | 19.823 |
| 1000 | 62 191 | 402.212 | 358.825 | 43.386 | −326.664 | −343.282 | 17.931 |
| 1100 | 62.220 | 408.141 | 363.043 | 49.607 | −328.382 | −344.863 | 16.376 |
| 1200 | 62.242 | 413.556 | 367.030 | 55.830 | −338.151 | −345.652 | 15.046 |
| 1300 | 62.259 | 418.538 | 370.803 | 62.055 | −339.282 | −346.231 | 13.912 |
| 1400 | 62.272 | 423.153 | 374.380 | 68.282 | −340.443 | −346.722 | 12.936 |
| 1500 | 62.283 | 427.449 | 377.776 | 74.510 | −341.642 | −347.129 | 12.088 |
| 1600 | 62.292 | 431.469 | 381.008 | 80.738 | −342.890 | −347.454 | 11.343 |
| 1700 | 62.300 | 435.246 | 384.088 | 86.968 | −344.197 | −347.700 | 10.684 |
| 1800 | 62.306 | 438.807 | 387.030 | 93.198 | −494.241 | −345.656 | 10.031 |
| 1900 | 62.311 | 442.176 | 389.845 | 99.429 | −494.267 | −337.401 | 9.276 |
| 2000 | 62.316 | 445.372 | 392.542 | 105.661 | −494.367 | −329.143 | 8.596 |
| 2100 | 62.320 | 448.413 | 395.131 | 111.892 | −494.543 | −320.877 | 7.981 |
| 2200 | 62.323 | 451.312 | 397.619 | 118.125 | −494.792 | −312.602 | 7.422 |
| 2300 | 62.326 | 454.083 | 400.014 | 124.357 | −495.111 | −304.314 | 6.911 |
| 2400 | 62.329 | 456.735 | 402.323 | 130.590 | −495.493 | −296.010 | 6.442 |
| 2500 | 62.331 | 459.280 | 404.550 | 136.823 | −495.933 | −287.690 | 6 011 |
| 2600 | 62.333 | 461.724 | 406.703 | 143.056 | −496.426 | −279.350 | 5.612 |
| 2700 | 62.335 | 464.077 | 408.784 | 149.289 | −496.966 | −270.991 | 5.243 |
| 2800 | 62.337 | 466.344 | 410.800 | 155.523 | −497.550 | −262.611 | 4.899 |
| 2900 | 62.338 | 468.531 | 412.753 | 161.757 | −498.174 | −254.209 | 4.579 |
| 3000 | 62.339 | 470.645 | 414.648 | 167.991 | −498.836 | −245.786 | 4.280 |
| 3100 | 62.341 | 472.689 | 416.487 | 174.225 | −499.535 | −237.339 | 3.999 |
| 3200 | 62.342 | 474.668 | 418.275 | 180.459 | −500.274 | −228.870 | 3.736 |
| 3300 | 62.343 | 476.586 | 420.013 | 186.693 | −501.054 | −220.376 | 3.488 |
| 3400 | 62.343 | 478.448 | 421.704 | 192.927 | −501.877 | −211.859 | 3.255 |
| 3500 | 62.344 | 480.255 | 423.351 | 199.162 | −502.748 | −203.316 | 3.034 |
| 3600 | 62.345 | 482.011 | 424.957 | 205.396 | −503.672 | −194.748 | 2.826 |
| 3700 | 62.346 | 483.719 | 426.522 | 211.631 | −504.653 | −186.153 | 2.628 |
| 3800 | 62.346 | 485.382 | 428.049 | 217.865 | −505.695 | −177.531 | 2.440 |
| 3900 | 62.347 | 487.001 | 429.540 | 224.100 | −506.805 | −168.881 | 2.262 |
| 4000 | 62.348 | 488.580 | 430.996 | 230.335 | −507.986 | −160.202 | 2.092 |
| 4100 | 62.348 | 490.119 | 432.420 | 236.569 | −509.243 | −151.492 | 1.930 |
| 4200 | 62.349 | 491.622 | 433.811 | 242.804 | −510.580 | −142.750 | 1.775 |
| 4300 | 62.349 | 493.089 | 435.173 | 249.039 | −512.000 | −133.976 | 1.627 |
| 4400 | 62.349 | 494.522 | 436.506 | 255.274 | −513.502 | −125.168 | 1.486 |
| 4500 | 62.350 | 495.924 | 437.810 | 261.509 | −515.076 | −116.325 | 1.350 |
| 4600 | 62.350 | 497.294 | 439.089 | 267.744 | −516.745 | −107.446 | 1.220 |
| 4700 | 62.350 | 498.635 | 440.341 | 273.979 | −518.504 | −98.530 | 1.095 |
| 4800 | 62.351 | 499.948 | 441.570 | 280.214 | −520.349 | −89.574 | 0.975 |
| 4900 | 62.351 | 501.233 | 442.774 | 286.449 | −522.279 | −80.580 | 0.859 |
| 5000 | 62.351 | 502.493 | 443.956 | 292.684 | −524.290 | −71.546 | 0.747 |
| 5100 | 62.352 | 503.728 | 445.116 | 298.919 | −526.381 | −62.470 | 0.640 |
| 5200 | 62.352 | 504.938 | 446.255 | 305.155 | −528.544 | −53.353 | 0.536 |
| 5300 | 62.352 | 506.126 | 447.373 | 311.390 | −530.783 | −44.194 | 0.436 |
| 5400 | 62.352 | 507.291 | 448.472 | 317.625 | −533.090 | −34.991 | 0.338 |
| 5500 | 62.352 | 508.436 | 449.552 | 323.860 | −535.461 | −25.746 | 0.245 |
| 5600 | 62.353 | 509.559 | 450.613 | 330.096 | −537.881 | −16.457 | 0.154 |
| 5700 | 62.353 | 510.663 | 451.657 | 336.331 | −540.362 | −7.124 | 0.065 |
| 5800 | 62.353 | 511.747 | 452.684 | 342.566 | −542.892 | 2.253 | −0.020 |
| 5900 | 62.353 | 512.813 | 453.694 | 348.801 | −545.465 | 11.674 | −0 103 |
| 6000 | 62.353 | 513.861 | 454.688 | 355.037 | −548.075 | 21.139 | −0.184 |

PREVIOUS June 1974 (1 atm) CURRENT. June 1974 (1 bar)

$S°(298.15\ K) = 38.212 \pm 0.13\ J·K^{-1}·mol^{-1}$
$T_{fus} = 3200 \pm 50\ K$

$\Delta_f H°(0\ K) = -631.76 \pm 0.88\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -635.09 \pm 0.88\ kJ·mol^{-1}$
$\Delta_{fus} H° = [79.5]\ kJ·mol^{-1}$

### Enthalpy of Formation

Huber and Holley[1] determined the enthalpy of combustion of calcium metal in a bomb calorimeter and derived the enthalpy of formation of calcium oxide (cr) as −151.9 kcal·mol$^{-1}$ which is adopted in the tabulation. The adopted value is in good agreement with the value, −151.9 kcal·mol$^{-1}$ [2] derived from solution calorimetry.

### Heat Capacity and Entropy

Gmelin[3] measured low temperature $C_p$ data from 4 to 300 K in an adiabatic calorimeter. We use his smoothed $C_p$ values to derive $S°(298.15\ K) = 9.133 \pm 0.03$ cal·K$^{-1}$·mol$^{-1}$ based on $S° = 0.0001$ cal·K$^{-1}$·mol$^{-1}$ at 4 K. Lander[4] determined high temperature enthalpy data from 563.6 to 1176.4 K by drop calorimetry. The low temperature $C_p$ and high temperature enthalpy data are smoothly joined at 298.15 K by a polynomial curve fitting method. The deviations of the observed enthalpies from the adopted values are about 0.2–1%, except the enthalpy value at 753 K (2.0%). Heat capacities above 1200 K are extrapolated from the adopted $C_p$ functions. The extrapolated $C_p$ at the melting point (2887 K), 14.8 J·K·mol$^{-1}$, is in reasonable agreement with the value $2 \times 7.25$ cal·K$^{-1}$ g-atom$^{-1}$ suggested by Kubaschewski.[5]

Combination of the earlier low temperature $C_p$ measurements of Nernst and Schwers (28–90 K)[6] and Parks and Kelley (87–293 K)[7] yields $S°(298.15\ K) = 9.5 \pm 0.2$ cal·K$^{-1}$·mol$^{-1}$, based on $S°(298.15\ K) = 0.04$ cal·K$^{-1}$·mol$^{-1}$.[8] These $C_p$ measurements are less accurate than those of Gmelin,[3] and are not adopted in the tabulation.

Fischer and Ertmer[9] determined high temperature enthalpy data by drop calorimetry in the temperature range from 0° to 1716°C. The accuracy was claimed to be approximately ±4%. We have not adopted their enthalpy data in the tabulation since the heat capacities which we derive from their data are always less than those of MgO[10] when the temperature is above 1000 K. The deviations between their enthalpy data and the adopted values are approximately 1.8% at 693 K, 3.3% at 1283 K and 5.3% at 1989 K.

### Fusion Data

Schneider[11] adjusted earlier melting points[12–15] to IPTS–48, yielding values ranging from 2565° to 2630°C. Recent studies by Foex,[16, 17] using solar energy to melt the center of a rotating crucible of oxide, gave values higher by about 300°C. Apparently the earlier values were depressed by formation of tungstates with the tungsten supports of the sample. Unfortunately, Foex reported three values: 2910°C (1968),[16] 2950°C(1968),[16] and 2900°C(1969).[17] We adopt an intermediate value of 2927°C = 3200 K and arbitrarily assign an uncertainty of 50 K.

The enthalpy of melting is assumed to be 19 kcal·mol$^{-1}$ which is calculated from the estimated $\Delta_{fus} S° = 6$ cal·K$^{-1}$·mol$^{-1}$ at the melting point. The latter is estimated to be the same as that of MgO.[10]

### References


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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 | −6.749 | −631.760 | −631.760 | INFINITE |
| 100 | 14.715 | 6.222 | 69.166 | −6.294 | −633.739 | −624.099 | 325.996 |
| 200 | 33.677 | 23.041 | 41.825 | −3.757 | −634.925 | −613.887 | 160.331 |
| 298.15 | 42.120 | 38.212 | 38.212 | 0. | −635.089 | −603.501 | 105.731 |
| 300 | 42.242 | 38.473 | 38.213 | 0.078 | −635.086 | −603.305 | 105.045 |
| 400 | 46.626 | 51.300 | 39.932 | 4.547 | −634.738 | −592.755 | 77.406 |
| 500 | 48.982 | 61.980 | 43.305 | 9.338 | −634.242 | −582.316 | 60.834 |
| 600 | 50.480 | 71.052 | 47.193 | 14.315 | −633.787 | −571.975 | 49.795 |
| 700 | 51.555 | 78.917 | 51.175 | 19.419 | −633.449 | −561.701 | 41.915 |
| 800 | 52.400 | 85.858 | 55.085 | 24.618 | −634.112 | −551.362 | 36.000 |
| 900 | 53.112 | 92.072 | 58.856 | 29.894 | −634.064 | −541.024 | 31.400 |
| 1000 | 53.735 | 97.700 | 62.463 | 35.237 | −634.273 | −530.677 | 27.720 |
| 1100 | 54.300 | 102.849 | 65.904 | 40.639 | −634.749 | −520.297 | 24.707 |
| 1200 | 54.831 | 107.596 | 69.183 | 46.096 | −643.226 | −509.239 | 22.167 |
| 1300 | 55.329 | 112.005 | 72.309 | 51.604 | −643.009 | −498.082 | 20.013 |
| 1400 | 55.810 | 116.123 | 75.293 | 57.161 | −642.759 | −486.943 | 18.168 |
| 1500 | 56.275 | 119.989 | 78.146 | 62.766 | −642.475 | −475.823 | 16.570 |
| 1600 | 56.727 | 123.636 | 80.876 | 68.416 | −642.159 | −464.723 | 15.172 |
| 1700 | 57.174 | 127.088 | 83.494 | 74.111 | −641.810 | −453.644 | 13.939 |
| 1800 | 57.609 | 130.369 | 86.007 | 79.850 | −790.102 | −440.375 | 12.779 |
| 1900 | 58.045 | 133.495 | 88.425 | 85.633 | −788.275 | −420.996 | 11.574 |
| 2000 | 58.471 | 136.483 | 90.754 | 91.459 | −786.423 | −401.713 | 10.492 |
| 2100 | 58.894 | 139.346 | 93.000 | 97.327 | −784.547 | −382.523 | 9.515 |
| 2200 | 59.317 | 142.096 | 95.170 | 103.238 | −782.651 | −363.423 | 8.629 |
| 2300 | 59.735 | 144.742 | 97.268 | 109.190 | −780.739 | −344.411 | 7.822 |
| 2400 | 60.149 | 147.293 | 99.299 | 115.184 | −778.816 | −325.481 | 7.084 |
| 2500 | 60.563 | 149.757 | 101.269 | 121.220 | −776.887 | −306.632 | 6.407 |
| 2600 | 60.978 | 152.140 | 103.180 | 127.297 | −774.958 | −287.860 | 5.783 |
| 2700 | 61.388 | 154.449 | 105.036 | 133.415 | −773.036 | −269.161 | 5.207 |
| 2800 | 61.798 | 156.689 | 106.841 | 139.575 | −771.126 | −250.534 | 4.674 |
| 2900 | 62.208 | 158.865 | 108.597 | 145.775 | −769.238 | −231.976 | 4.178 |
| 3000 | 62.618 | 160.981 | 110.308 | 152.016 | −767.378 | −213.481 | 3.717 |
| 3100 | 63.024 | 163.040 | 111.976 | 158.298 | −765.554 | −195.048 | 3.287 |
| 3200 | 63.434 | 165.048 | 113.604 | 164.621 | −763.774 | −176.673 | 2.884 |
| 3200.000 | 63.434 | 165.048 | 113.604 | 164.621 | --- CRYSTAL <---> LIQUID --- | | |
| 3300 | 63.839 | 167.006 | 115.192 | 170.985 | −762.047 | −158.353 | 2.507 |
| 3400 | 64.245 | 168.918 | 116.744 | 177.389 | −760.379 | −140.084 | 2.152 |
| 3500 | 64.651 | 170.786 | 118.262 | 183.834 | −758.779 | −121.864 | 1.819 |
| 3600 | 65.057 | 172.613 | 119.746 | 190.319 | −757.254 | −103.688 | 1.504 |

PREVIOUS: June 1971 CURRENT: June 1973

## Calcium Oxide (CaO) LIQUID $M_r = 56.0794$ Calcium Oxide (CaO) $Ca_1O_1(l)$

$S°(298.15\ K) = [62.321]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 3200 \pm 50\ K$

$\Delta_f H°(298.15\ K) = [-557.335]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [79.5]\ kJ·mol^{-1}$

### Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from $\Delta_f H°$(cr, 298.15 K) by adding $\Delta_{fus}H$ and the difference in enthalpy, $H°(3200\ K)-H°(298.15\ K)$, between the crystal and liquid.

### Heat Capacity and Entropy

A glass transition is assumed at 2100 K. Heat capacities of the liquid below 2100 K are assumed to be the same as those of the crystal. Above 2100 K the heat capacity is assumed to be constant at 7.50 $cal·K^{-1}$ $g\text{-}atom^{-1}$.

The entropy at 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.

### Decomposition

CaO does not vaporize simply to CaO(g); extensive dissociation of CaO(g) to Ca(g) was found mass-spectrometrically.[1]

### Reference

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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 | 42.120 | 62.321 | 62.321 | 0. | −557.335 | −532.935 | 93.368 |
| 300 | 42.242 | 62.582 | 62.322 | 0.078 | −557.332 | −532.783 | 92.766 |
| 400 | 46.626 | 75.409 | 64.041 | 4.547 | −556.984 | −524.644 | 68.511 |
| 500 | 48.982 | 86.089 | 67.413 | 9.338 | −556.488 | −516.616 | 53.971 |
| 600 | 50.480 | 95.160 | 71.301 | 14.315 | −556.033 | −508.686 | 44.285 |
| 700 | 51.555 | 103.026 | 75.284 | 19.419 | −555.695 | −500.823 | 37.372 |
| 800 | 52.400 | 109.966 | 79.194 | 24.618 | −556.358 | −492.895 | 32.183 |
| 900 | 53.112 | 116.180 | 82.964 | 29.894 | −556.310 | −484 968 | 28.147 |
| 1000 | 53.735 | 121.809 | 86.572 | 35.237 | −556.519 | −477.032 | 24.918 |
| 1100 | 54.300 | 126.957 | 90.012 | 40.639 | −556.995 | −469.062 | 22.274 |
| 1200 | 54.831 | 131.705 | 93.291 | 46.096 | −565.472 | −460.415 | 20.041 |
| 1300 | 55.329 | 136.114 | 96.418 | 51.604 | −565.255 | −451.669 | 18.148 |
| 1400 | 55.810 | 140.232 | 99.402 | 57.161 | −565.005 | −442.941 | 16.526 |
| 1500 | 56.275 | 144.098 | 102.254 | 62.766 | −564.721 | −434.232 | 15 121 |
| 1600 | 56.727 | 147.744 | 104.984 | 68.416 | −564.405 | −425.543 | 13.893 |
| 1700 | 57.174 | 151.197 | 107.602 | 74.111 | −564.056 | −416.874 | 12.809 |
| 1800 | 57.609 | 154.477 | 110.116 | 79.850 | −712.348 | −406.017 | 11.782 |
| 1900 | 58.045 | 157.604 | 112.534 | 85.633 | −710.521 | −389 048 | 10.696 |
| 2000 | 58.471 | 160.592 | 114.862 | 91.459 | −708.669 | −372.176 | 9.720 |
| 2100 | 58.894 | 163.455 | 117.109 | 97.327 | −706.793 | −355.397 | 8.840 |
| 2100.000 | 58.894 | 163.455 | 117.109 | 97.327 | GLASS <--> LIQUID TRANSITION | | |
| 2100.000 | 62.760 | 163.455 | 117.109 | 97.327 | | | |
| 2200 | 62.760 | 166.374 | 119.282 | 103.603 | −704.531 | −338.717 | 8.042 |
| 2300 | 62.760 | 169.164 | 121.391 | 109.879 | −702.296 | −322.140 | 7.316 |
| 2400 | 62.760 | 171.835 | 123.437 | 116.155 | −700.092 | −305.659 | 6.652 |
| 2500 | 62.760 | 174.397 | 125.425 | 122.431 | −697.922 | −289.269 | 6.044 |
| 2600 | 62.760 | 176.859 | 127.356 | 128.707 | −695.794 | −272.965 | 5.484 |
| 2700 | 62.760 | 179.227 | 129.234 | 134.983 | −693.714 | −256.741 | 4.967 |
| 2800 | 62.760 | 181.510 | 131.060 | 141.259 | −691.688 | −240.594 | 4 488 |
| 2900 | 62.760 | 183.712 | 132.838 | 147.535 | −689.724 | −224.519 | 4.044 |
| 3000 | 62.760 | 185.840 | 134.569 | 153.811 | −687.829 | −208.510 | 3.630 |
| 3100 | 62.760 | 187.898 | 136.257 | 160.087 | −686.011 | −192.562 | 3.245 |
| 3200 | 62.760 | 189.890 | 137.902 | 166.363 | −684.278 | −176.673 | 2.884 |
| 3200.000 | 62.760 | 189.890 | 137.902 | 166.363 | --- CRYSTAL <--> LIQUID --- | | |
| 3300 | 62.760 | 191.821 | 139.507 | 172.639 | −682.638 | −160.836 | 2.546 |
| 3400 | 62.760 | 193.695 | 141.073 | 178.915 | −681.099 | −145.047 | 2.228 |
| 3500 | 62.760 | 195.514 | 142.603 | 185.191 | −679.668 | −129.302 | 1.930 |
| 3600 | 62.760 | 197.282 | 144.097 | 191.467 | −678.352 | −113.596 | 1.648 |
| 3700 | 62.760 | 199.002 | 145.558 | 197.743 | −677.158 | −97.925 | 1.382 |
| 3800 | 62.760 | 200.676 | 146.986 | 204.019 | −676.092 | −82.285 | 1.131 |
| 3900 | 62.760 | 202.306 | 148.384 | 210.295 | −675.160 | −66.670 | 0.893 |
| 4000 | 62.760 | 203.895 | 149.752 | 216.571 | −674.364 | −51.079 | 0.667 |
| 4100 | 62.760 | 205.444 | 151.091 | 222.847 | −673.711 | −35.505 | 0.452 |
| 4200 | 62.760 | 206.957 | 152.404 | 229.123 | −673.202 | −19.946 | 0.248 |
| 4300 | 62.760 | 208.434 | 153.690 | 235.399 | −672.840 | −4.396 | 0.053 |
| 4400 | 62.760 | 209.876 | 154.950 | 241.675 | −672.622 | 11.146 | −0.132 |
| 4500 | 62.760 | 211.287 | 156.187 | 247.951 | −672.538 | 26.683 | −0.310 |

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0 to 3200 K crystal
above 3200 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 | −6.749 | −631.760 | −631.760 | INFINITE |
| 100 | 14.715 | 6.222 | 69.166 | −6.294 | −633.739 | −624.099 | 325.996 |
| 200 | 33.677 | 23.041 | 41.825 | −3.757 | −634.925 | −613.887 | 160.331 |
| 298.15 | 42.120 | 38.212 | 38.212 | 0. | −635.089 | −603.501 | 105.731 |
| 300 | 42.242 | 38.473 | 38.213 | 0.078 | −635.086 | −603.305 | 105.045 |
| 400 | 46.626 | 51.300 | 39.932 | 4.547 | −634.738 | −592.755 | 77.406 |
| 500 | 48.982 | 61.980 | 43.305 | 9.338 | −634.242 | −582.316 | 60.834 |
| 600 | 50.480 | 71.052 | 47.193 | 14.315 | −633.787 | −571.975 | 49.795 |
| 700 | 51.555 | 78.917 | 51.175 | 19.419 | −633.449 | −561.701 | 41.915 |
| 800 | 52.400 | 85.858 | 55.085 | 24.618 | −634.112 | −551.362 | 36.000 |
| 900 | 53.112 | 92.072 | 58.856 | 29.894 | −634.064 | −541.024 | 31.400 |
| 1000 | 53.735 | 97.700 | 62.463 | 35.237 | −634.273 | −530.677 | 27.720 |
| 1100 | 54.300 | 102.849 | 65.904 | 40.639 | −634.749 | −520.297 | 24.707 |
| 1200 | 54.831 | 107.596 | 69.183 | 46.096 | −643.226 | −509.239 | 22.167 |
| 1300 | 55.329 | 112.005 | 72.309 | 51.604 | −643.009 | −498.082 | 20.013 |
| 1400 | 55.810 | 116.123 | 75.293 | 57.161 | −642.759 | −486.943 | 18.168 |
| 1500 | 56.275 | 119.989 | 78.146 | 62.766 | −642.475 | −475.823 | 16.570 |
| 1600 | 56.727 | 123.636 | 80.876 | 68.416 | −642.159 | −464.723 | 15.172 |
| 1700 | 57.174 | 127.088 | 83.494 | 74.111 | −641.810 | −453.644 | 13.939 |
| 1800 | 57.609 | 130.369 | 86.007 | 79.850 | −790.102 | −440.375 | 12.779 |
| 1900 | 58.045 | 133.495 | 88.425 | 85.633 | −788.275 | −420.996 | 11.574 |
| 2000 | 58.471 | 136.483 | 90.754 | 91.459 | −786.423 | −401.713 | 10.492 |
| 2100 | 58.894 | 139.346 | 93.000 | 97.327 | −784.547 | −382.523 | 9.515 |
| 2200 | 59.317 | 142.096 | 95.170 | 103.238 | −782.651 | −363.423 | 8.629 |
| 2300 | 59.735 | 144.742 | 97.268 | 109.190 | −780.739 | −344.411 | 7.822 |
| 2400 | 60.149 | 147.293 | 99.299 | 115.184 | −778.816 | −325.481 | 7.084 |
| 2500 | 60.563 | 149.757 | 101.269 | 121.220 | −776.887 | −306.632 | 6.407 |
| 2600 | 60.978 | 152.140 | 103.180 | 127.297 | −774.958 | −287.860 | 5.783 |
| 2700 | 61.388 | 154.449 | 105.036 | 133.415 | −773.036 | −269.161 | 5.207 |
| 2800 | 61.798 | 156.689 | 106.841 | 139.575 | −771.126 | −250.534 | 4.674 |
| 2900 | 62.208 | 158.865 | 108.597 | 145.775 | −769.238 | −231.976 | 4.178 |
| 3000 | 62.618 | 160.981 | 110.308 | 152.016 | −767.378 | −213.481 | 3.717 |
| 3100 | 63.024 | 163.040 | 111.976 | 158.298 | −765.554 | −195.048 | 3.287 |
| 3200 | 63.434 | 165.048 | 113.604 | 164.621 | −763.774 | −176.673 | 2.884 |
| 3200.000 | 63.434 | 165.048 | 113.604 | 164.621 | CRYSTAL <--> LIQUID TRANSITION | | |
| 3200.000 | 62.760 | 189.890 | 113.604 | 244.117 | | | |
| 3300 | 62.760 | 191.821 | 115.945 | 250.393 | −682.638 | −160.836 | 2.546 |
| 3400 | 62.760 | 193.695 | 118.204 | 256.669 | −681.099 | −145.047 | 2.228 |
| 3500 | 62.760 | 195.514 | 120.387 | 262.945 | −679.668 | −129.302 | 1.930 |
| 3600 | 62.760 | 197.282 | 122.499 | 269.221 | −678.352 | −113.596 | 1.648 |
| 3700 | 62.760 | 199.002 | 124.543 | 275.497 | −677.158 | −97.925 | 1.382 |
| 3800 | 62.760 | 200.676 | 126.525 | 281.773 | −676.092 | −82.285 | 1.131 |
| 3900 | 62.760 | 202.306 | 128.447 | 288.049 | −675.160 | −66.670 | 0.893 |
| 4000 | 62.760 | 203.895 | 130.313 | 294.325 | −674.364 | −51.079 | 0.667 |
| 4100 | 62.760 | 205.444 | 132.127 | 300.601 | −673.711 | −35.505 | 0.452 |
| 4200 | 62.760 | 206.957 | 133.891 | 306.877 | −673.202 | −19.946 | 0.248 |
| 4300 | 62.760 | 208.434 | 135.607 | 313.153 | −672.840 | −4.396 | 0.053 |
| 4400 | 62.760 | 209.876 | 137.279 | 319.429 | −672.622 | 11.146 | −0.132 |
| 4500 | 62.760 | 211.287 | 138.908 | 325.705 | −672.538 | 26.684 | −0.310 |

PREVIOUS: CURRENT June 1973

$S°(298\ 15\ K) = 219.717 \pm 0.42\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 45.1 \pm 21\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 43.9 \pm 21\ kJ·mol^{-1}$

| Source | State | Electronic and Molecular Constants ($\sigma$ = 1) $\epsilon_e$, $cm^{-1}$ | $g_e$ | $r_e$, Å | $B_e$, $cm^{-1}$ | $\alpha_e$, $cm^{-1}$ | $\omega_e$, $cm^{-1}$ | $\omega_e x_e$, $cm^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 1-3 | $X^1\Sigma^+$ | 0.0 | 1 | 1.822 | 0.44452 | 0.00338 | 733.4 | 5.28 |
| 1 | $a^3\Pi$ | 8225. | 6 | 2.097 | 0.3353 | 0.0015 | 556.2 | 3.30 |
| 1 | $A'^1\Pi$ | 8612. | 2 | 2.092 | 0.3372 | 0.0021 | 545.7 | 2.54 |
| 1,4,5 | $^3\Sigma^+$ | [10000] | 3 | [1.906] | [0.4059] | [0.0014] | [719] | [2.1] |
| 1-3 | $A^1\Sigma^+$ | 11549. | 1 | 1.906 | 0.40592 | 0.00137 | 718.9 | 2.11 |
| 5 | $^3\Sigma^+$ | [21000] | 3 | [2.00] | [0.369] | [0.003] | [560] | [4.] |
| 5 | $^3\Delta$ | [21000] | 6 | [2.00] | [0.369] | [0.003] | [560] | [4.] |
| 5 | $^1\Delta$ | [23000] | 2 | [2.00] | [0.369] | [0.003] | [560] | [4.] |
| 5 | $^3\Sigma^-$ | [23000] | 3 | [2.00] | [0.369] | [0.003] | [560] | [4.] |
| 5 | $^1\Sigma^-$ | [23000] | 1 | [2.00] | [0.369] | [0.003] | [560] | [4.] |
| 6 | $C^1\Sigma^+$ | 28772. | 1 | 1.989 | 0.3731 | 0.0032 | 560.9 | 4.0 |
| 5 | $^3\Pi$ | [24000] | 6 | [1.95] | [0.3882] | [0.0055] | [581] | [3.3] |
| 7 | $B^1\Pi$ | 25913. | 2 | 1.950 | 0.3882 | 0.0055 | 581.0 | [3.3] |

## Enthalpy of Formation

We adopt $D_0° = 91 \pm 5$ and $\Delta_f H°(298\ 15\ K) = 10.5 \pm 5\ kcal·mol^{-1}$ based on mass-spectrometric data[8,9] for four reactions analyzed below. We give "<" or ">" for $\Delta H°$ and $D_0°$ values which may be biased due to our auxiliary data. JANAF differences in $\Delta_f H°(298.15\ K)$ for $WO_3$–$WO_2$ and $MoO_3$–$MoO_2$[5] may be biased by up to −3.5 and + 4.1 $kcal·mol^{-1}$, respectively, leading to bias of the opposite sign in $D_0°$ values derived from reactions B and C. Adjustments for this possible bias would improve the agreement in $D_0°$ but leave the mean value almost unchanged. Kalff[10] used spectrometry of CO–$N_2O$ flames to derive $D_0° = 86.5 \pm 4.6\ kcal·mol^{-1}$. This value becomes –89.5 $kcal·mol^{-1}$ when adjusted to be consistent with JANAF Gibbs energy functions. Our adopted $D_0° = 91 \pm 5$ is similar to that of Rosen[6] and is comparable with other selected values,[8,11] considering the difference in CaO functions.

The controversy over $D_0°$ of alkaline earth oxides has been reviewed in detail.[8,11-13] Uncertainty in the electronic partition function of CaO due to triplet states now is much reduced.[1] Schofields's criticism[12] of flame studies is supported by new evidence for importance of hydroxides;[10,14,15] thus, we dismiss higher flame values for $D_0°$.[12] Valid criticism[8] also causes us to dismiss higher $D_0°$ values derived from vaporization data. A linear Birge–Sponer extrapolation yields a very low estimate for $D_0°$, just as it does for the alkali halides,[13] unless $X^1\Sigma$ fails to dissociate to an excited state atom as predicted.[17,1]

| Source | Method | Reaction[a] | T/K | Data Points | δS cal·$K^{-1}$$mol^{-1}$ | $\Delta_f H°$(298.15 K), kcal·$mol^{-1}$ 2nd law | 3rd law | kcal·mol $\Delta_f H°$(298.15 K) | $D_0°$ |
|---|---|---|---|---|---|---|---|---|---|
| 8 | Knudsen mass spec. | A | 2168–2410 | 4 | −2.3 ± 9.7 | 24 ± 22 | 29.4 ± 3 | 12.7 | 88.8 |
| | Knudsen mass spec. | B | 2328–2334 | 2 | 67 | 209 | 51.9 ± 3 | >6.5 | <95.0 |
| | Knudsen mass spec. | C | 2393–2410 | 3 | 12 ± 83 | 85 ± 100 | 55.8 ± 3 | ≤15.5 | <85.9 |
| 9 | Knudsen mass spec. | D | 2180–2386 | 3 | 1 ± 31 | 31 ± 72 | 27.9 ± 6 | 5.6 | 95.8[b] |

[a]Reactions: A) $Ca(g) + O_2(g) = CaO(g) + O(g)$; C) $Ca(g) + MoO_3(g) = CaO(g) + MoO_2(g)$;
B) $Ca(g) + WO_3(g) = CaO(g) + WO_2(g)$; D) $Ca(g) + SO(g) = CaO(g) + S(g)$.

[b]Ion intensities and $D_0°$ reported [9] at 2180 K are discrepant by −8 $kcal·mol^{-1}$, we use ion intensities.

## Heat Capacity and Entropy

Electronic levels ($T_e$) and vibrational–rotational constants of the observed states are from (1, 2, 3, 6, 7) The long–sought $a^3\Pi$ and $A'^1\Pi$ states of CaO, SrO and BaO were characterized by Field[1] using a new method for assignment of perturbations This study resolved the long–standing controversy over low–lying electronic levels and confirmed that $X^1\Sigma^+$ is the ground state. We estimate the other potentially low–lying state ($^3\Sigma^+$) at 10000 $cm^{-1}$ by assuming that it lies 1500 ± 1200 $cm^{-1}$ [1,14] below the isoconfigurational order of MgO.[5] Rotational analysis of a band near 5470 Å was attributed[16] to CaO, but we question this assignment. Our thermodynamic functions are calculated using first–order anharmonic corrections to $Q_1'$ and $Q_1''$ in the partition function $Q = Q_t\ \Sigma_e\ Q_1'\ Q_1''\ g_e \exp(-c_2\epsilon_e/T)$.

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[5]JANAF Thermochemical Tables: CaO(g), MgO(g), BeO(g) 12–31–74, SrO(g), BaO(g) 6–30–74, $WO_2(g)$, $WO_3(g)$ 9–30–66, $MoO_2(g)$, $MoO_3$ (g) 6–30–68.


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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 | −8.953 | 45.057 | 45 057 | INFINITE |
| 100 | 29.136 | 186.730 | 247.175 | −6.044 | 45.533 | 37.122 | −19.390 |
| 200 | 30.381 | 207.194 | 222.620 | −3.085 | 44.768 | 28.975 | −7.568 |
| 298.15 | 32.455 | 219.717 | 219.717 | 0. | 43.932 | 21.405 | −3.750 |
| 300 | 32.491 | 219.918 | 219.717 | 0.060 | 43.917 | 21.266 | −3.703 |
| 400 | 34.089 | 229.499 | 221.013 | 3.394 | 43.131 | 13.835 | −1.807 |
| 500 | 35.139 | 237.226 | 223.508 | 6.859 | 42.301 | 6.604 | −0.690 |
| 600 | 35.833 | 243 699 | 226.348 | 10.410 | 41.330 | −0.447 | 0.039 |
| 700 | 36.313 | 249.260 | 229.233 | 14.019 | 40.172 | −7.321 | 0.546 |
| 800 | 36.663 | 254.133 | 232.047 | 17.669 | 37.960 | −13.911 | 0.908 |
| 900 | 36.947 | 258.468 | 234.747 | 21.349 | 36.412 | −20.305 | 1.178 |
| 1000 | 37.218 | 262.375 | 237.317 | 25.058 | 34.569 | −26.510 | 1.385 |
| 1100 | 37.532 | 265.936 | 239.760 | 28.794 | 32.428 | −32.517 | 1.544 |
| 1200 | 37.947 | 269.219 | 242.079 | 32.567 | 22.266 | −37.694 | 1.641 |
| 1300 | 38.518 | 272.278 | 244.286 | 36.389 | 20.797 | −42.630 | 1.713 |
| 1400 | 39.291 | 275.159 | 246.389 | 40.278 | 19.378 | −47.456 | 1.771 |
| 1500 | 40.298 | 277.903 | 248.399 | 44.255 | 18.035 | −52.182 | 1.817 |
| 1600 | 41.551 | 280.542 | 250.326 | 48.345 | 16.792 | −56.822 | 1.855 |
| 1700 | 43.046 | 283.105 | 252.179 | 52.573 | 15.674 | −61.388 | 1.886 |
| 1800 | 44.755 | 285.613 | 253.967 | 56.962 | −133.969 | −63.682 | 1.848 |
| 1900 | 46.639 | 288.082 | 255.698 | 61.530 | −133.357 | −59.793 | 1.644 |
| 2000 | 48.642 | 290.525 | 257.378 | 66.293 | −132.567 | −55 941 | 1.461 |
| 2100 | 50.703 | 292.948 | 259.015 | 71.260 | −131.592 | −52.133 | 1.297 |
| 2200 | 52.757 | 295.354 | 260.612 | 76 434 | −130.433 | −48.375 | 1.149 |
| 2300 | 54.742 | 297.744 | 262.174 | 81.810 | −129.098 | −44.674 | 1.015 |
| 2400 | 56.603 | 300.113 | 263.706 | 87.378 | −127.601 | −41.036 | 0.893 |
| 2500 | 58.293 | 302.459 | 265.209 | 93.125 | −125.962 | −37.462 | 0.783 |
| 2600 | 59.778 | 304.775 | 266.686 | 99.030 | −124.204 | −33.956 | 0.682 |
| 2700 | 61.036 | 307.055 | 268.139 | 105.072 | −122.357 | −30.520 | 0.590 |
| 2800 | 62.057 | 309.294 | 269.569 | 111.229 | −120.451 | −27.153 | 0.507 |
| 2900 | 62.844 | 311.486 | 270.977 | 117.476 | −118.515 | −23.856 | 0.430 |
| 3000 | 63.404 | 313.627 | 272.363 | 123.790 | −116.582 | −20.624 | 0.359 |
| 3100 | 63.755 | 315.712 | 273.728 | 130.150 | −114.681 | −17.457 | 0.294 |
| 3200 | 63.918 | 317.739 | 275.072 | 136.535 | −112.839 | −14.350 | 0.234 |
| 3300 | 63.917 | 319.706 | 276.395 | 142.928 | −111.082 | −11.300 | 0.179 |
| 3400 | 63.776 | 321.613 | 277.697 | 149.314 | −109.433 | −8.301 | 0.128 |
| 3500 | 63.520 | 323.458 | 278.978 | 155.679 | −107.913 | −5.350 | 0.080 |
| 3600 | 63.172 | 325.243 | 280.239 | 162.015 | −106.538 | −2.439 | 0 035 |
| 3700 | 62.754 | 326.968 | 281.478 | 168.311 | −105.323 | 0.435 | −0 006 |
| 3800 | 62.283 | 328.635 | 282.698 | 174.564 | −104.281 | 3.280 | −0.045 |
| 3900 | 61.777 | 330.247 | 283.896 | 180.767 | −103.420 | 6.099 | −0.082 |
| 4000 | 61.250 | 331.804 | 285.075 | 186.918 | −102.750 | 8.898 | −0.116 |
| 4100 | 60.713 | 333.310 | 286.233 | 193.017 | −102.274 | 11.683 | −0.149 |
| 4200 | 60.175 | 334.767 | 287.371 | 199.061 | −101.997 | 14.458 | −0.180 |
| 4300 | 59.644 | 336.176 | 288.490 | 205.052 | −101.920 | 17.230 | −0.209 |
| 4400 | 59.125 | 337.542 | 289.589 | 210.990 | −102.040 | 20.001 | −0.237 |
| 4500 | 58.624 | 338.865 | 290.670 | 216.877 | −102.344 | 22.777 | −0.264 |
| 4600 | 58.142 | 340.148 | 291.731 | 222.715 | −102.851 | 25.562 | −0.290 |
| 4700 | 57.683 | 341.393 | 292.775 | 228.507 | −103.554 | 28.361 | −0.315 |
| 4800 | 57.246 | 342.603 | 293.800 | 234.253 | −104.443 | 31.177 | −0.339 |
| 4900 | 56.834 | 343.779 | 294.808 | 239.957 | −105.514 | 34.014 | −0.363 |
| 5000 | 56.446 | 344.923 | 295.799 | 245.620 | −106.760 | 36.873 | −0.385 |
| 5100 | 56.081 | 346 037 | 296.773 | 251.246 | −108.175 | 39.760 | −0.407 |
| 5200 | 55.739 | 347.123 | 297.731 | 256.837 | −109.748 | 42.675 | −0.429 |
| 5300 | 55.418 | 348.182 | 298.673 | 262.395 | −111.478 | 45.623 | −0.450 |
| 5400 | 55.119 | 349.215 | 299.600 | 267.922 | −113.355 | 48.604 | −0.470 |
| 5500 | 54.840 | 350.224 | 300.511 | 273.419 | −115.371 | 51.621 | −0.490 |
| 5600 | 54.580 | 351.209 | 301.408 | 278.890 | −117.507 | 54.676 | −0.510 |
| 5700 | 54.337 | 352.173 | 302.290 | 284.336 | −119.775 | 57.771 | −0.529 |
| 5800 | 54.110 | 353.116 | 303.158 | 289.758 | −122.158 | 60.907 | −0.549 |
| 5900 | 53.899 | 354.040 | 304.013 | 295.159 | −124.648 | 64.083 | −0.567 |
| 6000 | 53.702 | 354.944 | 304 854 | 300.539 | −127.237 | 67.304 | −0.586 |

PREVIOUS: December 1974 (1 atm) CURRENT: December 1974 (1 bar)

$S°(298.15\ K) = 56.6 \pm 1.3\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = [2798]\ K$

$\Delta_f H°(0\ K) = -472.1 \pm 2.9\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -473.2 \pm 2.9\ kJ \cdot mol^{-1}$

### Enthalpy of Formation

Sabatier,[1] Mourlot,[2] and von Wartenberg,[3] all measured the enthalpy of solution of CaS in hydrochloric acid solution. Sabatier determined $\Delta_r H°(238.8) = -26.3 \pm 1.0$ kcal·mol$^{-1}$ while Mourlot determined $\Delta_r H°(291) = -26.7 \pm 1.0$ kcal·mol$^{-1}$ for CaS(cr) + 2HCl(100 $H_2O$, aq) → $CaCl_2$(100 $H_2O$, aq) + $H_2S$(aq). We derive $\Delta_f H°$(CaS, cr, 298.15 K) = −112.7 ± 2.0 kcal·mol$^{-1}$ and $\Delta_f H°$(CaS, cr, 298.15 K) = −112.3 ± 2.0 kcal·mol$^{-1}$ respectively, based on the following auxiliary data: $\Delta_f H°$(HCl·100 $H_2O$, aq, 298.15 K) = −39.657 kcal·mol$^{-1}$,[4] $\Delta_f H°$($H_2S$, aq, 298.15 K) = −9.5 kcal·mol$^{-1}$,[4] and $\Delta_f H°$($CaCl_2$100 $H_2O$, aq, 298.15 K) = −208.849 kcal·mol$^{-1}$.[5] Von Wartenberg measured $\Delta_r H$(293.15) = −20.6 ± 0.4 kcal·mol$^{-1}$ for CaS(cr) + 2HCl(30 $H_2O$, aq) → $CaCl_2$(30 $H_2O$, aq) + $H_2S$(g). We derive $\Delta_f H°$(CaS, cr, 298.15 K) = −113.9 ± 0.6 kcal·mol$^{-1}$ based on the following auxiliary data. $\Delta_f H°$(HCl·30 $H_2O$, aq, 298.15 K) = −39.357 kcal·mol$^{-1}$,[4] $\Delta_f H°$($H_2S$, g, 298.15 K) = −4.90 kcal·mol$^{-1}$,[4,18] and $\Delta_f H°$($CaCl_2$·30 $H_2O$, aq, 298.15 K) = −208.33 kcal·mol$^{-1}$.[5]

| Source | Method | Reaction[a] | T/K | Data Points | δS cal·K$^{-1}$mol$^{-1}$ | $\Delta_r H$(298.15 K), kcal·mol$^{-1}$ 2nd law | 3rd law | $\Delta_f H°$(298.15 K) kcal·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| [6] | Vap. Press. | A | 1400–1700 | Equation | −3.94 | 112.3 | 118.39 ± 1.0 | −88.9 ± 30 |
| [7] | Equilibrium | B | 1019–1704 | 15 | 1.06 ± 0.1 | 15.6 ± 0.1 | 14.14 ± 0.5 | −113.01 ± 0.8 |
| [8] | Equilibrium | B | 1031–1698 | 12 | 1.01 ± 0.2 | 15.4 ± 0.3 | 14.02 ± 0.5 | −112.89 ± 0.8 |
| [9] | Equilibrium | B | 1173–1373 | Equation | 0.18 | 14.3 | 14.04 ± 1.0 | −112.91 ± 1.0 |
| [9] | Equilibrium | C | 926–1026 | Equation | 0.03 | −23.02 | −23.06 ± 1.0 | −113.31 ± 2.0 |
| [10] | Equilibrium | D | 1124–1348 | 6 | 5.5 ± 0.6 | −51.2 ± 0.8 | −58.0 ± 1.0 | −111.98 ± 2.0 |
| [11] | Equilibrium | D | 1173–1393 | 10 | 7.3 ± 3.2 | −76.3 ± 4.2 | −66.8 ± 1.6 | −103.2 ± 4 |
| [11] | Equilibrium | E | 1173–1393 | 10 | −0.95 ± 5 | 254.06 ± 6.5 | 255.2 ± 1.9 | −117.9 ± 4 |
| [12] | Equilibrium | C | 1400–1650 | 7 | −2.8 ± 0.3 | 17.3 ± 0.5 | 22.3 ± 0.5 | −114.04 ± 0.6 |
| [13] | Mass Spec. | F | 1709 | 1 | | | 212.5 ± 10 | −103.4 ± 10 |
| [14] | Mass Spec. | G | 1849–2155 | 7 | −11.8 ± 2.0 | −1.4 ± 4.0 | 22.0 ± 2.0 | −116.3 ± 8 |

[a]Reactions:
A) CaS(c) = CaS(g)
B) CaS(c) + $H_2O$(g) = CaO(c) + $H_2S$(g)
C) CaS(c) + 0.5$O_2$(g) = CaO(c) + 0.5$S_2$(g)
D) CaS(c) + 2$SO_2$(g) = $CaSO_4$(c) + $S_2$(g)
E) CaS(c) + 3$CaSO_4$(c) = 4CaO(c) + 4$SO_2$(g)
F) CaS(c) + CaS(c) = Ca(g) + S(g)
G) CaS(c) + 3S(g) = Ca(g) + 2$S_2$(g)

The calculated 3rd-law $\Delta_r H°$(298.15 K) may have an uncertainty of 0.5 kcal·mol$^{-1}$ since the JANAF Gibbs energy functions are partially based on the estimated $C_p°$ data (above 300 K). The results of the majority of the equilibrium studies,[7–12] are in very good agreement with the enthalpy of solution[1–5] studies within combined experimental errors. The mass spectrometric studies[13,14] are not as reliable in condensed phase equilibrium as they are in gas phase equilibrium.[18] A weighted average, $\Delta_f H°$(CaS, cr, 298.15 K) = −113.1 ± 0.7 kcal·mol$^{-1}$ is adopted in the tabulation.

### Heat Capacity and Entropy

Anderson[15] measured the low temperature heat capacities of CaS(cr) from 58.1 – 294.9 K in an isothermal calorimeter. We have smoothed his $C_p°$ data by a polynomial curve fitting technique and obtain $S°(298.15\ K) = 13.5 \pm 0.3$ cal·K$^{-1}$·mol$^{-1}$ based on $S°$ (60 K) = 1.192 cal K$^{-1}$·mol$^{-1}$. The value of $S°$(60 K) is calculated from the combination of Debye and Einstein functions ($\theta_D$ = 284 and = $\theta_E$ = 369). The $C_p°$ values above 300 K are estimated by graphical extrapolation combined with a variant of method B of Kubaschewski *et al.*[16]

### Fusion Data

The melting point of CaS(cr) is given as 2525°C.[17]

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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 | −8.999 | −472.061 | −472.061 | INFINITE |
| 100 | 25.945 | 14.477 | 94.617 | −8.014 | −472.746 | −471.345 | 246.206 |
| 200 | 42.204 | 38.610 | 60.808 | −4.440 | −473.083 | −469.779 | 122.694 |
| 298.15 | 47.442 | 56.601 | 56.601 | 0. | −473.210 | −468.129 | 82.014 |
| 300 | 47.447 | 56.895 | 56.602 | 0.088 | −473.213 | −468.098 | 81.503 |
| 400 | 49.204 | 70.796 | 58.486 | 4.924 | −475.608 | −466.281 | 60.890 |
| 500 | 50.501 | 81.919 | 62.096 | 9.911 | −477.314 | −463.765 | 48.449 |
| 600 | 51.547 | 91.223 | 66.196 | 15.016 | −478.737 | −460.916 | 40.126 |
| 700 | 52.342 | 99.230 | 70.357 | 20.211 | −480.027 | −457.844 | 34.165 |
| 800 | 53.011 | 106.265 | 74.415 | 25.480 | −482.164 | −454.483 | 29.675 |
| 900 | 53.555 | 112.540 | 78.308 | 30.808 | −536.618 | −449.864 | 26.109 |
| 1000 | 54.099 | 118.211 | 82.020 | 36.192 | −536.911 | −440.212 | 22.994 |
| 1100 | 54.586 | 123.391 | 85.548 | 41.626 | −537.471 | −430.517 | 20.444 |
| 1200 | 55.020 | 128.159 | 88.903 | 47.107 | −546.037 | −420.137 | 18.288 |
| 1300 | 55.391 | 132.578 | 92.095 | 52.628 | −545.919 | −409.650 | 16.460 |
| 1400 | 55.731 | 136.695 | 95.135 | 58.184 | −545.780 | −399.173 | 14.893 |
| 1500 | 55.987 | 140.549 | 98.036 | 63.769 | −545.629 | −388.706 | 13.536 |
| 1600 | 56.317 | 144.172 | 100.807 | 69.384 | −545.462 | −378.250 | 12.349 |
| 1700 | 56.761 | 147.600 | 103.460 | 75.038 | −545.271 | −367.805 | 11.301 |
| 1800 | 57.195 | 150.857 | 106.003 | 80.736 | −693.723 | −355.161 | 10.306 |
| 1900 | 57.629 | 153.961 | 108.446 | 86.477 | −692.057 | −336.397 | 9.248 |
| 2000 | 58.032 | 156.927 | 110.797 | 92.261 | −690.367 | −317.722 | 8.298 |
| 2100 | 58.382 | 159.767 | 113.062 | 98.081 | −688.659 | −299.131 | 7.440 |
| 2200 | 58.743 | 162.491 | 115.247 | 103.938 | −686.936 | −280.623 | 6.663 |
| 2300 | 59.115 | 165.111 | 117.358 | 109.830 | −685.201 | −262.193 | 5.955 |
| 2400 | 59.496 | 167.634 | 119.401 | 115.761 | −683.456 | −243.839 | 5.307 |
| 2500 | 59.899 | 170.071 | 121.379 | 121.731 | −681.704 | −225.557 | 4.713 |
| 2600 | 60.291 | 172.428 | 123.298 | 127.740 | −679.950 | −207.346 | 4.166 |
| 2700 | 60.668 | 174.711 | 125.160 | 133.788 | −678.201 | −189.202 | 3.660 |
| 2800 | 61.045 | 176.924 | 126.969 | 139.874 | −676.464 | −171.123 | 3.192 |
| 2900 | 61.421 | 179.073 | 128.729 | 145.997 | −674.747 | −153.105 | 2.758 |
| 3000 | 61.798 | 181.161 | 130.442 | 152.158 | −673.058 | −135.147 | 2.353 |

PREVIOUS: December 1971  CURRENT: September 1977

$S°(298.15\ K) = 232.589 \pm 0.42\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -124.39 \pm 8.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -123.60 \pm 8.4\ kJ·mol^{-1}$

| Source | 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$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| | | Electronic and Molecular Constants ($\sigma = 1$) | | | | | | |
| 3 | $X^1\Sigma^+$ | 0.0 | 1 | 2.3178 | 0.17667 | 0.000837 | 462.23 | 1.76 |
| 4 | $^3\Pi$ | [6800.] | 6 | [2.63] | [0.137] | [0.0006] | [330] | [1.5] |
| 4 | $^1\Pi$ | [7200.] | 2 | [2.63] | [0.137] | [0.0006] | [330] | [1.5] |
| 3,4 | $^3\Sigma^+$ | [14000.] | 3 | [2.3864] | [0.16666] | [0.000605] | [409.04] | [0.818] |
| 3 | $A^1\Sigma^+$ | 15194.44 | 1 | 2.3864 | 0.16666 | 0.000605 | 409.04 | 0.818 |

## Enthalpy of Formation

The adopted value for the enthalpy of formation, $\Delta_f H°$(CaS, g, 298.15 K) = 29.54 ± 2 kcal·mol$^{-1}$, is based on the Knudsen mass spectrometric studies analyzed below. The two independent studies are in very good agreement and we have adopted the average value. Our value is intermediate between $\Delta_f H°(298.15\ K) = 32$ kcal·mol$^{-1}$ obtained by NBS[5] and $\Delta_f H°(298.15\ K) = 27.9 \pm 5$ kcal·mol$^{-1}$ obtained by Mills[6] in a recent critical compilation. Using auxiliary JANAF data[4] and a recommended value for $D°_0(S_2, g) = 100.69 \pm 01$ kcal·mol$^{-1}$,[4] we calculate $D°_0$(CaS, g) = 78.7 ± 2 kcal·mol$^{-1}$.

| Source | Method | Reaction[a] | $T$/K | Data Points | $\delta S$ cal·K$^{-1}$mol$^{-1}$ | $\Delta_f H°(298.15\ K)$, kcal·mol$^{-1}$ 2nd law | 3rd law | $\Delta_f H°(298.15\ K)$ kcal·mol$^{-1}$ | $D°_0$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Mass Spec | A | 2058–2319 | 9 | 2.83 ± 3.5 | 28.32 ± 7.5 | 22.32 ± 7.5 | 29.72 ± 1.7 | 78.6 ± 2 |
| 2 | Mass Spec | A | 1709–1962 | 2 | 0.22 | 22.37 | 21.97 ± 2 | 29.37 ± 2 | 78.9 ± 2 |

[a]Reaction: A) Ca(g) + $S_2$(g) = CaS(g) + (g)

## Heat Capacity and Entropy

Electronic levels ($T_\infty$) and vibrational–rotational constants for the observed states are from the optical study of Blues and Barrow.[3] Other low-lying electronic states and their vibrational–rotational constants are estimated in isoconfigurational groups by analogy with CaO[4] and from trends observed in the known states of the other alkaline–earth oxides and sulfides.[4] Uncertainty in the energy and constants for the estimated states may contribute as much as 2–3 cal·K$^{-1}$·mol$^{-1}$ to $S°$ at 3000 K. The molecular constants have been corrected to the natural isotopic abundances. The thermodynamic functions are calculated using first order anharmonic corrections to $Q_i^r$ and $Q_i^v$ in the partition function $Q = Q_i \Sigma_i Q_i^r Q_i^v g_i \exp(-c_2\epsilon_i/T)$.

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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 | −9.358 | 124.385 | 124.385 | INFINITE |
| 100 | 29.604 | 197.623 | 262.034 | −6.441 | 125.632 | 108.719 | −56.789 |
| 200 | 32.744 | 219.086 | 235.716 | −3.326 | 124.837 | 92.045 | −24.040 |
| 298.15 | 34.803 | 232.589 | 232.589 | 0. | 123.595 | 76.206 | −13.351 |
| 300 | 34.830 | 232.804 | 232.590 | 0.064 | 123.570 | 75.912 | −13.217 |
| 400 | 35.897 | 242.987 | 233.971 | 3.606 | 119.880 | 60.331 | −7.878 |
| 500 | 36.487 | 251.066 | 236.610 | 7.228 | 116.808 | 45.785 | −4.783 |
| 600 | 36.850 | 257.753 | 239.592 | 10.896 | 113.949 | 31.852 | −2.773 |
| 700 | 37.106 | 263.454 | 242.604 | 14.595 | 111.162 | 18.389 | −1.372 |
| 800 | 37.336 | 268.423 | 245.527 | 18.317 | 107.479 | 5.432 | −0.355 |
| 900 | 37.624 | 272.837 | 248.321 | 22.064 | 51.444 | −6.070 | 0.352 |
| 1000 | 38.061 | 276.822 | 250.975 | 25.847 | 49.550 | −12.362 | 0.646 |
| 1100 | 38.732 | 280.478 | 253.493 | 29.684 | 47.393 | −18.450 | 0.876 |
| 1200 | 39.703 | 283.888 | 255.885 | 33.603 | 37.265 | −23.710 | 1.032 |
| 1300 | 41.007 | 287.115 | 258.164 | 37.636 | 35.895 | −28.734 | 1.155 |
| 1400 | 42.641 | 290.212 | 260.344 | 41.815 | 34.657 | −33.659 | 1.256 |
| 1500 | 44.564 | 293.218 | 262.435 | 46.174 | 33.581 | −38.500 | 1.341 |
| 1600 | 46.705 | 296.161 | 264.452 | 50.736 | 32.695 | −43.275 | 1.413 |
| 1700 | 48.971 | 299.060 | 266.402 | 55.519 | 32.015 | −48.001 | 1.475 |
| 1800 | 51.260 | 301.924 | 268.296 | 60.530 | −117.123 | −50.483 | 1.465 |
| 1900 | 53.474 | 304.756 | 270.141 | 65.768 | −115.961 | −46.811 | 1.287 |
| 2000 | 55.523 | 307.552 | 271.942 | 71.220 | −114.603 | −43.206 | 1.128 |
| 2100 | 57.336 | 310.306 | 273.703 | 76.865 | −113.070 | −39.673 | 0.987 |
| 2200 | 58.863 | 313.009 | 275.429 | 82.677 | −111.390 | −36.217 | 0.860 |
| 2300 | 60.079 | 315.654 | 277.120 | 88.627 | −109.598 | −32.840 | 0.746 |
| 2400 | 60.977 | 318.231 | 278.780 | 94.683 | −107.728 | −29.542 | 0.643 |
| 2500 | 61.569 | 320.733 | 280.408 | 100.812 | −105.816 | −26.324 | 0.550 |
| 2600 | 61.878 | 323.155 | 282.006 | 106.987 | −103.897 | −23.182 | 0.466 |
| 2700 | 61.936 | 325.492 | 283.573 | 113.180 | −102.004 | −20.114 | 0.389 |
| 2800 | 61.781 | 327.742 | 285.111 | 119.367 | −100.165 | −17.115 | 0.319 |
| 2900 | 61.449 | 329.905 | 286.619 | 125.530 | −98.409 | −14.180 | 0.255 |
| 3000 | 60.977 | 331.980 | 288.096 | 131.652 | −96.758 | −11.304 | 0.197 |
| 3100 | 60.399 | 333.971 | 289.544 | 137.722 | −95.232 | −8.481 | 0.143 |
| 3200 | 59.743 | 335.878 | 290.963 | 143.729 | −93.848 | −5.705 | 0.093 |
| 3300 | 59.036 | 337.706 | 292.352 | 149.669 | −92.622 | −2.970 | 0.047 |
| 3400 | 58.298 | 339.457 | 293.711 | 155.536 | −91.564 | −0.269 | 0.004 |
| 3500 | 57.547 | 341.136 | 295.043 | 161.328 | −90.685 | 2.403 | −0.036 |
| 3600 | 56.796 | 342.747 | 296.345 | 167.045 | −89.993 | 5.052 | −0.073 |
| 3700 | 56.057 | 344.293 | 297.621 | 172.687 | −89.494 | 7.685 | −0.108 |
| 3800 | 55.336 | 345.778 | 298.868 | 178.257 | −89.193 | 10.307 | −0.142 |
| 3900 | 54.639 | 347.207 | 300.090 | 183.755 | −89.094 | 12.923 | −0.173 |
| 4000 | 53.972 | 348.581 | 301.285 | 189.186 | −89.198 | 15.540 | −0.203 |
| 4100 | 53.335 | 349.906 | 302.455 | 194.551 | −89.508 | 18.162 | −0.231 |
| 4200 | 52.730 | 351.184 | 303.600 | 199.854 | −90.023 | 20.794 | −0.259 |
| 4300 | 52.159 | 352.418 | 304.721 | 205.098 | −90.742 | 23.441 | −0.285 |
| 4400 | 51.620 | 353.611 | 305.819 | 210.287 | −91.660 | 26.106 | −0.310 |
| 4500 | 51.114 | 354.765 | 306.894 | 215.423 | −92.763 | 28.794 | −0.334 |
| 4600 | 50.639 | 355.884 | 307.946 | 220.511 | −94.069 | 31.508 | −0.358 |
| 4700 | 50.194 | 356.968 | 308.978 | 225.552 | −95.568 | 34.254 | −0.381 |
| 4800 | 49.778 | 358.020 | 309.989 | 230.550 | −97.253 | 37.034 | −0.403 |
| 4900 | 49.390 | 359.042 | 310.979 | 235.509 | −99.117 | 39.851 | −0.425 |
| 5000 | 49.027 | 360.037 | 311.951 | 240.429 | −101.153 | 42.707 | −0.446 |
| 5100 | 48.689 | 361.004 | 312.903 | 245.315 | −103.356 | 45.606 | −0.467 |
| 5200 | 48.374 | 361.946 | 313.837 | 250.168 | −105.714 | 48.549 | −0.488 |
| 5300 | 48.080 | 362.865 | 314.754 | 254.990 | −108.226 | 51.539 | −0.508 |
| 5400 | 47.806 | 363.761 | 315.653 | 259.784 | −110.882 | 54.578 | −0.528 |
| 5500 | 47.552 | 364.636 | 316.536 | 264.552 | −113.673 | 57.668 | −0.548 |
| 5600 | 47.315 | 365.491 | 317.402 | 269.295 | −116.582 | 60.809 | −0.567 |
| 5700 | 47.095 | 366.326 | 318.253 | 274.016 | −119.617 | 64.003 | −0.587 |
| 5800 | 46.890 | 367.143 | 319.089 | 278.715 | −122.764 | 67.252 | −0.606 |
| 5900 | 46.699 | 367.943 | 319.910 | 283.394 | −126.014 | 70.556 | −0.625 |
| 6000 | 46.522 | 368.727 | 320.718 | 288.055 | −129.358 | 73.915 | −0.643 |

PREVIOUS. September 1977 (1 atm)  CURRENT: September 1977 (1 bar)

$D_0^\circ$ = 12.740 ± 0.010 kJ·mol$^{-1}$ (natural abundance)
$S^\circ$(298.15 K) = 257.18 ± 0.5 J·K$^{-1}$·mol$^{-1}$

$\Delta_f H$(0 K) = 341.92 ± 0.80 kJ·mol$^{-1}$
$\Delta_f H$(298.15 K) = 341.64 ± 0.8 kJ·mol$^{-1}$

| State | Spectroscopic Constants for $^{40}Ca_2$ in cm$^{-1}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $T_e$ | $D_0^\circ$ | $\omega_e$ | $\omega_e x_e$ | $B_e$ | $10^3 \cdot \alpha_e$ | $10^6 \cdot D_e$ | $r_e$, Å |
| $^1\Sigma_g^+$ | 0 | 1063.1 | 65.046 | 1.0815[a] | 0.46086 | 0.6966[c] | 0.090731[e] | 3.807 |
| $^1\Sigma_u^+$ | 18964 | 22912 | 136.61 | 0.71797[b] | 0.058178 | 0.2970[d] | 0.043361[f] | 4.277 |

[a] + 3.1093 × 10$^{-3}$ (v + 1/2)$^3$ + 7.0080 × 10$^{-6}$ (v + 1/2)$^4$ − 2.4380 × 10$^{-8}$ (v + 1/2)$^5$
[b] − 2.8198 × 10$^{-3}$ (v + 1/2)$^3$ − 1.4773 × 10$^{-6}$ (v + 1/2)$^4$ + 1.692 × 10$^{-6}$ (v + 1/2)$^5$ − 5.545 × 10$^{-9}$ (v + 1/2)$^6$
[c] − 1.619 × 10$^{-5}$ (v + 1/2)$^2$ + 1.60 × 10$^{-6}$ (v + 1/2)$^3$
[d] − 3.202 × 10$^{-6}$ (v + 1/2)$^2$ − 6.58 × 10$^{-8}$ (v + 1/2)$^3$
[e] + 1.330336 × 10$^{-9}$ (v + 1/2) + 7.192454 × 10$^{-10}$ (v + 1/2)$^2$
[f] + 3.283167 × 10$^{-10}$ (v + 1/2) + 4.881575 × 10$^{-4}$ (v + 1/2)$^2$

### Enthalpy of Formation

The ground state dissociation energy for $^{40}Ca_2$ was determined by Vidal (1) to be $D_e$ = 1095.4 ± 0.5 cm$^{-1}$ which gives $D_0^\circ$ = 1063.1 cm$^{-1}$ using the spectroscopic data above. The adopted value for natural abundance $Ca_2$ was obtained from the $^{40}Ca_2$ value by correcting for the presence of the minor isotopic species.[14] Using this value and the recommended value for $\Delta_f H^\circ$(Ca, g, 0 K) = 177.33 kJ·mol$^{-1}$ as deduced from CODATA,[2] we calculate the adopted value of $\Delta_f H^\circ$($Ca_2$, g, 0 K) = 341.92 kJ·mol$^{-1}$. Note that Brewer and Winn[3] calculated a value of $D_0^\circ$ ($Ca_2$, natural abundance) = 12.47 ± 1.7 kJ·mol$^{-1}$ based on some earlier spectroscopic work of Balfour and Whitlock.[4] Gurvich[9] adopted a value of $\Delta_f H^\circ$(0 K) = 342.266 ± 2.6 kJ·mol$^{-1}$ which is also based on the earlier study of.[4]

### Heat Capacity and Entropy

The thermal functions are calculated using a direct summation technique, analogous to the alkali dimers.[13] Included in the calculation are the ground state ($^1\Sigma_g^+$) and the $^1\Sigma_u^+$ excited state at $T_e$ = 18964 cm$^{-1}$. Spectroscopic constants for both states are taken from a detailed experimental investigation by Vidal[1] and are considered to be the most accurate. Presumably, other excited states, lower in energy than the $^1\Sigma_u^+$ state, exist as in the case of $Mg_2$(g),[5] however no known experimental or theoretical constants have been published. The effect in the heat capacity of these missing states would probably be to cause the second $C_p$ maximum to occur at lower temperatures, similiar to $Mg_2$(g).[5] As with other diatomics possessing relatively shallow ground states, $Ca_2$(g) is another example where the traditional integration methods of calculating thermal functions fail.

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] For the ground state only, we included the so-called quasibound rotational levels above the dissociation limit[8] with $J_{lim}$ = 209 and $v_{max}$ = 34 as determined by Gurvich.[9] Instead of performing separate calculations on all 21 isotopic species (made up of all possible dimeric combinations of the six isotopes), we adjust the spectroscopic constants of $^{40}Ca_2$ to a hypothetical natural abundance molecule using a standard reduced mass scaling routine.[10] Thermal functions calculated in this manner should be trivially different from the exact procedure of performing the calculation on each isotope and combining the results according to the natural abundances of each species. The adopted value of $S^\circ$(298.15 K) is 0.39 J·K$^{-1}$·mol$^{-1}$ smaller than that calculated by.[9] It should also be noted that the minor controversy in the literature over the correct assignment of the ground state[11] has apparently been satisfactorily resolved with the currently used data.[12]

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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 | −11.189 | 341.920 | 341.920 | INFINITE |
| 100 | 38.200 | 214.556 | 291.717 | −7.716 | 343.432 | 325.170 | −169.851 |
| 200 | 39.844 | 241.757 | 260.663 | −3.781 | 342.830 | 307.074 | −80.199 |
| 250 | 38.647 | 250.545 | 257.797 | −1.813 | 342.297 | 298.193 | −62.304 |
| 298.15 | 36.577 | 257.183 | 257.183 | 0. | 341.637 | 289.757 | −50.764 |
| 300 | 36.490 | 257.409 | 257.184 | 0.068 | 341.608 | 289.435 | −50.395 |
| 350 | 34.120 | 262.855 | 257.619 | 1.833 | 340.761 | 280.804 | −41.908 |
| 400 | 31.951 | 267.266 | 258.558 | 3.483 | 339.754 | 272.305 | −35.559 |
| 450 | 30.117 | 270.920 | 259.735 | 5.033 | 338.579 | 263.943 | −30.638 |
| 500 | 28.619 | 274.013 | 261.012 | 6.500 | 337.240 | 255.721 | −26.715 |
| 600 | 26.434 | 279.023 | 263.615 | 9.245 | 334.100 | 239.702 | −20.868 |
| 700 | 25.000 | 282.983 | 266.109 | 11.812 | 330.390 | 224.254 | −16.734 |
| 800 | 24.030 | 286.254 | 268.428 | 14.260 | 324.450 | 209.584 | −13.684 |
| 900 | 23.352 | 289.043 | 270.567 | 16.628 | 319.766 | 195.500 | −11.347 |
| 1000 | 22.862 | 291.476 | 272.539 | 18.937 | 314.435 | 181.972 | −9.505 |
| 1100 | 22.498 | 293.637 | 274.361 | 21.204 | 308.456 | 169.010 | −8.026 |
| 1200 | 22.221 | 295.583 | 276.050 | 23.439 | 286.371 | 157.865 | −6.872 |
| 1300 | 22.005 | 297.352 | 277.621 | 25.650 | 281.582 | 147.350 | −5.921 |
| 1400 | 21.835 | 298.977 | 279.089 | 27.842 | 276.774 | 137.205 | −5.119 |
| 1500 | 21.697 | 300.478 | 280.466 | 30.018 | 271.950 | 127.404 | −4.437 |
| 1600 | 21.585 | 301.875 | 281.761 | 32.182 | 267.114 | 117.926 | −3.850 |
| 1700 | 21.492 | 303.180 | 282.983 | 34.336 | 262.268 | 108.750 | −3.341 |
| 1800 | 21.415 | 304.407 | 284.139 | 36.481 | −39.934 | 104.281 | −3.026 |
| 1900 | 21.350 | 305.563 | 285.237 | 38.619 | −41.969 | 112.348 | −3.089 |
| 2000 | 21.295 | 306.656 | 286.281 | 40.752 | −44.021 | 120.523 | −3.148 |
| 2100 | 21.248 | 307.694 | 287.276 | 42.879 | −46.093 | 128.801 | −3.204 |
| 2200 | 21.209 | 308.682 | 288.227 | 45.002 | −48.191 | 137.179 | −3.257 |
| 2300 | 21 177 | 309.624 | 289.137 | 47.121 | −50.323 | 145.652 | −3.308 |
| 2400 | 21.150 | 310.525 | 290.009 | 49.237 | −52.496 | 154.219 | −3.356 |
| 2500 | 21.130 | 311.388 | 290.847 | 51.351 | −54.721 | 162.878 | −3.403 |
| 2600 | 21.115 | 312.216 | 291.653 | 53.463 | −57.009 | 171.627 | −3.448 |
| 2700 | 21.106 | 313.013 | 292.430 | 55.574 | −59.371 | 180.465 | −3.491 |
| 2800 | 21.103 | 313.780 | 293.178 | 57.685 | −61.823 | 189.392 | −3.533 |
| 2900 | 21.105 | 314.521 | 293.902 | 59.795 | −64.379 | 198.409 | −3.574 |
| 3000 | 21.115 | 315.236 | 294.601 | 61.906 | −67.053 | 207.516 | −3.613 |
| 3100 | 21.131 | 315.929 | 295.278 | 64.018 | −69.861 | 216.714 | −3.652 |
| 3200 | 21.154 | 316.600 | 295.934 | 66.132 | −72.820 | 226.006 | −3.689 |
| 3300 | 21.184 | 317.252 | 296.570 | 68.249 | −75.944 | 235.392 | −3.726 |
| 3400 | 21.222 | 317.884 | 297.188 | 70.369 | −79.250 | 244.875 | −3.762 |
| 3500 | 21.267 | 318.500 | 297.788 | 72.494 | −82.752 | 254.459 | −3.798 |
| 3600 | 21.320 | 319.100 | 298.371 | 74.623 | −86.464 | 264.146 | −3.833 |
| 3700 | 21.380 | 319.685 | 298.940 | 76.758 | −90.399 | 273.938 | −3.867 |
| 3800 | 21.449 | 320.256 | 299.493 | 78.899 | −94.569 | 283.841 | −3.902 |
| 3900 | 21.525 | 320.814 | 300.033 | 81.048 | −98.985 | 293.856 | −3 936 |
| 4000 | 21.609 | 321.360 | 300.559 | 83.205 | −103.654 | 303.987 | −3.970 |
| 4100 | 21.700 | 321.895 | 301.073 | 85.370 | −108.585 | 314.239 | −4.003 |
| 4200 | 21.799 | 322.419 | 301.575 | 87.545 | −113 783 | 324.614 | −4.037 |
| 4300 | 21.904 | 322.933 | 302.066 | 89.730 | −119.252 | 335.116 | −4.071 |
| 4400 | 22.017 | 323.438 | 302.546 | 91.926 | −124.987 | 345.748 | −4.105 |
| 4500 | 22.135 | 323.934 | 303.016 | 94.133 | −130.965 | 356.512 | −4.138 |
| 4600 | 22.260 | 324.422 | 303.476 | 96.353 | −137.225 | 367.412 | −4.172 |
| 4700 | 22.391 | 324.902 | 303.926 | 98.586 | −143.757 | 378.453 | −4.206 |
| 4800 | 22.527 | 325.375 | 304.368 | 100.831 | −150.548 | 389.635 | −4.240 |
| 4900 | 22.667 | 325.841 | 304.802 | 103.091 | −157.590 | 400.961 | −4.274 |
| 5000 | 22.812 | 326.300 | 305.227 | 105.365 | −164.874 | 412.434 | −4.309 |
| 5100 | 22.961 | 326.753 | 305.645 | 107.654 | −172.393 | 424.054 | −4.343 |
| 5200 | 23 113 | 327.201 | 306.055 | 109.957 | −180.128 | 435.823 | −4.378 |
| 5300 | 23.269 | 327.642 | 306.458 | 112.277 | −188.082 | 447.744 | −4.413 |
| 5400 | 23.427 | 328.079 | 306.855 | 114.611 | −196.236 | 459.817 | −4.448 |
| 5500 | 23.586 | 328.510 | 307.244 | 116.962 | −204.578 | 472.043 | −4.483 |
| 5600 | 23 748 | 328.937 | 307.628 | 119.329 | −213.076 | 484.420 | −4.518 |
| 5700 | 23.910 | 329.358 | 308.005 | 121.712 | −221.751 | 496.952 | −4.554 |
| 5800 | 24.073 | 329.776 | 308.377 | 124.111 | −230.574 | 509.637 | −4.590 |
| 5900 | 24.237 | 330.189 | 308.743 | 126.526 | −239.532 | 522.476 | −4.626 |
| 6000 | 24.400 | 330.597 | 309.104 | 128.958 | −248.611 | 535.468 | −4.662 |

PREVIOUS: December 1974 (1 atm) CURRENT: September 1983 (1 bar)

## Continued from page 716

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