

Lithium (Li)

$A_1 = 6.941$  Lithium (Li)

REFERENCE STATE

0 to 453.69 K crystal  
 453.69 to 1620.120 K liquid  
 above 1620.120 K ideal monatomic gas

Refer to the individual tables for details.

$Li_1(\text{ref})$

T/K	$C_p$	Enthalpy Reference Temperature = $T_r = 298.15$ K		Standard State Pressure = $p^\circ = 0.1$ MPa		$\log K_f$
		$S^\circ - [C_p^\circ - F(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	
0	0	INFINITE	0	0	0	0
100	13.560	7.342	-4.622	0	0	0
107.250	16.491	8.370	-4.127	0	0	0
107.250	16.494	8.370	-4.021	0	0	0
200	21.573	19.826	-2.286	0	0	0
298.15	24.623	29.085	0	0	0	0
300	24.669	29.237	0.046	0	0	0
400	27.610	36.698	2.646	0	0	0
453.690	29.387	40.288	4.178	CRYSTAL $\leftarrow$ LIQUID	TRANSITION	
453.690	30.392	46.902	7.178	CRYSTAL $\leftarrow$ LIQUID	TRANSITION	
500	30.125	49.843	8.579	0	0	0
600	29.539	55.283	11.562	0	0	0
700	28.987	59.794	14.487	0	0	0
800	28.937	63.661	17.384	0	0	0
900	28.886	67.066	20.275	0	0	0
1000	28.836	70.107	23.161	0	0	0
1100	28.786	72.853	26.042	0	0	0
1200	28.736	75.356	28.918	0	0	0
1300	28.702	77.655	31.790	0	0	0
1400	28.619	79.779	34.656	0	0	0
1500	28.535	81.750	37.514	0	0	0
1600	28.451	83.589	40.363	0	0	0
1620.120	28.431	83.945	40.936	LIQUID $\leftarrow$ IDEAL GAS	FUGACITY = 1 bar	
1620.120	20.794	173.965	186.779	0	0	0
1700	20.799	174.966	188.441	0	0	0
1800	20.810	176.155	190.571	0	0	0
1900	20.826	177.281	192.603	0	0	0
2000	20.849	178.349	194.687	0	0	0
2100	20.882	179.367	196.773	0	0	0
2200	20.925	180.340	198.863	0	0	0
2300	20.980	181.271	200.958	0	0	0
2400	21.049	182.165	203.060	0	0	0
2500	21.132	183.026	205.169	0	0	0
2600	21.231	183.857	207.287	0	0	0
2700	21.347	184.660	209.415	0	0	0
2800	21.479	185.439	211.556	0	0	0
2900	21.628	186.195	213.712	0	0	0
3000	21.794	186.931	215.883	0	0	0
3100	21.977	187.649	218.071	0	0	0
3200	22.177	188.350	220.278	0	0	0
3300	22.391	189.035	222.506	0	0	0
3400	22.622	189.707	224.757	0	0	0
3500	22.868	190.366	227.031	0	0	0
3600	23.130	191.014	229.331	0	0	0
3700	23.406	191.652	231.658	0	0	0
3800	23.697	192.280	234.013	0	0	0
3900	24.003	192.899	236.398	0	0	0
4000	24.323	193.511	238.814	0	0	0
4100	24.658	194.115	241.263	0	0	0
4200	25.009	194.714	243.746	0	0	0
4300	25.375	195.307	246.265	0	0	0
4400	25.696	195.889	248.800	0	0	0
4500	26.069	196.470	251.386	0	0	0
4600	26.464	197.047	254.012	0	0	0
4700	26.873	197.621	256.679	0	0	0
4800	27.297	198.191	259.387	0	0	0
4900	27.736	198.758	262.139	0	0	0
5000	28.191	199.323	264.935	0	0	0
5200	29.134	200.446	270.661	0	0	0
5400	30.152	201.564	276.588	0	0	0
5600	31.233	202.680	282.726	0	0	0
5800	32.377	203.796	289.086	0	0	0
6000	33.581	204.914	295.681	0	0	0

PREVIOUS June 1982 (1 atm)

CURRENT June 1982 (1 bar)

Lithium (Li)

$Li_1(\text{ref})$

## CRYSTAL

## Lithium (Li)

$$S^{\circ}(298.15 \text{ K}) = 29.085 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$T_{\text{fus}} = 453.69 \text{ K}$$

## Enthalpy of Formation

Zero by definition.

## Heat Capacity and Entropy

Heat capacities have been reported by the following authors for the temperature ranges indicated. Roberts,<sup>1</sup> 1.5 to 20 K (Li 99.5% pure); Simon and Swain<sup>2</sup> 15 to 300 K; Martin<sup>3</sup> 22 to 300 K (Li 99.95% pure); Douglas *et al.*,<sup>4</sup> 289.15 K to 1200 K (Li 99.98% pure). Martin<sup>3</sup> in a series of determinations, found that  $C_p$  depended on the thermal history of the sample, a peak at roughly 107 K was ascribed to a martensitic transformation. There is excellent continuity between the results of Roberts<sup>1</sup> and of Martin,<sup>3</sup> while those of Martin<sup>3</sup> and Douglas *et al.*<sup>4</sup> differ by 1% at 300 K and have been smoothly joined. The values of Simon and Swain<sup>2</sup> were not used as they were 5% lower than Martin<sup>3</sup> and did not show the peak at 107 K; also their values for  $\text{Al}_2\text{O}_3$ , reported at the same time, are lower than recent measurements. Heat capacities between 1200 K and the normal boiling point were obtained from the enthalpy equation given by Douglas *et al.*<sup>4</sup> between 420–900°C.

## Fusion Data

Douglas *et al.*<sup>4</sup> report the triple point to be 180.54°C, which is here adopted as the melting point since the densities of solid and liquid lithium at 180°C are not available for calculating  $dT_{\text{fus}}/dP$ . The same authors<sup>4</sup> give the enthalpy of melting as  $432.3 \pm 2.2 \text{ J} \cdot \text{g}^{-1}$ .

## Sublimation Data

Lithium vapor contains an appreciable amount of dimer, whose enthalpy of dissociation has been selected by Evans,<sup>5</sup> from spectroscopic and molecular beam measurements to be  $25.76 \pm 0.10 \text{ kcal} \cdot \text{mol}^{-1}$  at 0 K. This enthalpy of dissociation, together with the thermodynamic functions calculated in this work, has been used to find the partial pressures of Li(g) and Li<sub>2</sub>(g) from the measured total vapor pressures. Hartmann and Schneider<sup>6</sup> report values from 1204 to 1353 K; while Mancherat<sup>7</sup> reports effusion measurements from 735 to 915 K. Mancherat's<sup>7</sup> pressures are calculated on the assumption of monatomic vapor and have been recalculated to fine the true total pressures. Effusion measurements by Lewis<sup>8</sup> and Bogros<sup>9</sup> have been disregarded. Mancherat<sup>7</sup> considers them to be inaccurate because of impurities in the lithium used, and Lewis<sup>8</sup> used a doubtful calibration method. Enthalpy of sublimation to monatomic vapor calculated from the vapor pressures of Hartmann and Schneider<sup>6</sup> and of Mancherat<sup>7</sup> agree to within 2% and the average value has been adopted. The enthalpy of sublimation of the dimer was then calculated using this value.

## References

- <sup>1</sup>L. M. Roberts, Proc. Phys. Soc. 70, 744 (1957).
- <sup>2</sup>F. Simon and R. C. Swain, Z. phys. Chem. B28, 189 (1935).
- <sup>3</sup>D. L. Martin, Proc. Roy. Soc. A254, 444 (1960).
- <sup>4</sup>T. B. Douglas, L. F. Epstein, J. L. Dever, and W. H. Howland, J. Am. Chem. Soc. 77, 2144 (1955).
- <sup>5</sup>W. H. Evans, R. Jacobson, T. R. Munson, and D. D. Wagman, J. Res. Natl. Bur. of Stand. 55, 83 (1955).
- <sup>6</sup>H. Hartmann and R. Schneider, Z. anorg. allgem. Chem. 180, 275 (1929).
- <sup>7</sup>M. Mancherat, C. Rendus 208, 499 (1939).
- <sup>8</sup>L. C. Lewis, Z. Physik 69, 786 (1931).
- <sup>9</sup>A. Bogros, C. Rendus 191, 560 (1930), Ann. Phys. 17, 199 (1932).

## Lithium (Li)

$$A_r = 6.941$$

Li<sub>2</sub>(cr)

T/K	C <sub>p</sub> <sup>a</sup>	Enthalpy Reference Temperature = T <sub>r</sub> = 298.15 K		Standard State Pressure = p <sup>o</sup> = 0.1 MPa		log K <sub>r</sub>
		S <sup>o</sup> - [C <sub>p</sub> <sup>a</sup> - f(T <sub>r</sub> )]/T	H <sup>o</sup> - f(T <sub>r</sub> )]/T	Δ <sub>r</sub> H <sup>o</sup>	Δ <sub>r</sub> G <sup>o</sup>	
0	0	INFINITE	-4.622	0	0	0
100	13.360	48.615	-4.127	0	0	0
107.250	16.491	8.370	-4.021	0	0	0
107.250	16.494	8.370	-4.021	0	0	0
200	21.573	19.876	-2.286	0	0	0
250	23.406	24.854	-1.157	0	0	0
298.15	24.623	29.085	0	0	0	0
300	24.669	29.237	0.046	0	0	0
350	25.930	33.128	1.308	0	0	0
400	27.610	36.698	2.646	0	0	0
450	29.280	40.049	4.069	0	0	0
453.690	29.387	40.288	4.178	---	---	---
500	30.217	43.188	5.559	---	---	---
600	30.380	48.714	8.591	-2.972	0.970	-0.084
700	30.384	53.397	11.629	-2.859	1.619	-0.121
800	30.384	57.455	14.667	-2.716	2.249	-0.147
900	30.384	61.033	17.706	-2.569	2.860	-0.166
1000	30.384	64.235	20.744	-2.417	3.456	-0.180

PREVIOUS

CURRENT: June 1962

## Lithium (Li)

Li<sub>2</sub>(cr)

Li(l)

Lithium (Li)

LIQUID

Lithium (Li)

$S^\circ(298.15\text{ K}) = [33.938] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$   
 $T_{\text{fus}} = 1843\text{ K}$

$\Delta_f H^\circ(298.15\text{ K}) = [2.380] \text{ kJ}\cdot\text{mol}^{-1}$   
 $\Delta_{\text{vap}} H^\circ = 3.000 \pm 0.015 \text{ kJ}\cdot\text{mol}^{-1}$

**Enthalpy of Formation**

$\Delta_f H^\circ(\text{Li, l, } 298.15\text{ K})$  is calculated from that of the crystal by adding the enthalpy of fusion and the difference in enthalpy,  $H^\circ(453.69\text{ K}) - H^\circ(298.15\text{ K})$ , between the crystal and liquid.

**Heat Capacity and Entropy**

The liquid heat capacity values are derived from the enthalpy measurements of Douglas *et al.*<sup>1</sup> The heat capacity curve was extrapolated to 298.15 K and 2000 K in a reasonable manner.

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

**Fusion Data**

The enthalpy of fusion and the melting point were measured by Douglas *et al.*<sup>1</sup>

**Vaporization Data**

Lithium vaporizes to a mixture of monatomic and diatomic gas. The total vapor pressure reaches 1 atm at 1620 K; the vapor pressure of the monatomic gas reaches 1 atm at 1638 K and the enthalpy of vaporization to monatomic gas is  $35.16 \text{ kcal}\cdot\text{mol}^{-1}$ .

**Reference**

<sup>1</sup>T. B. Douglas, L. F. Epstein, J. L. Dever, and W. H. Howland, *J. Am. Chem. Soc.* **77**, 2144 (1955).

T/K	$C_p^\circ$	$S^\circ - [C_p^\circ - H^\circ(T)]/T$	$H^\circ - H^\circ(T)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K <sub>r</sub>
0						
100						
200						
250						
298.15	31.300	33.938	0.	2.380	0.933	-0.163
300	31.284	34.131	0.058	2.392	0.924	-0.161
350	31.000	36.933	1.615	2.686	0.655	-0.098
400	30.711	43.053	3.159	2.891	0.349	-0.046
450	30.414	46.653	36.240	2.996	0.024	-0.003
453.690	30.392	46.902	36.335	4.794	---	---
500	30.125	49.843	37.444	6.199	0.	0.
600	29.539	55.283	39.979	9.182	0.	0.
700	28.987	59.793	42.497	12.108	0.	0.
800	28.637	63.661	44.906	15.004	0.	0.
900	28.886	67.066	47.185	17.895	0.	0.
1000	28.836	70.107	49.226	20.781	0.	0.
1100	28.786	72.853	51.342	23.662	0.	0.
1200	28.736	75.356	53.240	26.538	0.	0.
1300	28.702	77.655	55.031	29.410	0.	0.
1400	28.619	79.779	56.724	32.276	0.	0.
1500	28.535	81.750	58.327	35.134	0.	0.
1600	28.451	83.589	59.850	37.983	0.	0.
1620.120	28.431	83.945	60.147	38.556	---	---
1700	28.368	85.311	61.297	40.824	-145.237	-0.220
1800	28.326	86.931	62.677	43.658	-144.483	-0.468
1900	28.326	88.463	63.994	46.491	-143.732	-0.688
2000	28.326	89.916	65.254	49.323	-142.983	-0.885
2100	28.326	91.298	66.462	52.156	-142.237	-1.062
2200	28.326	92.615	67.621	54.989	-141.495	-1.223

PREVIOUS:

CURRENT: June 1962

Lithium (Li)

Li(l)

0 to 453.69 K crystal  
above 453.69 K liquid

Refer to the individual tables for details.

T/K	C <sub>p</sub> <sup>a</sup>	Enthalpy Reference Temperature = T <sub>r</sub> = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K <sub>r</sub>
		S° - J·K <sup>-1</sup> ·mol <sup>-1</sup>	-(G° - H°(T <sub>r</sub> ))/T	H° - H°(T <sub>r</sub> )	ΔG°	
0	0	0	INFINITE	-4.622	0	0
100	13.360	7.342	48.615	-4.127	0	0
107.250	16.491	8.370	45.859	-4.021	0	0
107.250	16.494	8.370	45.859	-4.021	0	0
200	21.573	19.826	31.255	-2.286	0	0
250	23.406	24.854	29.484	-1.157	0	0
298.15	24.623	29.085	29.085	0	0	0
300	24.669	29.237	29.085	0.046	0	0
350	25.930	33.128	29.390	1.308	0	0
400	27.610	36.698	30.083	2.646	0	0
450	29.280	40.049	31.006	4.069	0	0
453.690	29.387	40.288	31.080	4.178	0	0
453.690	30.392	46.902	31.080	7.178	0	0
500	30.125	49.843	32.684	8.579	0	0
600	29.539	55.283	36.013	11.562	0	0
700	28.987	59.794	39.097	14.487	0	0
800	28.937	63.661	41.931	17.384	0	0
900	28.886	67.066	44.539	20.275	0	0
1000	28.836	70.107	46.946	23.161	0	0
1100	28.786	72.853	49.179	26.042	0	0
1200	28.736	75.356	51.257	28.918	0	0
1300	28.702	77.655	53.201	31.790	0	0
1400	28.619	79.779	55.024	34.656	0	0
1500	28.535	81.750	56.741	37.514	0	0
1600	28.451	83.589	58.362	40.363	0	0
1620.120	28.431	83.945	58.678	40.936	0	0
1700	28.368	85.311	59.897	43.204	-145.237	7.176
1800	28.326	86.931	61.555	46.038	-144.483	16.120
1900	28.326	88.463	62.741	48.871	-143.732	25.072
2000	28.326	89.916	64.064	51.703	-142.983	33.884
2100	28.326	91.298	65.328	54.536	-142.237	42.709
2200	28.326	92.615	66.539	57.368	-141.495	51.499

PREVIOUS:

CURRENT: June 1962

Lithium (Li)

Li<sub>1</sub>(cr,l)

Lithium (Li)

IP(Li, g) = 43487.150 ± 0.005 cm<sup>-1</sup>  
 S°(298.15 K) = 138.781 ± 0.025 J·K<sup>-1</sup>·mol<sup>-1</sup>

IDEAL GAS

A<sub>r</sub> = 6.941 Lithium (Li)

Δ<sub>r</sub>H°(298.15 K) = 157.7 ± 1.0 kJ·mol<sup>-1</sup>  
 Δ<sub>r</sub>H°(298.15 K) = 159.3 ± 1.0 kJ·mol<sup>-1</sup>

Electronic Levels and Quantum Weights	g <sub>e</sub>	g <sub>l</sub>
State	ε <sub>e</sub> , cm <sup>-1</sup>	B <sub>e</sub>
3S <sub>1/2</sub>	0	2
2P <sub>1/2</sub>	14903.66	4
2P <sub>3/2</sub>	14904.00	4
2S <sub>1/2</sub>	27206.12	2
.	.	.
.	.	.
2P <sub>3/2</sub>	43424.3	4
IP	43487.150	

Enthalpy of Formation

The enthalpy of formation of lithium gas is chosen to be the value recommended by CODATA.<sup>1</sup> This value was obtained from 2nd and 3rd law treatments of vapor pressure data. The reported vapor pressures were corrected for the effects of Li<sub>2</sub>(g), using D<sub>0</sub><sup>0</sup> = 101.02 kJ·mol<sup>-1</sup>. As stated by CODATA,<sup>2</sup> the selected value is the weighted average of the 3rd law values of Δ<sub>sub</sub>H°(298.15 K) calculated from the following data:

Source	Δ <sub>sub</sub> H°(298.15 K), kJ·mol <sup>-1</sup>
Hartmann and Schneider <sup>3</sup>	159.04 ± 1.56
Bohdansky and Schiins <sup>4</sup>	159.54 ± 1.85
Schiins <i>et al.</i> <sup>5</sup>	159.22 ± 1.81
Rigney <i>et al.</i> <sup>6</sup>	159.34 ± 1.85
Anisimov and Volyak <sup>7</sup>	159.60 ± 1.58
Shpilrain and Belova <sup>8</sup>	159.06 ± 1.99

The weighted average is Δ<sub>sub</sub>H°(298.15 K) = 159.3 ± 1.0 kJ·mol<sup>-1</sup>.

The 2nd law values calculated from the above sources lead to more positive values. 3rd law values in reasonable agreement with the selected value were calculated from the data of Bogros,<sup>9</sup> Maucherat,<sup>10</sup> Achenet,<sup>11</sup> Wu,<sup>12</sup> and Bomilla.<sup>13</sup>

Heat Capacity and Entropy

The thermal functions for the five alkali metal monatomic gases are calculated by the same procedure. Observed and estimated atomic energy levels are included in the partition function calculation, using an ionization potential lowering (IP-kT) technique as the cutoff procedure in the energy level summation.<sup>16</sup>

The lowest lying levels for these metals [14904 cm<sup>-1</sup> (Li), 16956 cm<sup>-1</sup> (Na), 12578 cm<sup>-1</sup> (K), 12578 cm<sup>-1</sup> (Cs)] do not contribute to the thermal functions below ~1000 K; there is only a translational contribution below this temperature. Above this approximate temperature, the thermal functions become increasingly sensitive to the partition function cutoff procedure used, due to the combined effect of the observation of atomic energy levels of high principal quantum number and a low ionization potential. Energy levels have been observed up to n = 42 (Li), 59 (Na), 79 (K), 77 (Rb), and 73 (Cs). However, not all predicted levels have been observed for each of these principal quantum numbers. The ionization potentials vary from 43487.29 cm<sup>-1</sup> for Li to 31406.1 cm<sup>-1</sup> for Cs. In calculating the thermal functions with the inclusion of missing levels up to the high principal quantum numbers just mentioned, the Gibbs energy functions show significant differences (depending on the cutoff procedure) above 3000 K.<sup>16</sup>

The atomic energy levels have been taken from the compilation of Moore.<sup>14,15</sup> Our calculated values for the thermal functions are similar to those recommended by CODATA.<sup>1</sup> They do differ for two reasons, however. First, the entropy differs by 0.1094 J·K<sup>-1</sup>·mol<sup>-1</sup> because this table uses a reference pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, the entropies at 298.15 K for all alkali metal gases differs by ~0.004 J·K<sup>-1</sup>·mol<sup>-1</sup>, presumably due to the use of slightly different values for auxiliary data.

References

- J. D. Cox, chairman, CODATA Task Group on Key Values for Thermodynamics, *J. Chem. Thermodyn.* **10**, 903 (1978).
- J. D. Cox, chairman, CODATA Task Group on Key Values for Thermodynamics, CODATA Special Report No. 8, (1980).
- H. Hartmann and R. Schneider, *Z. anorg. allgem. Chem.* **180**, 275 (1929).
- J. Bohdanský and H. E. J. Schiins, *J. Appl. Phys.* **36**, 3683 (1965); *J. Phys. Chem.* **71**, 215 (1967).
- H. E. J. Schiins, R. W. M. van Wijk, and B. Dorpinza, *Z. Metallkunde* **62**, 330 (1971).

Continued on page 1527

Lithium (Li)

Li(g)

T/K	C <sub>p</sub> <sup>o</sup>	Enthalpy Reference Temperature = T <sub>r</sub> = 298.15 K		Standard State Pressure = P° = 0.1 MPa		log K <sub>r</sub>
		S° - [G° - IP(T <sub>r</sub> )]/T	H° - H°(T <sub>r</sub> )	Δ <sub>r</sub> H°	Δ <sub>r</sub> G°	
0	0	INFINITE	0	157.725	INFINITE	
100	20.786	116.074	-6.197	159.308	148.435	
200	20.786	130.481	-2.040	159.545	137.415	
250	20.786	135.120	-1.001	159.437	131.890	
298.15	20.786	138.781	0	159.300	126.594	-22.179
300	20.786	138.909	0.038	159.293	126.391	-22.007
350	20.786	142.114	1.078	159.069	120.924	-18.047
400	20.786	144.889	2.117	158.771	115.495	-15.082
450	20.786	147.337	3.156	158.387	110.107	-12.781
500	20.786	149.527	4.196	157.917	105.074	-10.977
600	20.786	153.317	6.274	154.012	95.192	-8.287
700	20.786	156.521	8.353	151.165	85.456	-6.377
800	20.786	159.297	10.431	148.348	75.839	-4.952
900	20.786	161.745	12.510	145.535	66.324	-3.649
1000	20.786	163.935	14.589	142.728	56.900	-2.972
1100	20.786	165.916	16.667	140.925	47.556	-2.258
1200	20.786	167.725	18.746	139.128	38.285	-1.666
1300	20.786	169.389	20.825	137.334	29.080	-1.168
1400	20.787	170.929	22.904	135.544	19.936	-0.744
1500	20.789	172.363	24.982	133.769	10.848	-0.378
1600	20.793	173.705	27.061	132.004	1.812	-0.059
1620.120	20.794	173.965	27.479	131.250	0	---
1700	20.799	174.966	29.141	130.500	0	---
1800	20.810	175.155	31.271	129.750	0	---
1900	20.826	175.281	33.303	129.000	0	---
2000	20.849	175.349	35.386	128.250	0	---
2100	20.882	175.367	37.473	127.500	0	---
2200	20.925	180.340	39.563	126.750	0	---
2300	20.980	181.271	41.658	126.000	0	---
2400	21.049	182.165	43.768	125.250	0	---
2500	21.132	183.026	45.868	124.500	0	---
2600	21.231	183.857	47.986	123.750	0	---
2700	21.347	184.660	50.115	123.000	0	---
2800	21.479	185.439	52.256	122.250	0	---
2900	21.628	186.195	54.412	121.500	0	---
3000	21.794	186.931	56.582	120.750	0	---
3100	21.977	187.649	58.771	120.000	0	---
3200	22.177	188.350	60.978	119.250	0	---
3300	22.391	189.035	63.206	118.500	0	---
3400	22.622	189.707	65.457	117.750	0	---
3500	22.868	190.366	67.731	117.000	0	---
3600	23.130	191.014	70.031	116.250	0	---
3700	23.406	191.652	72.358	115.500	0	---
3800	23.697	192.280	74.713	114.750	0	---
3900	24.003	192.899	77.098	114.000	0	---
4000	24.323	193.511	79.514	113.250	0	---
4100	24.658	194.115	81.963	112.500	0	---
4200	25.009	194.714	84.446	111.750	0	---
4300	25.375	195.309	86.965	111.000	0	---
4400	25.696	195.889	89.500	110.250	0	---
4500	26.069	196.470	92.086	109.500	0	---
4600	26.464	197.047	94.712	108.750	0	---
4700	26.873	197.621	97.379	108.000	0	---
4800	27.297	198.191	100.087	107.250	0	---
4900	27.736	198.758	102.839	106.500	0	---
5000	28.191	199.323	105.635	105.750	0	---
5100	28.650	199.885	108.472	105.000	0	---
5200	29.134	200.446	111.361	104.250	0	---
5300	29.635	201.006	114.299	103.500	0	---
5400	30.152	201.564	117.288	102.750	0	---
5500	30.684	202.122	120.330	102.000	0	---
5600	31.233	202.680	123.426	101.250	0	---
5700	31.798	203.238	126.577	100.500	0	---
5800	32.377	203.796	129.786	99.750	0	---
5900	32.972	204.354	133.053	99.000	0	---
6000	33.581	204.914	136.381	98.250	0	---

PREVIOUS: June 1962 (1 atm)      CURRENT: December 1983 (1 bar)

Lithium, Ion (Li<sup>+</sup>)

*M<sub>r</sub>* = 6.94045

$\Delta H^\circ(0\text{ K}) = 677.947 \pm 0.002\text{ kJ}\cdot\text{mol}^{-1}$   
 $\Delta H^\circ(298.15\text{ K}) = [685.719]\text{ kJ}\cdot\text{mol}^{-1}$

IDEAL GAS

Electronic Level and Quantum State	Weight <i>g<sub>i</sub></i>
<sup>1</sup> S <sub>0</sub>	1

$\Delta H^\circ(\text{Li}^+, \text{g}, 0\text{ K}) = 610079.0 \pm 0.1\text{ cm}^{-1}$   
 $S^\circ(298.15\text{ K}) = 133.017 \pm 0.02\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

Enthalpy of Formation

$\Delta H^\circ(\text{Li}^+, \text{g}, 0\text{ K})$  is calculated from  $\Delta H^\circ(\text{Li}, \text{g}, 0\text{ K})$  using the spectroscopic value of  $IP(\text{Li}) = 43487.150 \pm 0.005\text{ cm}^{-1}$  ( $520.222 \pm .000\text{ kJ}\cdot\text{mol}^{-1}$ ) from Moore.<sup>2</sup> The ionization limit is converted from  $\text{cm}^{-1}$  to  $\text{kJ}\cdot\text{mol}^{-1}$  using the factor,  $1\text{ cm}^{-1} = 0.01196266\text{ kJ}\cdot\text{mol}^{-1}$ , which is derived from the 1973 CODATA fundamental constants.<sup>3</sup> Rosenstock *et al.*<sup>4</sup> and Levin and Lias<sup>5</sup> have summarized additional ionization and appearance potential data.

$\Delta H^\circ(\text{Li}^+, \text{g}, 298.15\text{ K})$  is calculated from  $\Delta H^\circ(\text{Li}, \text{g}, 0\text{ K})$  with JANAF<sup>6</sup> enthalpies,  $H^\circ(0\text{ K}) - H^\circ(298.15\text{ K})$ , for  $\text{Li}(\text{g})$ ,  $\text{Li}^+(\text{g})$ , and  $e^-(\text{ref})$ .  $\Delta H^\circ(\text{Li}, \text{g})$  differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*<sup>4</sup>  $\Delta H^\circ(298.15\text{ K})$  should be changed by  $-6.197\text{ kJ}\cdot\text{mol}^{-1}$  if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,<sup>6</sup> 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<sup>7</sup> 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, the first excited state is approximately  $476046\text{ cm}^{-1}$  above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state. The reported uncertainty in  $S^\circ(298.15\text{ K})$  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.<sup>7</sup>

References

- <sup>1</sup>JANAF Thermochemical Tables:  $\text{Li}(\text{g})$ , 6-30-62;  $e^-(\text{ref})$ , 3-31-82.
- <sup>2</sup>C. E. Moore, U. S. Nat. Bur. Stand., NSRDS-NBS-34, (1970).
- <sup>3</sup>E. R. Cohen and B. N. Taylor, J. Phys. Chem. Ref. Data 2, 663 (1973).
- <sup>4</sup>H. M. Rosenstock, K. Draxl *et al.*, J. Phys. Chem. Ref. Data 6, Supp. 1 (1977).
- <sup>5</sup>R. D. Levin and S. G. Lias, U. S. Nat. Bur. Stand., NSRDS-NBS-71, (1982).
- <sup>6</sup>C. E. Moore, U. S. Nat. Bur. Stand., NSRDS-NBS-35, Volume 1, (1970) [Reprint of NBS Circular 467, Volume 1, 1949].
- <sup>7</sup>J. R. Downey, Jr., The Dow Chemical Company, AFOSR-TR-78-0960, Contract No. F44620-75-1-0048, (1978).

Li(g)

T/K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> - [C <sub>p</sub> <sup>o</sup> - H <sup>o</sup> (T)]/T	H <sup>o</sup> - H <sup>o</sup> (T)/T	Standard State Pressure = P <sup>o</sup> = 0.1 MPa	log K <sub>i</sub>
				kJ·mol <sup>-1</sup>	ΔG <sup>o</sup>
0	0	INFINITE	0	677.947	-113.611
100	20.786	110.309	-6.197	685.719	-112.870
200	20.786	124.717	-4.119	685.751	-95.803
250	20.786	129.356	-3.359	686.566	-82.988
298.15	20.786	133.017	0	687.507	-73.011
300	20.786	133.145	0.038	687.963	-72.709
350	20.786	136.349	1.078	685.552	-65.054
400	20.786	139.123	2.117	686.706	-51.108
450	20.786	141.575	3.156	690.105	-33.138
500	20.786	143.763	4.196	574.857	-23.090
600	20.786	147.553	6.274	516.755	-17.650
700	20.786	150.757	8.353	469.477	-15.509
800	20.786	153.533	10.431	428.181	-13.435
900	20.786	155.981	12.510	392.926	-11.811
1000	20.786	158.171	14.589	363.688	-10.473
1100	20.786	160.152	16.667	339.293	-9.349
1200	20.786	161.961	18.746	317.070	-8.552
1300	20.786	163.625	20.824	297.520	-8.091
1400	20.786	165.165	22.903	280.181	-7.863
1500	20.786	166.599	24.982	264.661	-7.705
1600	20.786	167.941	27.060	250.750	-7.630
1700	20.786	169.201	29.139	238.356	-7.630
1800	20.786	170.389	31.217	227.333	-7.722
1900	20.786	171.513	33.296	217.529	-7.883
2000	20.786	172.579	35.375	208.926	-8.111
2100	20.786	173.593	37.453	201.514	-8.401
2200	20.786	174.560	39.532	195.288	-8.755
2300	20.786	175.484	41.610	189.236	-9.172
2400	20.786	176.369	43.689	184.345	-9.643
2500	20.786	177.217	45.768	180.605	-10.166
2600	20.786	178.032	47.846	177.996	-10.741
2700	20.786	178.817	49.925	176.154	-11.363
2800	20.786	179.573	52.004	174.926	-12.032
2900	20.786	180.302	54.082	174.252	-12.747
3000	20.786	181.007	56.161	174.101	-13.507
3100	20.786	181.688	58.239	174.566	-14.311
3200	20.786	182.348	60.318	175.638	-15.160
3300	20.786	182.988	62.397	177.312	-16.054
3400	20.786	183.608	64.475	179.593	-17.000
3500	20.786	184.211	66.554	182.584	-18.000
3600	20.786	184.797	68.632	186.293	-19.060
3700	20.786	185.366	70.711	190.726	-20.180
3800	20.786	185.920	72.790	195.886	-21.360
3900	20.786	186.460	74.868	201.779	-22.600
4000	20.786	186.987	76.947	208.411	-23.910
4100	20.786	187.500	79.025	215.799	-25.280
4200	20.786	188.001	81.104	223.951	-26.710
4300	20.786	188.490	83.183	232.886	-28.200
4400	20.786	188.968	85.261	242.621	-29.750
4500	20.786	189.435	87.340	253.166	-31.360
4600	20.786	189.892	89.418	264.531	-33.030
4700	20.786	190.339	91.497	276.726	-34.760
4800	20.786	190.776	93.576	289.761	-36.550
4900	20.786	191.205	95.654	303.646	-38.400
5000	20.786	191.625	97.733	318.381	-40.310
5100	20.786	192.036	99.811	333.976	-42.280
5200	20.786	192.440	101.890	350.441	-44.310
5300	20.786	192.836	103.969	367.786	-46.400
5400	20.786	193.225	106.047	386.031	-48.550
5500	20.786	193.606	108.126	405.186	-50.760
5600	20.786	193.981	110.204	425.261	-53.030
5700	20.786	194.348	112.283	446.266	-55.360
5800	20.786	194.710	114.362	468.211	-57.750
5900	20.786	195.065	116.440	491.106	-60.200
6000	20.786	195.415	118.519	515.051	-62.710

PREVIOUS March 1965 (1 atm)

CURRENT: December 1983 (1 bar)

Lithium, Ion (Li<sup>+</sup>)

Li(g)

Lithium, ion (Li<sup>+</sup>)

EA(Li, g) = 0.6180 ± 0.0005 eV  
 S°(298.15 K) = 133.019 ± 0.005 J·K<sup>-1</sup>·mol<sup>-1</sup>

IDEAL GAS

Electronic Level and Quantum Weight State	ε <sub>n</sub> , cm <sup>-1</sup>	g <sub>n</sub>
<sup>1</sup> S <sub>0</sub>	0.0	1

Enthalpy of Formation

The enthalpy of formation, at 0 K, for Li<sup>+</sup>(g) is calculated from the adopted electron affinity, EA(Li, g) = 0.6180 ± 0.0005 eV (59.627 ± 0.048 kJ·mol<sup>-1</sup>). This value, recommended by Hotop and Lineberger,<sup>1</sup> was measured by a tunable laser photodetachment threshold technique.<sup>2,3</sup> Additional discussion on Li<sup>+</sup>(g) may be obtained in the critical discussions of Hotop and Lineberger,<sup>1,4</sup> Rosenstock *et al.*,<sup>5</sup> and Massey.<sup>6</sup>  
 ΔH°(Li<sup>+</sup>, g, 298.15 K) is obtained from ΔH°(Li, g, 0 K) by using EA(Li, g) with JANAF<sup>7</sup> enthalpies, H°(0 K)–H°(298.15 K), for Li<sup>+</sup>(g), Li(g), and e<sup>-</sup> (ref). ΔH°(Li<sup>+</sup> → Li + e<sup>-</sup>, 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.*<sup>5</sup> ΔH°(298.15 K) should be changed by +6.197 kJ·mol<sup>-1</sup> if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state configuration for Li<sup>+</sup>(g) is given by Hotop and Lineberger<sup>1,4</sup> and Rosenstock *et al.*<sup>5</sup> Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

References

1. H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data*, **14**, 731 (1985).
2. D. Feldman, *Z. Physik A*, **277**, 19 (1976).
3. Y. K. Bae and J. R. Peterson, *Phys. Rev. A*, to be published.
4. H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data*, **4**, 539 (1975).
5. H. M. Rosenstock, K. Draxl *et al.*, *J. Phys. Chem. Ref. Data*, **6**, Supp. 1 (1977).
6. H. S. W. Massey, "Negative Ions," 3rd ed., Cambridge University Press, Cambridge, (1976).
7. JANAF Thermochemical Tables: Li(g), 3–31–82; e<sup>-</sup> (ref), 3–31–82.

M<sub>r</sub> = 6.94155 Lithium, ion (Li<sup>+</sup>)

Li<sup>+</sup>(g)

T/K	C <sub>p</sub> <sup>o</sup>	Enthalpy Reference Temperature = T <sub>r</sub> = 298.15 K		Standard State Pressure = P° = 0.1 MPa		log K <sub>r</sub>
		S° – (G° – H°(T <sub>r</sub> ))/T	H° – H°(T <sub>r</sub> )/T	ΔH°	ΔG°	
0	0	INFINITE	-6.197	98.097		
100	20.786	110.311	-4.119		68.742	-12.043
200	20.786	134.920	-2.040		64.589	-11.942
250	20.786	129.357	-1.001		64.548	-9.633
298.15	20.786	133.019	0		60.692	-7.926
300	20.786	133.147	0.038		57.010	-6.618
350	20.786	136.351	1.078		53.797	-5.620
400	20.786	139.834	2.117		47.859	-4.166
450	20.786	141.575	3.156		42.415	-3.165
500	20.786	143.765	4.196		37.388	-2.441
600	20.786	147.555	6.274		32.724	-1.899
700	20.786	150.827	8.353		28.381	-1.482
800	20.786	153.535	10.431		24.328	-1.155
900	20.786	155.983	12.510		20.536	-0.894
1000	20.786	158.173	14.589		16.984	-0.682
1100	20.786	160.154	16.667		13.653	-0.509
1200	20.786	161.963	18.746		10.527	-0.367
1300	20.786	163.627	20.824		7.591	-0.248
1400	20.786	165.167	22.903		4.865	-0.160
1500	20.786	166.601	24.982		2.409	-0.098
1600	20.786	167.943	27.060		0.200	-0.053
1700	20.786	169.203	29.139		-18.361	-0.683
1800	20.786	170.391	31.217		-31.407	-0.820
1900	20.786	171.515	33.296		-44.871	-1.065
2000	20.786	172.581	35.375		-58.716	-1.278
2100	20.786	173.595	37.453		-72.913	-1.465
2200	20.786	174.562	39.532		-87.436	-1.631
2300	20.786	175.486	41.610		-102.284	-1.781
2400	20.786	176.371	43.689		-117.451	-1.916
2500	20.786	177.219	45.768		-132.931	-2.040
2600	20.786	178.034	47.846		-148.722	-2.154
2700	20.786	178.819	49.925		-164.828	-2.259
2800	20.786	179.575	52.004		-181.242	-2.359
2900	20.786	180.304	54.082		-197.966	-2.450
3000	20.786	181.009	56.161		-215.000	-2.536
3100	20.786	181.690	58.239		-232.344	-2.618
3200	20.786	182.350	60.318		-250.000	-2.695
3300	20.786	182.990	62.397		-267.966	-2.768
3400	20.786	183.610	64.475		-286.242	-2.838
3500	20.786	184.213	66.554		-304.828	-2.905
3600	20.786	184.799	68.632		-323.722	-2.970
3700	20.786	185.368	70.711		-342.922	-3.033
3800	20.786	185.922	72.790		-362.428	-3.095
3900	20.786	186.462	74.868		-382.242	-3.157
4000	20.786	186.989	76.947		-402.366	-3.218
4100	20.786	187.502	79.025		-422.798	-3.279
4200	20.786	188.003	81.104		-443.538	-3.339
4300	20.786	188.492	83.183		-464.584	-3.399
4400	20.786	188.970	85.261		-485.936	-3.459
4500	20.786	189.437	87.340		-507.594	-3.519
4600	20.786	189.894	89.418		-529.558	-3.579
4700	20.786	190.341	91.497		-551.828	-3.639
4800	20.786	190.778	93.576		-574.404	-3.699
4900	20.786	191.207	95.654		-597.286	-3.759
5000	20.786	191.627	97.733		-620.474	-3.819
5100	20.786	192.038	99.811		-643.968	-3.879
5200	20.786	192.442	101.890		-667.768	-3.939
5300	20.786	192.838	103.969		-691.874	-3.999
5400	20.786	193.227	106.047		-716.286	-4.059
5500	20.786	193.608	108.126		-741.004	-4.119
5600	20.786	193.982	110.204		-766.036	-4.179
5700	20.786	194.350	112.283		-791.382	-4.239
5800	20.786	194.712	114.362		-817.042	-4.299
5900	20.786	195.067	116.440		-843.018	-4.359
6000	20.786	195.417	118.519		-869.306	-4.419

PREVIOUS:

CURRENT: December 1983 (1 bar)

Lithium, ion (Li<sup>+</sup>)

Li<sup>+</sup>(g)

IDEAL GAS

Lithium Nitride (LiN)

Lithium Nitride (LiN)

Li<sub>3</sub>N<sub>2</sub>(g)

$\Delta_f H^\circ(0 \text{ K}) = 334.7 \pm 167 \text{ kJ mol}^{-1}$   
 $\Delta_f H^\circ(298.15 \text{ K}) = 334.7 \pm 167 \text{ kJ mol}^{-1}$

$S^\circ(298.15 \text{ K}) = [208.245] \text{ J K}^{-1} \text{ mol}^{-1}$

Electronic Level and Quantum State	Weight $g_i$
$[\Sigma]$	0
$[\Sigma]$	3

$\omega_e x_e = [7] \text{ cm}^{-1}$   
 $B_e = [1.25] \text{ cm}^{-1}$   
 $\sigma = 1$   
 $r_e = [1.71] \text{ \AA}$

Enthalpy of Formation

The adopted  $\Delta_f H^\circ(298.15 \text{ K}) = 80 \pm 40 \text{ kcal mol}^{-1}$  is calculated from the following estimates:

Method	$D_0^\circ, \text{ kcal mol}^{-1}$	$\Delta_f H^\circ(298.15 \text{ K}), \text{ kcal mol}^{-1}$
Estimate $D_0^\circ$ from geometric means for Li <sub>2</sub> and N <sub>2</sub>	76	75
Estimate from $D_0^\circ$ for series N <sub>2</sub> (g), CN(g), BN(g), and BeN(g)	40 - 100	110 - 50
Estimate from $D_0^\circ$ for series HN(g), HO(g), HF(g), LiF(g) and LiO(g)	20 - 60	130 - 90

Margrave and Shapitanonda<sup>1</sup> report estimated dissociation energies in the range 111-178 kcal mol<sup>-1</sup> based on approximate ionic binding energies calculated from ionic radii for N<sup>-</sup> in the range 0.70 to 1.08 Å.

Heat Capacity and Entropy

The molecular constants,  $\omega_e$ ,  $r_e$ , and  $\omega_e x_e$  are estimated by comparison with those of CN, BN, CO, BO and LiO. The values of  $\alpha_e$  and  $B_e$  are calculated from the above constants. The ground state configuration is assumed to be  $\Sigma$  by analogy with NH and OH<sup>+</sup>.

Reference

<sup>1</sup>J. L. Margrave and P. Shapitanonda, J. Phys. Chem. 59, 1231 (1955).

T/K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> - [C <sub>p</sub> <sup>o</sup> - (T <sub>o</sub> )/T]	H <sup>o</sup> - H <sup>o</sup> (T <sub>o</sub> )	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K <sub>c</sub>
0	0	INFINITE	0	INFINITE	334.678	INFINITE
100	29.167	175.034	235.957	-8.999	334.678	334.678
200	30.651	195.587	211.181	-6.092	335.639	-170.734
250	31.812	202.552	208.780	-3.119	335.316	-83.095
298.15	32.838	208.245	208.245	-1.557	335.021	-65.587
300	32.875	208.448	208.246	0.	334.720	-34.288
350	33.762	213.585	208.649	0.061	334.708	309.713
400	34.479	218.142	209.556	1.727	334.383	-53.926
450	35.056	222.237	210.742	3.434	334.022	-45.604
500	35.521	225.956	212.080	5.173	333.605	-39.369
600	36.215	232.497	214.952	6.938	333.123	-34.526
700	36.702	238.118	217.870	10.577	329.238	298.562
800	37.084	243.034	220.715	14.174	328.438	328.438
900	37.345	247.626	223.444	17.863	327.676	273.171
1000	37.574	251.373	226.043	21.584	326.918	228.735
1100	37.767	254.964	228.511	25.330	326.158	15.528
1200	37.935	258.257	230.855	29.098	325.396	-11.981
1300	38.084	261.300	233.081	32.883	324.631	-10.694
1400	38.221	264.127	235.199	36.684	323.864	-9.609
1500	38.347	266.768	237.216	40.499	323.095	-8.680
1600	38.466	269.247	239.142	44.328	322.323	-7.877
1700	38.578	271.582	240.982	48.169	321.573	-7.177
1800	38.686	273.791	242.744	52.021	320.841	-6.580
1900	38.790	275.885	244.434	55.884	320.123	-6.081
2000	38.890	277.877	246.056	59.754	319.423	-5.679
2100	38.989	279.777	247.617	63.642	318.741	-5.273
2200	39.085	281.593	249.121	67.536	318.077	-4.865
2300	39.179	283.333	250.570	71.440	317.431	-4.455
2400	39.273	285.002	251.974	75.351	316.801	-4.043
2500	39.364	286.607	253.324	79.270	316.186	-3.630
2600	39.455	288.153	254.634	83.207	315.586	-3.215
2700	39.545	289.643	255.903	87.148	314.999	-2.800
2800	39.634	291.083	257.134	91.098	314.424	-2.385
2900	39.722	292.476	258.329	95.057	313.861	-1.970
3000	39.810	293.824	259.490	99.025	313.309	-1.555
3100	39.898	295.131	260.619	103.002	312.767	-1.140
3200	39.984	296.399	261.717	106.987	312.235	-0.725
3300	40.071	297.630	262.787	110.981	311.711	-0.310
3400	40.157	298.828	263.829	114.984	311.195	0.105
3500	40.243	299.993	264.846	118.995	310.686	0.420
3600	40.328	301.128	265.838	123.015	310.184	0.735
3700	40.414	302.234	266.807	127.044	309.688	1.050
3800	40.499	303.313	267.753	131.081	309.197	1.365
3900	40.584	304.366	268.679	135.127	308.711	1.680
4000	40.668	305.395	269.584	139.181	308.230	1.995
4100	40.753	306.400	270.470	143.243	307.754	2.310
4200	40.837	307.383	271.337	147.314	307.283	2.625
4300	40.921	308.345	272.186	151.394	306.817	2.940
4400	41.006	309.287	273.019	155.482	306.356	3.255
4500	41.090	310.209	273.835	159.578	305.899	3.570
4600	41.173	311.113	274.636	163.683	305.447	3.885
4700	41.257	311.999	275.421	167.796	304.999	4.200
4800	41.341	312.869	276.192	171.918	304.556	4.515
4900	41.422	313.722	276.950	176.048	304.117	4.830
5000	41.508	314.560	277.693	180.186	303.681	5.145
5100	41.592	315.383	278.424	184.332	303.250	5.460
5200	41.675	316.191	279.143	188.487	302.823	5.775
5300	41.759	316.986	279.849	192.651	302.401	6.090
5400	41.842	317.767	280.544	196.822	301.984	6.405
5500	41.925	318.536	281.228	201.003	301.571	6.720
5600	42.009	319.292	281.901	205.191	301.162	7.035
5700	42.092	320.036	282.564	209.388	300.758	7.350
5800	42.175	320.769	283.216	213.593	300.359	7.665
5900	42.258	321.491	283.859	217.806	300.000	7.980
6000	42.341	322.201	284.492	222.028	299.641	8.295

PREVIOUS December 1966 (1 atm)

CURRENT December 1966 (1 bar)

Lithium Nitride (LiN)

Li<sub>3</sub>N<sub>2</sub>(g)



Lithium Oxynitride (LiON)

IDEAL GAS

Lithium Oxynitride (LiON)

$M_r = 36.9471$

$\Delta_f H^\circ(0 \text{ K}) = [181.91 \pm 41.8] \text{ kJ mol}^{-1}$   
 $\Delta_f H^\circ(298.15 \text{ K}) = [179.91 \pm 41.8] \text{ kJ mol}^{-1}$

$S^\circ(298.15 \text{ K}) = 245.332 \text{ J K}^{-1} \text{ mol}^{-1}$

T/K	$C_p^\circ$	$S^\circ - (C_p^\circ - H^\circ(T))/T$	$H^\circ - H^\circ(T)$	$\Delta_f H^\circ$	Standard State Pressure = $p^\circ = 0.1 \text{ MPa}$	$\log K_r$
0	0	INFINITE	-11.301	181.910	INFINITE	
100	34.974	202.507	281.906	179.012	181.910	
200	40.335	228.423	249.272	176.518	179.012	-93.506
250	42.576	237.671	246.053	180.890	176.518	-46.102
298.15	44.424	245.332	245.332	180.380	175.484	-36.665
300	44.490	245.607	245.333	179.912	175.584	-30.586
350	46.144	252.592	245.881	179.895	174.551	-30.392
400	47.585	258.850	247.117	179.432	173.698	-25.923
450	48.838	264.529	248.741	178.961	172.910	-22.980
500	49.975	269.732	250.584	178.457	172.184	-19.987
600	51.676	278.997	254.566	177.909	171.823	-17.950
700	52.982	287.066	258.645	177.399	171.599	-14.913
800	53.962	294.208	262.653	176.925	171.401	-12.755
900	54.706	300.608	266.521	176.485	171.229	-11.144
1000	55.280	306.403	270.224	176.080	171.079	-9.896
1100	55.729	311.694	273.757	175.711	170.948	-8.902
1200	56.085	316.539	277.124	175.377	170.832	-8.093
1300	56.371	321.060	280.332	175.066	170.730	-7.421
1400	56.605	325.246	283.393	174.784	170.641	-6.855
1500	56.797	329.158	286.315	174.530	170.579	-6.372
1600	56.957	332.829	289.108	174.303	170.540	-5.955
1700	57.092	336.286	291.783	174.101	170.520	-5.592
1800	57.206	339.553	294.347	173.921	170.515	-5.278
1900	57.304	342.649	296.808	173.761	170.520	-5.009
2000	57.388	345.590	299.174	173.619	170.536	-4.780
2100	57.461	348.392	301.452	173.493	170.560	-4.592
2200	57.525	351.066	303.647	173.381	170.590	-4.444
2300	57.581	353.625	305.765	173.281	170.623	-4.331
2400	57.630	356.076	307.810	173.191	170.660	-4.248
2500	57.674	358.430	309.788	173.110	170.700	-4.189
2600	57.713	360.693	311.703	173.037	170.743	-4.151
2700	57.747	362.871	313.558	172.971	170.789	-4.130
2800	57.779	364.971	315.357	172.911	170.837	-4.125
2900	57.807	367.000	317.103	172.857	170.886	-4.135
3000	57.832	368.960	318.799	172.808	170.936	-4.156
3100	57.855	370.857	320.448	172.764	170.987	-4.187
3200	57.876	372.694	322.052	172.724	171.038	-4.228
3300	57.895	374.475	323.614	172.688	171.089	-4.277
3400	57.913	376.204	325.135	172.656	171.140	-4.333
3500	57.929	377.883	326.618	172.627	171.191	-4.394
3600	57.943	379.515	328.067	172.600	171.242	-4.460
3700	57.957	381.103	329.477	172.575	171.293	-4.531
3800	57.970	382.649	330.856	172.551	171.344	-4.606
3900	57.981	384.155	332.204	172.528	171.395	-4.685
4000	57.992	385.623	333.521	172.506	171.446	-4.767
4100	58.002	387.055	334.809	172.485	171.497	-4.851
4200	58.011	388.453	336.070	172.465	171.548	-4.937
4300	58.020	389.818	337.304	172.446	171.600	-5.024
4400	58.028	391.152	338.513	172.427	171.651	-5.112
4500	58.035	392.456	339.697	172.409	171.702	-5.201
4600	58.042	393.732	340.858	172.392	171.753	-5.291
4700	58.049	394.980	341.996	172.376	171.804	-5.382
4800	58.055	396.202	343.113	172.361	171.855	-5.473
4900	58.061	397.399	344.208	172.346	171.906	-5.564
5000	58.067	398.572	345.284	172.332	171.957	-5.655
5100	58.072	399.722	346.340	172.318	172.008	-5.746
5200	58.077	400.850	347.378	172.305	172.059	-5.837
5300	58.081	401.956	348.397	172.292	172.110	-5.928
5400	58.086	403.042	349.399	172.280	172.161	-6.019
5500	58.090	404.108	350.384	172.268	172.212	-6.110
5600	58.094	405.154	351.353	172.257	172.263	-6.201
5700	58.097	406.183	352.306	172.246	172.314	-6.292
5800	58.101	407.191	353.243	172.235	172.365	-6.383
5900	58.104	408.186	354.166	172.225	172.416	-6.474
6000	58.107	409.163	355.075	172.215	172.467	-6.565

PREVIOUS: September 1966 (1 atm)

CURRENT: September 1966 (1 bar)

Vibrational Frequencies and Degeneracies  
 $\nu, \text{ cm}^{-1}$   
 1350(1)  
 330(1)  
 650(1)

Ground State Quantum Weight: [1]  
 Point Group:  $C_2$   
 Bond Distances: O-Li =  $1.63 \pm 0.07 \text{ \AA}$  O-N =  $1.30 \pm 0.05 \text{ \AA}$   
 Bond Angle: Li-O-N =  $100 \pm 10^\circ$   
 Product of the Moments of Inertia:  $I_A I_B I_C = 2.65370 \times 10^{-116} \text{ g}^3 \cdot \text{cm}^6$

Enthalpy of Formation

In order to estimate the  $\Delta_f H^\circ(298.15 \text{ K})$  of LiON(g) a comparison with the known  $\Delta_f H^\circ(\text{LiOH}, g, 298.15 \text{ K}) = -59 \text{ kcal mol}^{-1}$  was made. This was estimated from bond energies using  $D(\text{Li-O}) = 88 \text{ kcal mol}^{-1}$ , the average value in  $\text{Li}_2\text{O}(g)$ , and  $D(\text{O-H}) = 111 \text{ kcal mol}^{-1}$ , the average value in  $\text{H}_2\text{O}(g)$ , which yields an estimated  $\Delta_f H^\circ(\text{LiOH}, g, 298.15 \text{ K}) = -49 \text{ kcal mol}^{-1}$  or a difference of  $-10 \text{ kcal mol}^{-1}$ . Using  $D(\text{N-O}) = 69 \text{ kcal mol}^{-1}$  from  $\text{NO}_2\text{Cl}(g)$ (equation 1) and  $D(\text{Li-O}) = 88 \text{ kcal mol}^{-1}$  from  $\text{Li}_2\text{O}(g)$ , the estimated  $\Delta_f H^\circ(298.15 \text{ K}) = 53 \text{ kcal mol}^{-1}$  of LiON(g) was obtained (equation 2). Thus adding the  $-10 \text{ kcal mol}^{-1}$  correction from the above comparison a  $\Delta_f H^\circ(298.15 \text{ K}) = 43 \text{ kcal mol}^{-1}$  for LiON(g) was obtained.

The justification for using a N=O bond energy is from the 1.7 bond order reported by Andrews and Pimentel<sup>1</sup> and a comparison of bond lengths.

- Equations:
- $\text{NO}_2\text{Cl}(g) \rightarrow \text{NOCl}(g) + \text{O}(g)$
  - $\text{LiON}(g) \rightarrow \text{Li}(g) + \text{O}(g) + \text{N}(g)$

Heat Capacity and Entropy

The vibration frequencies, bond distances and bond angle were obtained from Andrews and Pimentel.<sup>1</sup> The principal moments of inertia are:  $I_A = 1.2707 \times 10^{-39}$ ,  $I_B = 3.9785 \times 10^{-39}$  and  $I_C = 5.2492 \times 10^{-39} \text{ g cm}^2$ .

Reference

<sup>1</sup>W. L. S. Andrews and G. C. Pimentel, J. Chem. Phys. 44, 2361 (1966).

Lithium Oxynitride (LiON)

$\text{Li}_2\text{N}_2\text{O}_2(g)$

Lithium Sodium Oxide (LiONa)  $M_r = 45.93017$   $\Delta_f H_f^\circ(0\text{ K}) = [-100.16 \pm 125.5] \text{ kJ mol}^{-1}$   $\Delta_f H_f^\circ(298.15\text{ K}) = [-104.60 \pm 125.5] \text{ kJ mol}^{-1}$   $S^\circ(298.15\text{ K}) = [256.459] \text{ J K}^{-1} \text{ mol}^{-1}$   $\sigma = 1$

Vibrational Frequencies and Degeneracies

$\nu$ , $\text{cm}^{-1}$	[400](1)	[1000](1)	[900](1)
Ground State Quantum Weight: [1]			
Point Group $C_s$			
Bond Distances: O-Li = [1.82] Å O-Na = [2.21] Å			
Bond Angle: Li-O-Na = [105]°			
Product of the Moments of Inertia: $I_A I_B I_C = [3.182324 \times 10^{-11}] \text{ g}^3 \text{ cm}^6$			

**Enthalpy of Formation**  
 Estimated from bond energies derived from enthalpies of formation used in the JANAF Thermochemical Tables.

**Heat Capacity and Entropy**  
 The molecular constants have been estimated by comparison of similar molecules. The principal moments of inertia are:  $I_A = 1.9618 \times 10^{-39} \text{ g cm}^2$ ,  $I_B = 11.7930 \times 10^{-39} \text{ g cm}^2$ , and  $I_C = 13.7548 \times 10^{-39} \text{ g cm}^2$ .

T/K	Enthalpy Reference Temperature = $T_r = 298.15\text{ K}$			Standard State Pressure = $p^\circ = 0.1\text{ MPa}$			log $K_r$
	$C_p^\circ$	$S^\circ - [C_p^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H_f^\circ$	$\Delta_f G_f^\circ$		
0	0	INFINITE	-10.966	-100.156	INFINITE		
100	34.139	215.303	291.557	-100.102	-109.851		
200	38.470	240.232	260.252	-102.233	-118.826		
250	40.849	249.071	257.156	-103.432	-122.836		
298.15	43.079	256.459	256.459	-104.600	-126.468		
300	43.161	256.726	256.460	0.080	-126.604		
350	45.267	263.540	256.993	2.292	-105.887		
400	47.099	269.708	258.203	4.602	-109.831		
450	48.652	275.348	259.799	6.997	-111.180		
500	49.952	280.543	261.617	9.463	-115.534		
600	51.941	289.837	265.564	14.564	-118.012		
700	53.334	297.955	269.624	19.831	-120.249		
800	54.331	305.145	273.623	25.217	-122.337		
900	55.060	311.589	277.490	30.689	-124.340		
1000	55.607	317.419	281.196	36.223	-126.316		
1100	56.006	322.740	284.734	41.806	-128.278		
1200	56.353	327.629	288.108	47.425	-130.219		
1300	56.653	332.151	291.324	53.074	-132.142		
1400	56.922	336.354	294.397	58.746	-134.042		
1500	56.993	340.280	297.322	64.437	-135.928		
1600	57.134	344.963	300.123	70.144	-137.818		
1700	57.252	349.431	302.805	75.863	-139.709		
1800	57.352	353.706	305.376	81.594	-141.596		
1900	57.437	357.809	307.844	87.333	-143.478		
2000	57.510	356.757	310.217	93.081	-145.352		
2100	57.573	359.565	312.500	98.835	-147.219		
2200	57.628	362.244	314.701	104.595	-149.078		
2300	57.676	364.807	316.824	110.360	-150.928		
2400	57.718	367.262	318.875	116.130	-152.768		
2500	57.755	369.619	320.858	121.904	-154.600		
2600	57.788	371.885	322.777	127.681	-156.424		
2700	57.818	374.067	324.637	133.461	-158.242		
2800	57.844	376.170	326.440	139.244	-160.055		
2900	57.868	378.200	328.190	145.030	-161.862		
3000	57.890	380.162	329.890	150.818	-163.662		
3100	57.910	382.061	331.542	156.608	-165.456		
3200	57.927	383.900	333.150	162.400	-167.244		
3300	57.943	385.683	334.715	168.193	-169.026		
3400	57.958	387.413	336.240	173.988	-170.802		
3500	57.972	389.093	337.726	179.785	-172.573		
3600	57.984	390.726	339.175	185.583	-174.339		
3700	57.996	392.315	340.590	191.382	-176.101		
3800	58.006	393.862	341.972	197.182	-177.858		
3900	58.016	395.369	343.322	202.983	-179.611		
4000	58.025	396.838	344.641	208.785	-181.360		
4100	58.034	398.271	345.932	214.588	-183.105		
4200	58.041	399.669	347.195	220.392	-184.846		
4300	58.049	401.033	348.431	226.196	-186.582		
4400	58.056	402.369	349.642	232.002	-188.314		
4500	58.062	403.674	350.828	237.807	-190.042		
4600	58.068	404.950	351.991	243.614	-191.766		
4700	58.073	406.199	353.131	249.421	-193.485		
4800	58.079	407.422	354.249	255.229	-195.199		
4900	58.084	408.620	355.347	261.037	-196.908		
5000	58.088	409.793	356.424	266.845	-198.612		
5100	58.093	410.943	357.482	272.654	-200.312		
5200	58.097	412.072	358.521	278.464	-202.007		
5300	58.101	413.178	359.542	284.274	-203.697		
5400	58.104	414.264	360.545	290.084	-205.382		
5500	58.108	415.330	361.531	295.895	-207.062		
5600	58.111	416.378	362.502	301.705	-208.737		
5700	58.114	417.406	363.456	307.515	-210.407		
5800	58.117	418.417	364.398	313.328	-212.072		
5900	58.120	419.410	365.319	319.140	-213.732		
6000	58.123	420.387	366.228	324.952	-215.387		

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

IDEAL GAS

Lithium Oxide (LIO)

M<sub>r</sub> = 22.9404 Lithium Oxide (LIO)

Li<sub>2</sub>O(g)

ΔH<sup>0</sup>(0 K) = 84.12 ± 20.9 kJ·mol<sup>-1</sup>  
 ΔH<sup>0</sup>(298.15 K) = 84.10 ± 20.9 kJ·mol<sup>-1</sup>

S<sup>0</sup>(298.15 K) = [210.963] J·K<sup>-1</sup>·mol<sup>-1</sup>

Electronic Level and Quantum Weight State	ε <sub>i</sub> , cm <sup>-1</sup>	g <sub>i</sub>
[ <sup>1</sup> Π]	0	4

ω<sub>e</sub> = 745 cm<sup>-1</sup>  
 B<sub>e</sub> = [1.333] cm<sup>-1</sup>  
 ω<sub>e</sub>x<sub>e</sub> = [4.835] cm<sup>-1</sup>  
 α<sub>e</sub> = [0.01288] cm<sup>-1</sup>  
 σ = 1  
 r<sub>e</sub> = [1.62] Å

Enthalpy of Formation

White *et al.*<sup>1</sup> calculated the enthalpy of formation from their mass spectral data by two different methods. For the first calculation (a) they combined the slope of the log Π vs 1/T curve for LiO<sup>+</sup> with the slopes for Li<sup>+</sup> and Li<sub>2</sub>O<sup>+</sup> for the reaction Li<sub>2</sub>O(g) → Li(g) + LiO(g). For the second calculation (b) they assumed a cross section σ LiO<sup>+</sup>/Li<sub>2</sub>O = 1 and from this they calculated a partial pressure for LiO(g) at 1500 K and an equilibrium constant for the reaction Li<sub>2</sub>O(g) → Li(g) + LiO(g). They obtained (a) Δ<sub>f</sub>H<sup>0</sup>(298.15 K) = 18.3 kcal·mol<sup>-1</sup> and (b) Δ<sub>f</sub>H<sup>0</sup>(298.15 K) = 16.3 kcal·mol<sup>-1</sup>, and used the average value from the two methods for the enthalpy of formation of LiO(g). The JANAF enthalpy of formation, 20.1 ± 5 kcal·mol<sup>-1</sup>, was obtained in the same way using their data and the present tables i.e. (a) Δ<sub>f</sub>H<sup>0</sup>(298.15 K) = 22.0 kcal·mol<sup>-1</sup> and (b) Δ<sub>f</sub>H<sup>0</sup>(298.15 K) = 18.3 kcal·mol<sup>-1</sup>.

Heat Capacity and Entropy

The molecular constants, ω<sub>e</sub>x<sub>e</sub>, B<sub>e</sub> and α<sub>e</sub>, were calculated from ω<sub>e</sub> and r<sub>e</sub>, reported by White *et al.*<sup>1</sup> The ground state configuration, <sup>2</sup>Π, was estimated by Gordon,<sup>2</sup> Buchler and Stauffer<sup>3</sup> and White *et al.*<sup>1</sup>

References

1. D. White, K. S. Seshadri, D. F. Dever, and D. E. Mann, and M. J. Linevsky, *J. Chem. Phys.* **39**, 2463 (1963).
2. J. S. Gordon, Thiokol Chemical Corp., Reaction Motor Division, Denville, N.J., "Thermodynamic Data for Combustion Products," (January 1960).
3. A. Buchler and J. L. Stauffer, *J. Chem. Phys.* **39**, 2299 (1963).

T/K	Enthalpy Reference Temperature = T <sub>r</sub> = 298.15 K		Standard State Pressure = p <sup>0</sup> = 0.1 MPa		log K <sub>f</sub>
	C <sub>p</sub> <sup>0</sup>	S <sup>0</sup> - [C <sub>p</sub> <sup>0</sup> - H <sup>0</sup> (T <sub>r</sub> )]/T	H <sup>0</sup> - H <sup>0</sup> (T <sub>r</sub> )	Δ <sub>f</sub> H <sup>0</sup>	
0	0	0	INFINITE	84.118	INFINITE
100	29.147	178.000	238.387	85.076	-40.031
200	30.343	198.439	213.861	84.737	-17.834
250	31.411	205.543	211.491	84.424	-13.435
298.15	32.406	210.963	210.963	84.098	-10.591
300	32.442	211.163	210.963	84.086	-10.500
350	33.332	216.233	211.362	83.729	-8.413
400	34.067	220.733	212.257	83.300	-6.855
450	34.664	224.872	213.427	82.867	-5.649
500	35.148	228.460	214.750	82.432	-4.722
600	35.872	234.936	217.589	81.408	-3.349
700	36.376	240.506	220.474	80.384	-2.280
800	36.744	245.389	223.290	79.359	-1.663
900	37.024	249.733	225.991	78.334	-1.311
1000	37.246	253.646	228.564	77.308	-1.075
1100	37.428	257.205	231.008	76.282	-0.922
1200	37.582	260.468	233.329	75.256	-0.832
1300	37.716	263.482	235.534	74.230	-0.790
1400	37.834	266.281	237.632	73.204	-0.772
1500	37.942	268.895	239.630	72.178	-0.772
1600	38.041	271.347	241.536	71.152	-0.785
1700	38.133	273.656	243.358	70.126	-0.805
1800	38.219	275.838	245.103	69.100	-0.830
1900	38.302	277.907	246.775	68.074	-0.859
2000	38.381	279.874	248.381	67.048	-0.892
2100	38.457	281.748	249.926	66.022	-0.928
2200	38.530	283.539	251.414	65.000	-0.967
2300	38.602	285.253	252.848	64.000	-1.007
2400	38.672	286.897	254.233	63.000	-1.047
2500	38.741	288.477	255.571	62.000	-1.087
2600	38.808	289.998	256.866	61.000	-1.127
2700	38.875	291.464	258.120	60.000	-1.167
2800	38.941	292.879	259.337	59.000	-1.207
2900	39.005	294.247	260.517	58.000	-1.247
3000	39.070	295.570	261.664	57.000	-1.287
3100	39.133	296.852	262.778	56.000	-1.327
3200	39.196	298.096	263.862	55.000	-1.367
3300	39.259	299.303	264.918	54.000	-1.407
3400	39.321	300.476	265.947	53.000	-1.447
3500	39.383	301.616	266.950	52.000	-1.487
3600	39.445	302.727	267.928	51.000	-1.527
3700	39.506	303.808	268.883	50.000	-1.567
3800	39.567	304.863	269.816	49.000	-1.607
3900	39.628	305.891	270.728	48.000	-1.647
4000	39.689	306.895	271.620	47.000	-1.687
4100	39.749	307.876	272.492	46.000	-1.727
4200	39.810	308.835	273.346	45.000	-1.767
4300	39.870	309.772	274.182	44.000	-1.807
4400	39.930	310.689	275.002	43.000	-1.847
4500	39.990	311.587	275.805	42.000	-1.887
4600	40.049	312.467	276.592	41.000	-1.927
4700	40.109	313.329	277.365	40.000	-1.967
4800	40.169	314.174	278.123	39.000	-2.007
4900	40.228	315.002	278.867	38.000	-2.047
5000	40.287	315.816	279.598	37.000	-2.087
5100	40.347	316.615	280.316	36.000	-2.127
5200	40.406	317.399	281.022	35.000	-2.167
5300	40.465	318.169	281.715	34.000	-2.207
5400	40.524	318.926	282.397	33.000	-2.247
5500	40.583	319.670	283.068	32.000	-2.287
5600	40.642	320.402	283.728	31.000	-2.327
5700	40.701	321.122	284.378	30.000	-2.367
5800	40.760	321.830	285.018	29.000	-2.407
5900	40.819	322.527	285.648	28.000	-2.447
6000	40.878	323.214	286.268	27.000	-2.487

PREVIOUS: March 1964 (1 atm)

CURRENT: March 1964 (1 bar)

## IDEAL GAS

Lithium Oxide, Ion (LiO<sup>-</sup>)M<sub>r</sub> = 22.94095Lithium Oxide, Ion (LiO<sup>-</sup>)Li<sub>2</sub>O(g)

$$S^{\circ}(298.15 \text{ K}) = [199.241 \pm 1.3] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H_f^{\circ}(0 \text{ K}) = [-60.7 \pm 62.8] \text{ kJ mol}^{-1}$$

$$\Delta H_f^{\circ}(298.15 \text{ K}) = [-66.944] \text{ kJ mol}^{-1}$$

Electronic Level and Quantum State	Weight g.
[Σ]	0

$$\omega_e = [750] \text{ cm}^{-1}$$

$$B_e = [1.360] \text{ cm}^{-1}$$

$$\sigma = 1$$

$$r_e = [1.6] \text{ \AA}$$

## Enthalpy of Formation

Data on the electron affinity of LiO(g) are unavailable, therefore the value of  $\Delta H_f^{\circ}(\text{LiO}^-, \text{g}, 298.15 \text{ K})$  is estimated. We first assume that the enthalpy change  $\Delta H_f^{\circ}(0 \text{ K})$  of the reaction (1)  $\text{LiO}^-(\text{g}) = \text{Li}(\text{g}) + \text{O}^-(\text{g})$  is close to the average of the  $\Delta H_f^{\circ}(0 \text{ K})$  values for the reactions (2)  $\text{LiO}(\text{g}) = \text{Li}(\text{g}) + \text{O}(\text{g})$  and (3)  $\text{LiF}(\text{g}) = \text{Li}(\text{g}) + \text{F}(\text{g})$ . The atom F(g) is isoelectronic with O<sup>-</sup>(g). In other words, the  $\Delta H_f^{\circ}(0 \text{ K})$  for reaction (1) is approximately  $1/2(76.91 + 135.84) = 106.4 \text{ kcal mol}^{-1}$ . Then we compare the  $\Delta H_f^{\circ}(0 \text{ K})$  values for the reactions (4)  $\text{HO}(\text{g}) = \text{H}(\text{g}) + \text{O}(\text{g})$ , (5)  $\text{HO}^-(\text{g}) = \text{H}(\text{g}) + \text{O}^-(\text{g})$ , and (6)  $\text{HF}(\text{g}) = \text{H}(\text{g}) + \text{F}(\text{g})$ , and find that  $\Delta H_f^{\circ}(0 \text{ K})$  for reaction (5) is experimentally determined as  $109.7 \text{ kcal mol}^{-1}$ , which is about  $8 \text{ kcal mol}^{-1}$  more negative than the average of  $\Delta H_f^{\circ}(0 \text{ K})$  values for reactions (4) and (6). Based on this fact we estimate  $\Delta H_f^{\circ}(0 \text{ K}) = 96.4 \text{ kcal mol}^{-1}$  for reaction (1), yielding  $\Delta H_f^{\circ}(\text{LiO}^-, \text{g}, 298.15 \text{ K}) = -15.5 \text{ kcal mol}^{-1}$ .

Applying the difference in electron affinity between H(g) and Li(g) to OH(g) gives an approximate value,  $EA = 1.7 \text{ eV}$  ( $39.2 \text{ kcal mol}^{-1}$ ) for LiO(g). The values of EA for H(g), Li(g) and OH(g) are taken from.<sup>1</sup> Based on  $\Delta H_f^{\circ}(0 \text{ K}) = 39.2 \text{ kcal mol}^{-1}$  for the reaction  $\text{LiO}^-(\text{g}) = \text{LiO}(\text{g}) + e^-(\text{g})$ , we derive  $\Delta H_f^{\circ}(298.15 \text{ K}) = -19.1 \text{ kcal mol}^{-1}$  for LiO<sup>-</sup>(g), which is in reasonable agreement with the above estimated value.

The value of  $\Delta H_f^{\circ}(298.15 \text{ K})$  for LiO<sup>-</sup>(g) is tentatively adopted as  $-16 \pm 15 \text{ kcal mol}^{-1}$ . Using this  $\Delta H_f^{\circ}(298.15 \text{ K})$  value, we derive  $EA = 1.6 \pm 0.7 \text{ eV}$  for LiO(g). The electron affinity of OH(g) is  $1.8 \pm 0.1 \text{ eV}$ .

## Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of LiF(g) which is isoelectronic with LiO<sup>-</sup>(g). The values of  $\omega_e$ ,  $\omega_e x_e$  and  $r_e$  are estimated by comparison with the observed data for LiF(g). The values of  $B_e$  and  $\alpha_e$  are calculated from  $r_e$ ,  $\omega_e$  and  $\omega_e x_e$  by use of the method suggested by Herzberg.<sup>2</sup>

## References

- U. S. Nat. Bur. Stand. Report 8628, (1965).
- G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, (1950).

T/K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> - [C <sup>o</sup> - H <sup>o</sup> (T)]/T	H <sup>o</sup> - H <sup>o</sup> (T)	ΔH <sup>o</sup>	log K <sub>r</sub>
0	.000	INFINITE	-8.939	-60.722	
100	29.145	166.304	-6.033		14.163
200	30.312	186.754	-3.076		14.090
250	31.369	193.680	-1.535		12.400
298.15	32.359	199.241	.000		11.119
300	32.395	199.442	.060	-66.944	10.995
350	33.284	204.504	1.703	-66.995	9.226
400	34.070	208.998	3.386	-67.035	
450	34.619	213.041	5.102	-67.066	
500	35.106	216.715	6.846	-67.095	
600	35.833	223.184	10.395	-67.129	
700	36.339	228.748	14.005	-67.158	
800	36.707	233.625	17.638	-67.182	
900	36.986	237.965	21.343	-67.201	
1000	37.207	241.874	25.054	-67.216	
1100	37.388	245.429	28.784	-67.227	
1200	37.541	248.689	32.530	-67.234	
1300	37.672	251.699	36.291	-67.238	
1400	37.789	254.495	40.064	-67.239	
1500	37.894	257.106	43.848	-67.238	
1600	37.991	259.555	47.643	-67.234	
1700	38.080	261.861	51.446	-67.227	
1800	38.165	264.046	55.259	-67.217	
1900	38.244	266.106	59.079	-67.204	
2000	38.321	268.069	62.908	-67.188	
2100	38.394	269.941	66.743	-67.169	
2200	38.465	271.728	70.586	-67.147	
2300	38.534	273.440	74.436	-67.123	
2400	38.602	275.081	78.293	-67.097	
2500	38.668	276.658	82.157	-67.069	
2600	38.732	278.176	86.027	-67.039	
2700	38.796	279.639	89.903	-67.007	
2800	38.859	281.051	93.786	-66.973	
2900	38.921	282.416	97.675	-66.937	
3000	38.982	283.736	101.570	-66.900	
3100	39.043	285.016	105.471	-66.862	
3200	39.104	286.256	109.379	-66.823	
3300	39.164	287.450	113.292	-66.783	
3400	39.223	288.606	117.211	-66.742	
3500	39.282	289.728	121.137	-66.700	
3600	39.341	290.876	125.068	-66.658	
3700	39.399	291.954	129.005	-66.615	
3800	39.458	293.006	132.948	-66.572	
3900	39.516	294.032	136.896	-66.529	
4000	39.573	295.033	140.851	-66.485	
4100	39.631	296.011	144.811	-66.441	
4200	39.689	296.966	148.777	-66.397	
4300	39.746	297.901	152.749	-66.353	
4400	39.803	298.815	156.726	-66.309	
4500	39.860	299.710	160.709	-66.265	
4600	39.917	300.587	164.698	-66.221	
4700	39.974	301.446	168.693	-66.177	
4800	40.031	302.288	172.693	-66.133	
4900	40.087	303.114	176.699	-66.089	
5000	40.144	303.925	180.710	-66.045	
5100	40.200	304.720	184.727	-66.001	
5200	40.257	305.501	188.750	-65.957	
5300	40.313	306.269	192.779	-65.913	
5400	40.369	307.023	196.813	-65.869	
5500	40.425	307.764	200.853	-65.825	
5600	40.482	308.493	204.898	-65.781	
5700	40.538	309.210	208.949	-65.737	
5800	40.594	309.915	213.006	-65.693	
5900	40.650	310.610	217.068	-65.649	
6000	40.706	311.294	221.135	-65.605	

PREVIOUS: December 1967 (1 atm)

CURRENT: December 1967 (1 bar)

Lithium Oxide, Ion (LiO<sup>-</sup>)Li<sub>2</sub>O(g)

Lithium (Li<sub>2</sub>) Li<sub>2</sub>(g)

**M<sub>r</sub> = 13.882 Lithium (Li<sub>2</sub>)**

Standard State Pressure = *p*<sup>o</sup> = 0.1 MPa

T/K	Enthalpy Reference Temperature = T <sub>r</sub> = 298.15 K		Standard State Pressure = <i>p</i> <sup>o</sup> = 0.1 MPa		log K <sub>t</sub>
	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> - [C <sub>p</sub> <sup>o</sup> - H(T <sub>r</sub> )/T]	H <sup>o</sup> - H(T <sub>r</sub> )	Δ <i>H</i> <sup>o</sup>	
0	0	INFINITE	-9.675	215.469	INFINITE
100	30.583	160.414	-6.717	217.417	-105.955
200	34.380	182.905	-3.470	217.001	-49.102
250	35.426	190.697	-1.773	216.492	-31.879
298.15	36.103	196.998	0	215.908	-30.573
300	36.125	197.222	0.067	174.251	-30.340
350	36.617	202.830	1.886	171.417	-24.978
400	36.985	207.744	3.726	160.595	-20.972
450	37.274	212.118	5.583	153.935	-17.868
500	37.513	216.058	7.453	148.009	-15.462
600	37.902	222.933	11.225	136.800	-11.800
700	38.225	228.809	15.031	125.507	-9.365
800	38.489	233.673	18.868	114.120	-7.490
900	38.714	238.527	22.729	108.080	-6.046
1000	38.843	242.557	26.608	106.186	-5.402
1100	38.859	246.261	30.494	104.310	-5.075
1200	38.744	249.638	34.375	102.439	-4.729
1300	38.498	252.731	38.238	100.558	-4.368
1400	38.133	255.571	42.071	98.658	-4.024
1500	37.675	258.187	45.862	96.734	-3.697
1600	37.155	260.602	49.604	94.777	-3.390
1700	36.607	262.838	53.292	92.790	-3.102
1800	36.067	264.915	56.976	90.780	-2.830
1900	35.569	266.851	60.507	88.750	-2.576
2000	35.142	268.665	64.042	86.637	-2.340
2100	34.814	270.371	67.539	84.457	-2.117
2200	34.610	271.985	71.009	82.210	-1.905
2300	34.447	273.522	74.465	79.916	-1.702
2400	34.324	275.000	77.924	77.580	-1.507
2500	34.309	276.412	81.400	75.200	-1.321
2600	35.350	277.790	84.911	72.762	-1.142
2700	35.970	279.135	88.411	70.270	-0.976
2800	36.765	280.450	91.911	67.730	-0.822
2900	37.728	281.763	95.344	65.150	-0.676
3000	38.846	283.061	98.662	62.530	-0.540
3100	40.103	284.355	103.068	60.000	-0.410
3200	41.479	285.649	107.686	57.630	-0.285
3300	42.948	286.948	112.520	55.410	-0.165
3400	44.483	288.253	117.578	53.330	-0.050
3500	46.057	289.565	122.850	51.390	0.050
3600	47.640	290.884	128.340	49.590	0.165
3700	49.201	292.211	134.050	47.930	0.285
3800	50.715	293.543	140.000	46.410	0.410
3900	52.149	294.879	146.190	45.020	0.540
4000	53.485	296.217	152.620	43.760	0.676
4100	54.702	297.553	159.290	42.630	0.822
4200	55.781	298.884	166.200	41.630	0.976
4300	56.711	300.208	173.350	40.750	1.142
4400	57.483	301.521	180.740	40.000	1.321
4500	58.092	302.820	188.360	39.390	1.507
4600	58.537	304.102	196.210	38.900	1.702
4700	58.822	305.364	204.370	38.510	1.905
4800	58.950	306.604	212.800	38.210	2.117
4900	58.930	307.820	221.500	37.990	2.340
5000	58.772	309.009	230.460	37.840	2.576
5100	58.487	310.170	239.680	37.750	2.830
5200	58.086	311.302	249.160	37.710	3.090
5300	57.582	312.404	258.900	37.710	3.360
5400	56.988	313.475	268.890	37.740	3.640
5500	56.317	314.514	279.130	37.790	3.930
5600	55.580	315.523	289.620	37.860	4.240
5700	54.789	316.499	299.360	37.940	4.570
5800	53.955	317.445	309.350	38.030	4.920
5900	53.087	318.360	319.580	38.130	5.290
6000	52.196	319.245	329.040	38.240	5.680

PREVIOUS: June 1962 (1 atm) CURRENT: December 1983 (1 bar)

*D*<sub>0</sub><sup>o</sup> = 99.833 ± 0.096 kJ·mol<sup>-1</sup> (natural abundance)  
*S*<sup>o</sup>(298.15 K) = 196.998 ± 0.030 J·K<sup>-1</sup>·mol<sup>-1</sup>

**IDEAL GAS**

State	T <sub>c</sub>	D <sub>0</sub> <sup>o</sup>	10 <sup>3</sup> α <sub>c</sub>	10 <sup>6</sup> D <sub>c</sub>	r <sub>c</sub> , Å	References
<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	0	8346.45	0.67257	9.8478 <sup>b</sup>	2.6730	<sup>3</sup> (D <sub>0</sub> ) <sup>9</sup>
<sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	8229.5	8346.45	0.26806	[20.706] <sup>d</sup>	4.234	<sup>10</sup>
<sup>1</sup> Π <sub>g</sub>	11942.5	23250.4	0.69368	[11.618] <sup>d</sup>	2.632	<sup>10</sup>
<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	14068.3	23250.4	0.4975	7.54	3.107	<sup>9</sup>
<sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	16614.5	23250.4	0.50134	[8.385] <sup>d</sup>	3.096	<sup>10</sup>

(a) -6.4724 × 10<sup>-3</sup> (v + 1/2)<sup>3</sup> - 9.712 × 10<sup>-5</sup> (v + 1/2)<sup>4</sup>  
 (b) -3.6071 × 10<sup>-5</sup> (v + 1/2)<sup>2</sup> - 4.2570 × 10<sup>-7</sup> (v + 1/2)<sup>3</sup>  
 (c) +5.672 × 10<sup>-3</sup> (v + 1/2) - 1.9002 × 10<sup>-2</sup> (v + 1/2)<sup>2</sup>  
 (d) These values of α<sub>c</sub> and D<sub>c</sub> were approximated: equations III, 118 and III, 123.<sup>4</sup>

**Enthalpy of Formation**  
 We adopt the Δ*H*<sup>o</sup>(Li<sub>2</sub>, g, 298.15 K) of 215.9 kJ·mol<sup>-1</sup> as recommended by NBS.<sup>12</sup> The value adopted for Δ*H*<sup>o</sup>(Li<sub>2</sub>, g, 0 K) was obtained using the values of *H*<sup>o</sup>(298.15 K) - *H*<sup>o</sup>(0 K) for Li<sub>2</sub>(g) and Li(cr), from JANAF and NBS,<sup>12</sup> respectively. This results in Δ*H*<sup>o</sup>(Li<sub>2</sub>, g, 0 K) = 215.474 kJ·mol<sup>-1</sup>. Note that this adoption of the NBS value results in a minor inconsistency in the value of *D*<sub>0</sub><sup>o</sup> for the ground state. In the calculation of *C*<sub>p</sub><sup>o</sup> and *S*<sup>o</sup> described below, we used *D*<sub>0</sub><sup>o</sup> = 99.846 kJ·mol<sup>-1</sup> (for <sup>1</sup>Li<sub>2</sub>) whereas the above procedure results in *D*<sub>0</sub><sup>o</sup> = 100.125 kJ·mol<sup>-1</sup> based on Δ*H*<sup>o</sup>(Li<sub>2</sub>, g, 0 K) from NBS.<sup>12</sup> This results in uncertainties in the calculated *C*<sub>p</sub><sup>o</sup> and *S*<sup>o</sup> of less than 0.002 J·K<sup>-1</sup>·mol<sup>-1</sup> at 6000 K.

**Heat Capacity and Entropy**  
 The thermal functions were calculated using a direct summation technique. Included in the calculation were the ground state plus the four lowest lying excited electronic states. Of these excited states, only the <sup>3</sup>Σ<sub>g</sub><sup>-</sup> has been observed spectroscopically. All spectroscopic data for <sup>1</sup>Li<sub>2</sub>, <sup>3</sup>Li<sub>2</sub>, and <sup>1</sup>Π<sub>g</sub> and the results were combined according to the natural abundances of the atoms, <sup>6</sup>Li: 92.3191%, <sup>7</sup>Li: 7.6809%.<sup>3</sup> Calculation of the <sup>1</sup>Li<sub>2</sub> and <sup>1</sup>Π<sub>g</sub> species were carried out by adjusting the spectroscopic constants for <sup>1</sup>Li<sub>2</sub> using a standard reduced mass scaling routine. The summation was extended to the dissociation limit of each state, and thus did not include any of the so-called quasi-bound levels above *D*<sup>o</sup> that owe their existence to rotational barriers. A detailed study of the effects of the quasi-bound levels on the thermodynamic properties of diatomic molecules has been recently performed by Mies and Julienne.<sup>11</sup> According to their approach, the metastable and "free" contribution to the Gibbs energy function for Li<sub>2</sub>(g) at 6000 K is only ca. 4 J·K<sup>-1</sup>·mol<sup>-1</sup>.<sup>11</sup>

The excited states contribute significantly to the heat capacity above 2000 K, but the effect on the Gibbs energy function is considerably less, only 0.5 J·K<sup>-1</sup>·mol<sup>-1</sup> larger than the ground state contribution at 6000 K. The ground state and <sup>3</sup>Σ<sub>g</sub><sup>-</sup> excited state rotational levels were weighted in accordance with the nuclear spin-rotation interaction<sup>3</sup> as follows: even *J* weight = 0.625, odd *J* weight = 0.375 for the <sup>1</sup>Li<sub>2</sub> species; even *J* weight = 0.667, odd *J* weight = 0.333 for the <sup>3</sup>Li<sub>2</sub> species. Note also that although the Dunham coefficients for the ground state are known to higher order than used here,<sup>5</sup> the neglect of these data leads to small errors in the computed functions as follows: *S*<sup>o</sup>(6000 K) is 0.4 J·K<sup>-1</sup>·mol<sup>-1</sup> larger than the nonrotated ro-vibrational constant calculation (based on a ground state calculation). The rotational levels were extrapolated to high *J* values according to the method of Khachkuruzov,<sup>6</sup> who proposed a simpler form of Wooley's method.<sup>7</sup> Splitting of the rotational levels in the <sup>3</sup>Σ<sub>g</sub><sup>-</sup> and <sup>1</sup>Π<sub>g</sub> states due to rotational-electronic coupling was taken into account only insofar as the electronic degeneracy of these states was increased accordingly. The errors invoked by this approximation are much less than the other uncertainties. The adopted value of *S*<sup>o</sup>(298.15 K) is only 0.013 J·K<sup>-1</sup>·mol<sup>-1</sup> lower than that adopted by NBS.<sup>12</sup>

**References**  
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<sup>10</sup>M. L. Olson and D. D. Konowalow, Chem. Phys. 21, 393 (1977); 22, 29 (1977).  
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Lithium (Li<sub>2</sub>)

Lithium Oxide (Li<sub>2</sub>O)Lithium Oxide (Li<sub>2</sub>O)M<sub>r</sub> = 29.8814

$\Delta H_f^\circ(0 \text{ K}) = -592.39 \pm 2.1 \text{ kJ}\cdot\text{mol}^{-1}$   
 $\Delta H_f^\circ(298.15 \text{ K}) = -598.73 \pm 2.1 \text{ kJ}\cdot\text{mol}^{-1}$   
 $\Delta_{\text{sub}}H^\circ = [58.576] \text{ kJ}\cdot\text{mol}^{-1}$

## CRYSTAL

Lithium Oxide (Li<sub>2</sub>O)

$S^\circ(298.15 \text{ K}) = 37.890 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$   
 $T_{\text{fus}} = 1843 \text{ K}$

## Enthalpy of Formation

The selected enthalpy of formation was calculated as follows:

Reaction	$\Delta H_f^\circ(298.15 \text{ K})$ kJ mol <sup>-1</sup>	Source
(A) Li(OH(aq)) + H <sub>2</sub> O(l) = 2 LiOH(aq, ∞)	-31.74 ± 0.08	1
(B) Li(cr) + 1/2 O <sub>2</sub> (g) = LiOH(aq, ∞)	-121.572 ± 0.019	2
(C) H <sub>2</sub> (g) + 1/2 O <sub>2</sub> (g) = H <sub>2</sub> O(l)	-68.3174	3
(D) 2 Li(cr) + 1/2 O <sub>2</sub> (g) = Li <sub>2</sub> O(cr)*	-143.1 ± 0.5	

\* Reaction (D) is the sum of -(A) + 2(B) - (C).

Kolesov *et al.*<sup>1</sup> measured the enthalpy of the reaction of Li<sub>2</sub>O with water at 20° in 5 experiments. The mean  $\Delta H_f^\circ$  was  $-31.41 \pm 0.08 \text{ kcal}\cdot\text{mol}^{-1}$ . This was brought to 298.15 K by Kolesov using enthalpy data of Johnston and Bauer<sup>4</sup> for Li<sub>2</sub>O, Osborne *et al.*<sup>5</sup> for H<sub>2</sub>O, Gucker and Schminke<sup>6</sup> for C<sub>2</sub> of LiOH(aq) and Rossini *et al.*<sup>3</sup> for aqueous LiOH. In addition to the above, Beketov<sup>7</sup> and Forcrand<sup>8</sup> have reported experimental enthalpies for Li<sub>2</sub>O. Rossini *et al.* and Johnston and Bauer<sup>4</sup> have reported enthalpies of formation for Li<sub>2</sub>O recalculated from older data. Fassolino<sup>9</sup> reported a  $\Delta H_f^\circ(298.15 \text{ K})$  of  $-141.1 \pm 4.2 \text{ kcal}\cdot\text{mol}^{-1}$ . He measured the enthalpy of combustion of Li(cr) in O (g) in a Parr bomb.

## Heat Capacity and Entropy

The low temperature C<sub>p</sub> data of Johnston and Bauer<sup>4</sup> from [179–298 K] was joined graphically to the high temperature C<sub>p</sub> data of Shomate and Cohen,<sup>10</sup> (425–1045 K) and Rodriga and Gornelskii,<sup>11</sup> (370–1125 K). S<sup>o</sup>(298.15 K) was reported by Johnston and Bauer using S<sup>o</sup>(16 K) = 0.003 cal K<sup>-1</sup>·mol<sup>-1</sup> (extrap.).

## Fusion Data

The melting point of Li<sub>2</sub>O is uncertain. The selected melting point, 1843 K, was measured by van Arkel *et al.*<sup>12</sup> Brewer and Margrave<sup>13</sup> reported the melting point 1700 K. They also stated that van Kooster and Jaeger<sup>14</sup> had reported 1700 (1973 K) as the melting point. The heat of melting, [14] kcal·mol<sup>-1</sup>, was estimated by Glassner.<sup>15</sup>

## Sublimation Data

Li<sub>2</sub>O(cr) vaporizes to Li<sub>2</sub>O(g), LiO(g), Li<sub>2</sub>O<sub>2</sub>(g) and O<sub>2</sub>(g).<sup>16–20</sup> The major species (0–1700 K) are reported to be Li<sub>2</sub>O(g), Li(g), and O<sub>2</sub>(g) with lesser amounts of LiO(g) and Li<sub>2</sub>O<sub>2</sub>(g). Hildenbrand *et al.*,<sup>16</sup> U-2298, have reported about equal amounts of Li<sub>2</sub>O\* and Li\* (1300 to 1550 K) and about 1/30th of this amount of LiO\*. White *et al.*<sup>17</sup> calculated  $\Delta_{\text{sub}}H^\circ$  from their mass spectra data. They made two different calculations: (I) for Li<sub>2</sub>O(cr) → Li<sub>2</sub>O(g), and (II) for Li<sub>2</sub>O(g) → 2 Li(g) + 1/2 O<sub>2</sub>(g), and found: (a) 102.5 kcal·mol<sup>-1</sup> and (b) 99.0 kcal·mol<sup>-1</sup>. They used a weighted average of (a) and (b) and obtained 101.6 kcal·mol<sup>-1</sup> at 0 K. The selected  $\Delta_{\text{sub}}H^\circ(298.15 \text{ K})$  of 102.3 ± 3 kcal·mol<sup>-1</sup> was obtained in the same manner using their data and the present JANAF functions, i.e., (a) 104.2 kcal·mol<sup>-1</sup> and (b) 100.3 kcal·mol<sup>-1</sup>. Knudson-effusion data of White *et al.*, corrected for dissociation gave 3rd law heats at 298 K of 101.9 kcal·mol<sup>-1</sup> and a 2nd law heat of 94 kcal·mol<sup>-1</sup>. Recalculation of Hildenbrand's dissociation pressure with JANAF values give Li<sub>2</sub>O pressures slightly different than those reported. The recalculated pressures give a 3rd law  $\Delta_{\text{sub}}H^\circ(298.15 \text{ K})$  of 101.7 kcal·mol<sup>-1</sup> for both cells. The corresponding 2nd law values are 85 and 95.5 kcal·mol<sup>-1</sup> for cell 7 and 8. The 3rd law treatment of both sets of data show relatively large trends of  $\Delta_{\text{sub}}H^\circ$  with T which are probably too large to be only due to errors in the function.

A sample of LiAlO<sub>2</sub> was melted 7 times in argon in an arc-image furnace. Prophet,<sup>21</sup> the sample decomposed on fusion and successive melting points approached that of Al<sub>2</sub>O<sub>3</sub>. The residue was found to be 95% Al<sub>2</sub>O<sub>3</sub> and 5% LiAl<sub>2</sub>O<sub>4</sub>. The sample and residue were characterized by X-ray diffraction. A reasonable assumption from this is that  $\Delta_f H^\circ(2000 \text{ K}) = 0$  for 2LiAlO<sub>2</sub>(cr) = Al<sub>2</sub>O<sub>3</sub>(cr) + Li<sub>2</sub>O(g). From this  $\Delta_f H^\circ$ , a  $\Delta_{\text{sub}}H^\circ(298.15 \text{ K})$  for Li<sub>2</sub>O of 50 kcal·mol<sup>-1</sup> was calculated. A vapor pressure study of the molecular species over the decomposing LiAlO<sub>2</sub> might help resolve the discrepancies in lithium oxide  $\Delta_{\text{sub}}H^\circ$  values.

## References

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Continued on page 1527

Lithium Oxide (Li<sub>2</sub>O)

PREVIOUS December 1960

CURRENT March 1964

Li<sub>2</sub>O(cr)

Lithium Oxide (Li<sub>2</sub>O)

Lithium Oxide (Li<sub>2</sub>O)

LIQUID

Lithium Oxide (Li<sub>2</sub>O)

Lithium Oxide (Li<sub>2</sub>O(l))

S°(298.15 K) = [55.083] J·K<sup>-1</sup>·mol<sup>-1</sup>  
 T<sub>fus</sub> = 1843 K

Δ<sub>liq</sub>H°(298.15 K) = [-553.247] kJ·mol<sup>-1</sup>  
 Δ<sub>liq</sub>H° = [58.576] kJ·mol<sup>-1</sup>

Enthalpy of Formation

Δ<sub>f</sub>H°(Li<sub>2</sub>O, l, 298.15 K) is calculated from Δ<sub>f</sub>H°(Li<sub>2</sub>O, cr, 298.15 K) by adding the enthalpy of fusion, Δ<sub>liq</sub>H°, and the difference in enthalpy, H°(1843 K) - H°(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity was estimated at 8 cal·K<sup>-1</sup>·mol<sup>-1</sup> from comparisons with similar compounds and from Kopp's rule. S°(Li<sub>2</sub>O, l, 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 vapor over Li<sub>2</sub>O(cr) at 1700 K is composed of Li<sub>2</sub>O(g), Li(g), O(g), LiO(g), and Li<sub>2</sub>O<sub>2</sub>(g). Thus a boiling point becomes almost meaningless. The value, T<sub>vap</sub> = 2836 K, listed above is the temperature at which the fugacity of Li<sub>2</sub>O(g) reaches one atm. Brewer<sup>1</sup> estimated a boiling point of 2600 K.

Reference

<sup>1</sup>L. Brewer, Chem. Rev. 52, (1953).

T/K	C <sub>p</sub> <sup>o</sup>	S°	-[C <sub>p</sub> <sup>o</sup> - H°(T)]/T	H° - H°(T <sub>r</sub> )	Δ <sub>liq</sub> H°	Δ <sub>cr</sub> G°	log K <sub>f</sub>
0							
100							
200							
298.15	54.087	55.083	55.083	0.	-553.247	-521.744	91.407
300	54.379	55.419	55.084	0.100	-553.265	-521.549	90.810
400	64.003	72.477	60.584	6.053	-553.999	-510.857	66.711
500	69.580	87.383	61.896	12.743	-560.704	-499.380	52.170
600	73.822	100.464	67.256	19.925	-561.069	-487.072	42.403
600.000	73.822	100.464	67.256	19.925	GLASS	LIQUID	
600.000	100.416	100.464	67.256	19.925	TRANSITION		
700	100.416	115.943	73.134	29.966	-558.505	-474.941	35.441
800	100.416	129.352	79.342	40.008	-555.924	-463.180	30.243
900	100.416	141.179	85.569	50.049	-553.568	-451.741	26.218
1000	100.416	151.759	91.668	60.091	-550.829	-440.855	23.014
1100	100.416	161.330	97.573	70.133	-548.304	-429.683	20.404
1200	100.416	170.067	103.255	80.174	-545.789	-419.010	18.239
1300	100.416	178.105	108.708	90.216	-543.284	-408.547	16.416
1400	100.416	185.546	113.934	100.257	-540.781	-398.277	14.860
1500	100.416	192.474	118.942	110.299	-538.275	-388.185	13.518
1600	100.416	198.955	123.742	120.341	-535.766	-378.261	12.349
1700	100.416	205.043	128.347	130.382	-533.255	-368.542	10.881
1800	100.416	210.782	132.769	140.424	-530.742	-359.022	9.479
1843.000	100.416	213.153	134.617	144.742	CRYSTAL	LIQUID	
1900	100.416	216.212	137.019	150.465	-515.694	-299.352	8.230
2000	100.416	221.362	141.109	160.507	-511.701	-272.280	7.111
2100	100.416	226.262	145.048	170.549	-507.725	-245.407	6.104
2200	100.416	230.833	148.847	180.590	-503.768	-218.712	5.192
2300	100.416	235.397	152.513	190.632	-500.833	-192.318	4.360
2400	100.416	239.670	156.056	200.673	-498.916	-166.384	3.610
2500	100.416	243.770	159.483	210.715	-497.033	-140.912	2.919
2600	100.416	247.708	162.801	220.757	-495.185	-115.936	2.284
2700	100.416	251.498	166.017	230.798	-493.368	-91.562	1.699
2800	100.416	255.150	169.135	240.840	-491.579	-67.787	1.158
2900	100.416	258.673	172.162	250.881	-489.814	-44.612	0.658
3000	100.416	262.078	175.103	260.923	-488.072	-21.042	0.192
3100	100.416	265.370	177.962	270.965	-486.351	1.929	-0.241
3200	100.416	268.558	180.744	281.006	-484.650	4.983	-0.645
3300	100.416	271.648	183.452	291.048	-482.977	8.034	-1.023
3400	100.416	274.646	186.090	301.089	-481.331	11.081	-1.377
3500	100.416	277.557	188.662	311.131	-479.712	14.126	-1.709
3600	100.416	280.386	191.171	321.173	-478.121	17.169	-2.022
3700	100.416	283.137	193.619	331.214	-476.558	20.211	-2.316
3800	100.416	285.815	196.011	341.256	-475.022	23.251	-2.593
3900	100.416	288.423	198.347	351.297	-473.512	26.289	-2.856
4000	100.416	290.965	200.631	361.339	-472.026	29.326	-3.104

PREVIOUS December 1960

CURRENT March 1964

Lithium Oxide (Li<sub>2</sub>O)

Li<sub>2</sub>O(l)

Lithium Oxide (Li<sub>2</sub>O)

M<sub>r</sub> = 29.8814 Lithium Oxide (Li<sub>2</sub>O)

Li<sub>2</sub>O(cr,l)

0 to 1843 K crystal  
above 1843 K liquid

Refer to the individual tables for details.

T/K	Enthalpy Reference Temperature = T <sub>r</sub> = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K <sub>f</sub>
	C <sub>p</sub> <sup>o</sup>	S° - (G° - H°(T <sub>r</sub> ))/T <sub>r</sub>	H° - H°(T <sub>r</sub> )	Δ <sub>f</sub> G°	
		kJ·mol <sup>-1</sup>			
0	0	0	INFINITE	-592.392	INFINITE
100	10.447	3.632	71.417	-594.565	305.465
200	37.204	19.581	42.362	-597.282	149.892
298.15	54.087	37.890	37.890	-598.730	98.478
300	54.379	38.226	37.891	-598.748	97.831
400	64.003	55.515	40.156	-599.472	71.753
500	69.580	70.232	44.714	-606.172	56.024
600	73.822	83.284	50.077	-606.553	45.466
700	77.404	94.940	55.668	-606.464	37.922
800	80.563	105.484	61.246	-606.026	32.267
900	83.429	115.137	66.705	-605.311	27.873
1000	86.211	124.073	72.001	-604.331	24.362
1100	88.805	132.415	77.118	-603.094	21.495
1200	91.211	140.244	82.055	-601.621	19.112
1300	93.199	147.625	86.818	-599.934	17.102
1400	94.872	154.595	91.413	-598.066	15.381
1500	96.232	161.189	95.847	-596.045	13.895
1600	97.320	167.434	100.127	-593.899	12.600
1700	98.332	173.364	104.262	-591.618	11.521
1800	99.434	179.017	108.260	-589.247	10.618
1843.000	99.914	181.370	109.938	-588.681	11.021
1843.000	100.416	213.153	109.938	-588.681	9.518
1900	100.416	216.212	113.081	-589.352	8.230
2000	100.416	221.362	118.367	-590.990	7.111
2100	100.416	226.262	123.389	-592.725	6.104
2200	100.416	230.933	128.172	-594.507	5.193
2300	100.416	235.397	132.738	-596.323	4.365
2400	100.416	239.670	137.105	-598.157	3.610
2500	100.416	243.769	141.290	-599.919	2.919
2600	100.416	247.708	145.308	-601.598	2.284
2700	100.416	251.498	149.171	-603.202	1.699
2800	100.416	255.150	152.891	-604.733	1.158
2900	100.416	258.673	156.478	-606.196	0.658
3000	100.416	262.077	159.942	-607.596	0.192
3100	100.416	265.370	163.290	-608.948	-0.241
3200	100.416	268.558	166.530	-610.259	-0.645
3300	100.416	271.648	169.669	-611.531	-1.023
3400	100.416	274.646	172.713	-612.772	-1.377
3500	100.416	277.557	175.667	-613.986	-1.709
3600	100.416	280.386	178.537	-615.169	-2.022
3700	100.416	283.137	181.327	-616.325	-2.316
3800	100.416	285.815	184.039	-617.456	-2.593
3900	100.416	288.433	186.684	-618.564	-2.856
4000	100.416	290.965	189.260	-619.648	-3.104

PREVIOUS:

CURRENT: March 1964

Lithium Oxide (Li<sub>2</sub>O)

Li<sub>2</sub>O(cr,l)



Li<sub>2</sub>O(g)

Li<sub>2</sub>O(g)

IDEAL GAS

Lithium Oxide (Li<sub>2</sub>O)

$\Delta H_f^\circ(0\text{ K}) = -165.84 \pm 10.5 \text{ kJ}\cdot\text{mol}^{-1}$   
 $\Delta H_f^\circ(298.15\text{ K}) = -166.94 \pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$

$S^\circ(298.15\text{ K}) = 229.108 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

Vibrational Frequencies and Degeneracies

$\nu_1, \text{cm}^{-1}$	
[760](1)	
[140](2)	
987 (1)	

$\sigma = 2$

Ground State Quantum Weight: [1]

Point Group: D<sub>2h</sub>

Bond Distance: Li-O = [1.59] Å

Bond Angle: Li-O-Li = 180°

Rotational Constant: B<sub>0</sub> = 0.480342 cm<sup>-1</sup>

**Enthalpy of Formation**

The enthalpy of formation was calculated from the enthalpy of formation of the crystal and the enthalpy of sublimation.

**Heat Capacity and Entropy**

White *et al.*<sup>1</sup> made an estimate of the bond distance Li-O = 1.59 Å based on an analysis of their vibrational spectra. They found that Li<sub>2</sub>O was a linear molecule. Buchler and Stauffer<sup>2</sup> have shown from electric deflection experiments that Li<sub>2</sub>O is very probably linear. They also report from the results of an effusion experiment evidence that the electron diffraction data and Li-O bond distance, 1.82 Å reported by Akshin and Rambidi<sup>3</sup> are for Mo-O in Li<sub>2</sub>MoO, rather than for Li-O in Li<sub>2</sub>O. Buchler and Stauffer<sup>2</sup> estimate a Li-O distance of 1.55 Å. White, *et al.*,<sup>1</sup> have estimated the vibrational frequencies  $\nu_1 = [760] \text{ cm}^{-1}$  and  $\nu_2 = [140] \text{ cm}^{-1}$  and assigned  $\nu_3 = 987 \text{ cm}^{-1}$  from their infrared matrix spectra.

**References**

- <sup>1</sup>D. White, K. S. Seshadri, D. F. Dever, D. E. Mann, and M. J. Linevsky, *J. Chem. Phys.* **39**, 2463 (1963).
- <sup>2</sup>A. Buchler and J. L. Stauffer, *J. Chem. Phys.* **39**, 2299 (1963).
- <sup>3</sup>P. A. Akshin and N. G. Rambidi, *Dokl. Akad. Nauk. SSSR* **118**, 973 (1958) [English Translation, Proc. Acad. Sci. USSR, Phys. Chem. Sect. **118**, 83 (1958)].

T/K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> - (G <sup>o</sup> - HF(T)) / T	H <sup>o</sup> - HF(T)	ΔH <sup>o</sup>	Standard State Pressure = p <sup>o</sup> = 0.1 MPa	log K <sub>r</sub>
0	0	INFINITE	-12.485	-165.840	INFINITE	
100	41.106	179.969	-9.061	-164.858	90.220	
200	45.797	210.079	-4.691	-163.627	47.106	
250	47.836	220.517	-2.350	-162.372	38.440	
298.15	49.758	229.108	0.	-166.942	32.818	
300	49.829	229.416	0.092	-166.968	32.638	
350	51.633	237.236	2.630	-167.694	28.477	
400	53.190	244.233	5.251	-168.495	25.341	
450	54.500	250.578	7.943	-169.407	22.890	
500	55.590	256.378	10.698	-170.444	20.854	
600	57.243	266.669	16.344	-173.344	17.766	
700	58.393	275.584	22.130	-180.036	15.538	
800	59.211	283.438	28.012	-181.615	13.851	
900	59.808	290.448	33.964	-183.147	12.528	
1000	60.254	296.774	39.968	-184.646	11.461	
1100	60.595	302.533	46.012	-186.120	10.581	
1200	60.861	307.818	52.085	-187.573	9.842	
1300	61.072	312.698	58.182	-189.012	9.211	
1400	61.242	317.230	64.298	-190.435	8.667	
1500	61.380	321.460	70.429	-191.840	8.191	
1600	61.495	325.425	76.573	-193.228	7.772	
1700	61.591	329.156	82.728	-194.604	7.399	
1800	61.672	332.679	88.891	-195.970	7.061	
1900	61.740	336.016	95.062	-197.322	6.754	
2000	61.799	339.184	101.239	-198.664	6.474	
2100	61.850	342.200	107.421	-199.997	6.222	
2200	61.895	345.079	113.608	-201.322	6.000	
2300	61.933	347.831	119.800	-202.640	5.804	
2400	61.968	350.467	126.000	-203.950	5.631	
2500	61.998	352.998	132.193	-205.252	5.474	
2600	62.025	355.430	138.394	-206.548	5.330	
2700	62.049	357.771	144.598	-207.830	5.197	
2800	62.070	360.018	150.804	-209.100	5.074	
2900	62.089	362.107	157.012	-210.358	4.960	
3000	62.107	364.312	163.222	-211.604	4.854	
3100	62.123	366.349	169.433	-212.838	4.756	
3200	62.137	368.321	175.646	-214.060	4.664	
3300	62.150	370.233	181.861	-215.272	4.578	
3400	62.162	372.089	188.076	-216.474	4.496	
3500	62.173	373.891	194.293	-217.666	4.418	
3600	62.183	375.643	200.511	-218.848	4.344	
3700	62.192	377.346	206.730	-220.020	4.274	
3800	62.201	379.005	212.949	-221.182	4.208	
3900	62.209	380.621	219.170	-222.336	4.146	
4000	62.216	382.196	225.391	-223.482	4.088	
4100	62.223	383.732	231.613	-224.620	4.034	
4200	62.229	385.232	237.841	-225.750	3.984	
4300	62.235	386.696	244.056	-226.872	3.938	
4400	62.241	388.127	250.283	-227.988	3.894	
4500	62.246	389.526	256.507	-229.100	3.851	
4600	62.251	390.894	262.732	-230.208	3.810	
4700	62.255	392.233	268.957	-231.312	3.770	
4800	62.259	393.544	275.183	-232.412	3.732	
4900	62.263	394.827	281.409	-233.508	3.696	
5000	62.267	396.085	287.636	-234.600	3.662	
5100	62.271	397.318	293.862	-235.688	3.630	
5200	62.274	398.528	300.090	-236.772	3.599	
5300	62.277	399.714	306.317	-237.852	3.570	
5400	62.280	400.878	312.545	-238.928	3.542	
5500	62.283	402.021	318.773	-240.000	3.516	
5600	62.285	403.143	325.002	-241.068	3.491	
5700	62.288	404.245	331.230	-242.132	3.467	
5800	62.290	405.329	337.459	-243.192	3.444	
5900	62.293	406.394	343.688	-244.248	3.422	
6000	62.295	407.441	349.918	-245.300	3.401	

PREVIOUS: March 1964 (1 atm)

CURRENT: March 1964 (1 bar)

Lithium Oxide (Li<sub>2</sub>O)

Li<sub>2</sub>O(g)

Lithium Peroxide (Li <sub>2</sub> O <sub>2</sub> )		CRYSTAL		Lithium Peroxide (Li <sub>2</sub> O <sub>2</sub> )		Li <sub>2</sub> O <sub>2</sub> (cr)	
M <sub>r</sub> = 45.8808							
S°(298.15 K) = [56.484 ± 4.2] J·K <sup>-1</sup> ·mol <sup>-1</sup>		ΔH <sub>f</sub> °(298.15 K) = [632.62 ± 8.4] kJ·mol <sup>-1</sup>		ΔH <sub>f</sub> °(0 K) = Unknown		ΔH <sub>f</sub> °(298.15 K) = [632.62 ± 8.4] kJ·mol <sup>-1</sup>	
Enthalpy of Formation Li <sub>2</sub> O <sub>2</sub> (aq)		based on the measured enthalpies of the reactions of Li <sub>2</sub> O <sub>2</sub> (cr) with HCl(aq) and LiOH(aq) with H <sub>2</sub> O(aq).					
Heat Capacity and Entropy		Both C <sub>p</sub> ° and S°(298.15 K) were estimated by comparison with those of the Na <sub>2</sub> O <sub>2</sub> (cr), respectively.					
Decomposition Data		T <sub>dec</sub> was reported to be about 300°C by Wiederhorn <i>et al.</i> <sup>2</sup> The value adopted, T <sub>dec</sub> = 468 K, was reported by <sup>3</sup> obtained from Centnerzwer and Blumenthal. <sup>4</sup>					
References		R. de Forcrand, <i>Compt. Rend.</i> 130, 1465 (1900).					
		N. M. Wiederhorn, N. F. Surprenant, and A. J. Leffler, "Research on New Methods of Separation of Air into O <sub>2</sub> and N <sub>2</sub> Components," <i>C.</i> 63825, First Quarterly Progress Report, September 1961, Arthur D. Little, Inc.					
		Bulletin of the National Research Council, No. 118, "Data on Chemicals for Ceramic Use", (June 1949).					
		M. Centnerzwer and M. Blumenthal, <i>Bull. Intern. Acad. Polonaise, Classe. Sci. Math. Nat., A</i> 499 (1933).					
T/K	C <sub>p</sub> °	S°	-(G° - HF(T))/T	H° - HF(T)	ΔH <sub>f</sub> °	ΔG°	log K <sub>r</sub>
0				0.			
100	70.626	56.484			-632.621	-570.954	100.029
200	70.919	56.922			-632.635	-570.571	99.345
250	82.676	79.021			-633.098	-549.799	71.796
300	90.793	98.369			-639.337	-528.332	55.194
400	97.445	115.520			-639.045	-506.147	44.064
500	103.428	130.995			-638.104	-484.063	36.121
600	109.077	143.178			-636.605	-462.154	30.176
700	114.432	158.336			-634.617	-440.462	25.564
800	119.704	170.666			-632.144	-419.017	21.887
900	124.892	182.319			-629.184	-397.844	18.892
1000	129.997	193.406			-625.740	-376.961	16.409
1200	134.980	204.008			-621.818	-356.385	14.320
1300	139.905	214.192			-617.419	-336.129	12.541
1400	144.766	224.010			-612.541	-316.205	11.011
1500	149.570	233.507			-607.190	-296.621	9.684
1600	154.318	242.717			-601.461	-277.364	8.082
1700	159.005	251.671			-595.352	-258.452	6.566
1800	163.628	260.392			-588.882	-239.947	5.222
1900	168.197	268.902			-582.100	-222.070	4.024
2000							

PREVIOUS: June 1963

CURRENT: September 1963

Lithium Oxide (Li<sub>2</sub>O)

IDEAL GAS

M<sub>r</sub> = 45.8808

Lithium Oxide ((LiO)<sub>2</sub>)

Li<sub>2</sub>O<sub>2</sub>(g)

S°(298.15 K) = [273.562] J·K<sup>-1</sup>·mol<sup>-1</sup>      Δ<sub>f</sub>H°(0 K) = [-240.60 ± 25.1] kJ·mol<sup>-1</sup>      log K<sub>r</sub>

S°(298.15 K) = [273.562] J·K<sup>-1</sup>·mol<sup>-1</sup>      Δ<sub>f</sub>H°(298.15 K) = [-242.67 ± 25.1] kJ·mol<sup>-1</sup>

Vibrational Frequencies and Degeneracies	
ν, cm <sup>-1</sup>	ν, cm <sup>-1</sup>
[400](1)	[270](1)
[250](1)	330 (1)
[300](1)	530 (1)

Ground State Quantum Weight: [1]  
 Point Group: [D<sub>2h</sub>]  
 Bond Distances: Li-O = [1.90] Å  
 Bond Angle: O-Li-O = [116]°  
 Product of the Moments of Inertia: I<sub>A</sub>I<sub>B</sub>I<sub>C</sub> = [5.200811 × 10<sup>-115</sup>] g<sup>3</sup>·cm<sup>6</sup>      σ = 4

Enthalpy of Formation

The enthalpy of formation, -58 kcal·mol<sup>-1</sup>, was calculated from an equilibrium constant for the reaction 1/2 O<sub>2</sub>(g) + Li<sub>2</sub>O(g) → Li<sub>2</sub>O<sub>2</sub>(g) and the current JANAF functions. The equilibrium constant, 0.39, was estimated by White *et al.*,<sup>1</sup> from their mass spectrometric data.

Heat Capacity and Entropy

White, *et al.*,<sup>1</sup> from their spectral data have assigned two observed frequencies and estimated the remaining frequencies using the ionic model calculations of Berkowitz<sup>2</sup> as a guide. They proposed a planar rhombic structure of D<sub>2h</sub> symmetry, similar to the alkali halide dimers, for the previously undetected Li<sub>2</sub>O<sub>2</sub> molecule, and estimated the angle, 116°, and bond distance, 1.90 Å, from their matrix spectra. The principal moments calculated from these molecular constants are I<sub>A</sub> = 2.3369 × 10<sup>-39</sup>, I<sub>B</sub> = 13.7955 × 10<sup>-39</sup>, and I<sub>C</sub> = 16.1324 × 10<sup>-39</sup> g·cm<sup>2</sup>.

References

1. D. White, K. S. Seshadri, D. F. Dever, and D. E. Mann, and M. J. Linevsky, *J. Chem. Phys.* **39**, 2463 (1963).
2. J. Berkowitz, *J. Chem. Phys.* **29**, 1386 (1958); **32**, 1519 (1960).

T/K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> - [C <sub>p</sub> <sup>o</sup> - H <sup>o</sup> (T)]/T	H <sup>o</sup> - H <sup>o</sup> (T)	H <sup>o</sup> - H <sup>o</sup> (T)	Δ <sub>f</sub> G <sup>o</sup>	log K <sub>r</sub>
Enthalpy Reference Temperature = T <sub>r</sub> = 298.15 K						
Standard State Pressure = P <sup>o</sup> = 0.1 MPa						
0	0	0	INFINITE	INFINITE	-240.598	INFINITE
100	43.954	208.779	331.528	-12.275	-240.914	126.926
200	63.946	246.153	279.984	-6.766	-241.999	63.884
250	69.312	261.042	274.742	-3.425	-245.208	51.233
298.15	72.730	273.562	273.562	0	-245.727	43.050
300	72.837	274.012	273.563	0.135	-245.746	42.788
350	75.223	285.431	274.460	3.840	-246.233	36.748
400	76.893	295.591	276.478	7.645	-246.674	32.212
450	78.098	304.720	279.117	11.521	-247.062	28.678
500	78.993	312.998	282.098	15.450	-247.465	25.780
600	80.201	327.516	288.491	23.415	-248.925	21.410
700	80.955	339.940	294.975	31.475	-250.670	18.274
800	81.454	350.784	301.288	39.597	-253.711	15.913
900	81.801	360.399	307.332	47.761	-257.002	14.069
1000	82.052	369.032	313.078	55.954	-260.582	12.588
1100	82.339	376.861	318.526	64.169	-264.444	11.371
1200	82.581	384.023	323.588	72.400	-268.599	10.353
1300	82.785	390.622	328.298	80.644	-273.057	9.487
1400	82.952	396.759	332.640	88.898	-277.811	8.743
1500	83.084	402.459	337.665	97.160	-282.864	8.094
1600	82.713	407.875	341.882	105.429	-288.226	7.525
1700	82.762	412.791	345.907	113.702	-293.899	6.979
1800	82.803	417.523	349.756	121.981	-300.000	6.434
1900	82.838	422.001	353.441	130.263	-306.548	5.899
2000	82.867	426.250	356.976	138.548	-313.644	5.372
2100	82.893	430.294	360.372	146.836	-321.292	4.851
2200	82.915	434.151	363.639	155.127	-329.494	4.342
2300	82.935	437.837	366.785	163.419	-338.250	3.846
2400	82.952	441.357	369.820	171.713	-347.561	3.362
2500	82.967	444.754	372.750	180.009	-357.427	2.890
2600	82.980	448.008	375.582	188.307	-367.849	2.430
2700	82.992	451.140	378.323	196.603	-378.827	1.982
2800	83.005	454.158	380.978	204.903	-390.361	1.546
2900	83.012	457.071	383.552	213.206	-402.450	1.121
3000	83.021	459.886	386.050	221.507	-415.104	0.703
3100	83.029	462.608	388.476	229.810	-428.323	0.293
3200	83.036	465.244	390.834	238.113	-442.107	-0.117
3300	83.042	467.799	393.127	246.417	-456.456	-0.536
3400	83.048	470.278	395.360	254.722	-471.375	-0.954
3500	83.053	472.686	397.535	263.027	-486.864	-1.372
3600	83.058	475.026	399.656	271.332	-502.932	-1.789
3700	83.063	477.301	401.724	279.638	-519.580	-2.206
3800	83.067	479.517	403.742	287.945	-536.810	-2.623
3900	83.071	481.674	405.712	296.252	-554.623	-3.040
4000	83.075	483.778	407.638	304.559	-573.020	-3.457
4100	83.078	485.829	409.520	312.867	-592.003	-3.874
4200	83.081	487.831	411.361	321.175	-611.572	-4.291
4300	83.084	489.786	413.162	329.483	-631.727	-4.708
4400	83.087	491.696	414.925	337.791	-652.468	-5.125
4500	83.089	493.563	416.652	346.100	-673.795	-5.542
4600	83.092	495.390	418.344	354.409	-695.708	-5.959
4700	83.094	497.177	420.002	362.719	-718.207	-6.376
4800	83.096	498.926	421.628	371.028	-741.292	-6.793
4900	83.098	500.639	423.224	379.338	-764.963	-7.210
5000	83.100	502.318	424.789	387.648	-789.220	-7.627
5100	83.101	503.964	426.325	395.958	-814.063	-8.044
5200	83.103	505.577	427.834	404.268	-839.497	-8.461
5300	83.105	507.160	429.316	412.578	-865.526	-8.878
5400	83.106	508.714	430.772	420.889	-892.150	-9.295
5500	83.107	510.239	432.203	429.199	-919.370	-9.712
5600	83.109	511.736	433.609	437.510	-947.193	-10.129
5700	83.110	513.207	434.993	445.821	-975.619	-10.546
5800	83.111	514.653	436.354	454.132	-1004.658	-10.963
5900	83.112	516.073	437.693	462.443	-1034.311	-11.380
6000	83.113	517.470	439.011	470.755	-1064.580	-11.797

PREVIOUS: March 1964 (1 atm)

CURRENT: March 1964 (1 bar)

Lithium Oxide ((LiO)<sub>2</sub>)

Li<sub>2</sub>O<sub>2</sub>(g)

Lithium Silicate (Li<sub>2</sub>SiO<sub>3</sub>)

CRYSTAL

M<sub>r</sub> = 89.9657

Lithium Silicate (Li<sub>2</sub>SiO<sub>3</sub>)

Li<sub>2</sub>O<sub>3</sub>Si<sub>1</sub>(cr)

S°(298.15 K) = 80.295 ± 1.3 J·K<sup>-1</sup>·mol<sup>-1</sup>  
T<sub>m</sub> = 1474 ± 1 K

T/K	C <sub>p</sub> <sup>a</sup>	S°	-[G°-H°(T)]/T	H°-H°(T)	Δ <sub>sub</sub> H°	Standard State Pressure = p° = 0.1 MPa	log K <sub>r</sub>
	J·K <sup>-1</sup> ·mol <sup>-1</sup>	J·K <sup>-1</sup> ·mol <sup>-1</sup>	J·K <sup>-1</sup> ·mol <sup>-1</sup>	J·K <sup>-1</sup> ·mol <sup>-1</sup>	J·mol <sup>-1</sup>	ΔG°	
0	0	0	INFINITE	-14554	-1638.567	-1638.567	INFINITE
100	27.669	12.276	148.950	-13.667	-1616.673	-1616.673	844.463
200	72.036	45.798	88.665	-8.573	-1588.278	-1588.278	414.816
298.15	100.567	80.295	80.295	0	-1649.500	-1649.500	273.085
300	101.010	80.919	80.297	0.186	-1649.524	-1558.739	271.303
400	118.826	112.628	84.499	11.252	-1650.237	-1527.594	199.483
500	127.809	140.155	92.946	23.604	-1656.617	-1496.277	156.315
600	134.306	164.049	102.850	36.720	-1656.584	-1464.203	127.470
700	139.649	185.161	113.129	50.422	-1656.061	-1432.175	106.870
800	144.433	204.128	123.328	64.632	-1655.158	-1400.249	91.427
900	148.565	221.382	133.288	79.285	-1653.958	-1368.455	79.423
1000	152.302	237.232	142.900	94.331	-1652.487	-1336.808	69.828
1100	155.576	251.903	152.151	109.728	-1650.773	-1305.321	61.985
1200	158.574	265.571	161.040	125.437	-1648.837	-1274.001	55.456
1300	161.293	278.371	169.578	141.431	-1646.703	-1242.850	49.938
1400	163.942	290.422	177.783	157.694	-1644.375	-1211.870	45.215
1474.000	165.856	298.915	183.653	169.896	---	CRYSTAL ← -> LIQUID	---
1500	166.523	301.821	185.676	174.217	-1641.853	-1181.064	41.128
1600	169.034	312.649	193.276	190.996	-1639.140	-1150.432	37.558
1700	171.502	322.971	200.604	208.023	-1636.890	-1105.177	33.958
1800	173.887	332.841	207.678	225.293	-1634.074	-1054.038	30.387
1900	176.188	342.305	214.517	242.798	-1630.661	-1003.172	27.579
2000	178.406	351.399	221.135	260.528	-1626.528	-952.574	24.879
2100	180.537	360.155	227.548	278.476	-1621.485	-902.241	22.442
2200	182.590	368.602	233.768	296.633	-1615.540	-852.168	20.233
2300	184.553	376.762	239.809	314.991	-1608.738	-802.351	18.272
2400	186.461	384.657	245.681	333.587	-1601.064	-752.786	16.384
2500	188.280	392.306	251.394	352.281	-1592.539	-703.467	14.698

PREVIOUS: March 1964

CURRENT: June 1967

Lithium Silicate (Li<sub>2</sub>SiO<sub>3</sub>)

Li<sub>2</sub>O<sub>3</sub>Si<sub>1</sub>(cr)

Enthalpy of Formation

The enthalpies of solution of LiCl(cr), Li<sub>2</sub>SO<sub>4</sub>(cr), SiO<sub>2</sub>(quartz) and Li<sub>2</sub>SiO<sub>3</sub>(cr) in 20 percent hydrofluoric acid at 74.7°C were measured by Kracek.<sup>1</sup> The authors derived two values of Δ<sub>sub</sub>H° of Li<sub>2</sub>O(cr) from those of LiCl(cr) and Li<sub>2</sub>SO<sub>4</sub>(cr), presumably employing auxiliary data from.<sup>2</sup> We recalculate Δ<sub>sub</sub>H° of Li<sub>2</sub>O(cr) as -58.74 (chloride scheme, originally -59.36) and -59.83 kcal mol<sup>-1</sup> (sulfate scheme, originally -60.86), using recent Δ<sub>sub</sub>H°(298.15 K) values for LiCl(cr), Li<sub>2</sub>SO<sub>4</sub>(cr), HCl(aq), H<sub>2</sub>SO<sub>4</sub>(aq) and Li<sub>2</sub>O(cr). The corresponding enthalpy changes, Δ<sub>sub</sub>H°(298.15 K), for the reaction Li<sub>2</sub>O(cr) + SiO<sub>2</sub>(quartz) = Li<sub>2</sub>SiO<sub>3</sub>(cr) are derived as -33.08 and -34.17 kcal mol<sup>-1</sup>. Adopting the weighted average Δ<sub>sub</sub>H°(298.15 K) = -33.44 kcal·mol<sup>-1</sup> with Δ<sub>sub</sub>H°(Li<sub>2</sub>O, cr, 298.15 K) = -143.1 kcal·mol<sup>-1</sup> and Δ<sub>sub</sub>H°(SiO<sub>2</sub>, quartz, 298.15 K) = -217.7 kcal·mol<sup>-1</sup>, we obtain Δ<sub>sub</sub>H°(298.15 K) = -394.24 kcal·mol<sup>-1</sup> for Li<sub>2</sub>SiO<sub>3</sub>(cr). This Δ<sub>sub</sub>H°(Li<sub>2</sub>SiO<sub>3</sub>, cr, 298.15 K) value is independent of future changes in Δ<sub>sub</sub>H°(298.15 K) of Li<sub>2</sub>O(cr) but the values of Δ<sub>sub</sub>H° and Δ<sub>sub</sub>H° are not independent.

The enthalpies of solution of LiOH(cr) and Li<sub>2</sub>SiO<sub>3</sub>(cr) in 20 percent HF(aq) at 50°C were measured by Hattner *et al.*<sup>3</sup> The Li<sub>2</sub>SiO<sub>3</sub> sample was prepared from lithium carbonate and silica by fusion under vacuum at 1500 K. Analysis gave 66.74 percent SiO<sub>2</sub> and 15.12 percent Li. The corresponding calculated values are 66.79 and 15.43. Also present were 0.5 percent K and 0.06 percent Na. Corrections were made for impurities in the enthalpy of formation measurements. The results are given as follows:

2 LiOH(cr, 25°C) + 2HF(sol, 50°C) + 2 LiF(sol, 50°C) + 2 H <sub>2</sub> O(sol, 50°C)	Δ <sub>sub</sub> H°(298.15 K)
3 H <sub>2</sub> O(sol, 50°C) + 6 HF(sol, 50°C) → H <sub>2</sub> SiF <sub>6</sub> (sol, 50°C) + 2 H <sub>2</sub> O(sol, 50°C)	-38.728
H <sub>2</sub> O(sol, 50°C) → H <sub>2</sub> O(l, 25°C)	-32.810
	+58.850
	-0.450
2 LiOH(cr, 25°C) + SiO <sub>2</sub> (cr, 25°C) → Li <sub>2</sub> SiO <sub>3</sub> (cr, 25°C) + H <sub>2</sub> O(l, 25°C)	-13.14 ± 0.70

The Δ<sub>sub</sub>H°(298.15 K) for the second reaction was determined by Torgeson and Sahama.<sup>4</sup> Based on the calculated enthalpy change for the overall reaction, Δ<sub>sub</sub>H°(298.15 K) = -13.14 kcal·mol<sup>-1</sup> and Δ<sub>sub</sub>H°(298.15 K) = -115.84 - 217.7 and -68.33 kcal·mol<sup>-1</sup> for LiOH(cr), SiO<sub>2</sub>(low quartz), and H<sub>2</sub>O(l), respectively, we derived Δ<sub>sub</sub>H°(Li<sub>2</sub>SiO<sub>3</sub>, cr, 298.15 K) = -394.21 ± 1.0 kcal·mol<sup>-1</sup>, which is in agreement with the adopted value.

Kroger and Fingas<sup>5</sup> measured the equilibrium pressure of CO<sub>2</sub> over a mixture of Li<sub>2</sub>CO<sub>3</sub>(cr), SiO<sub>2</sub>(quartz) and Li<sub>2</sub>SiO<sub>3</sub>(cr) from 585 to 781 K. The enthalpy change Δ<sub>sub</sub>H°(298.15 K) of the reaction Li<sub>2</sub>CO<sub>3</sub>(cr) + SiO<sub>2</sub>(cr) → Li<sub>2</sub>SiO<sub>3</sub>(cr) + CO<sub>2</sub>(g) is evaluated by the second and third law methods to be 30.94 and 29.47 kcal·mol<sup>-1</sup>, respectively. Using Δ<sub>sub</sub>H°(298.15 K) = -290.64, -217.7 and -94.05 kcal·mol<sup>-1</sup> for Li<sub>2</sub>CO<sub>3</sub>(cr), SiO<sub>2</sub>(cr), and CO<sub>2</sub>(g), respectively, and 3rd law Δ<sub>sub</sub>H°(298.15 K), we obtain Δ<sub>sub</sub>H°(Li<sub>2</sub>SiO<sub>3</sub>, cr, 298.15 K) = -384.82 ± 5 kcal·mol<sup>-1</sup>, which is not used.

Heat Capacity and Entropy

The low temperature heat capacities, 25-340 K, were measured by Hattner *et al.*<sup>3</sup> with an adiabatic vacuum calorimeter, using a nickel plated copper sample container. During the filling and sealing of the calorimeter, the compound was handled in an anhydrous, CO<sub>2</sub> free atmosphere so as to avoid contamination. The purity of the sample is not well established. The high temperature heat capacities are estimated by summation of the C<sub>p</sub>'s of the constituent oxides, Li<sub>2</sub>O and SiO<sub>2</sub>, and a subsequent correction based upon a comparison of the heat capacities of Na<sub>2</sub>SiO<sub>3</sub>(cr) and its constituent oxides. These estimated C<sub>p</sub>'s values are plotted and the resulting curve is joined smoothly with the low temperature C<sub>p</sub>'s curve at 298 K. The entropy, S°(298.15 K), is derived using the measured low temperature heat capacities, based on S°(25 K) = 0.023 cal·K<sup>-1</sup>·mol<sup>-1</sup>.

Fusion Data

Refer to the liquid table for details.

References

- <sup>1</sup>F. C. Kracek, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 69 (1953).
- <sup>2</sup>U. S. Nat. Bur. Stand. Circ. 500, (1952).
- <sup>3</sup>W. E. Hattner, D. L. Hildensbrand, G. C. Sinke and D. R. Stull, unpublished work, The Dow Chemical Co., Midland, Michigan, (1959).
- <sup>4</sup>D. R. Torgeson and T. G. Sahama, J. Amer. Chem. Soc. 70, 2156 (1948).
- <sup>5</sup>C. Kroger and E. Fingas, Z. anorg. allg. Chem. 213, 12 (1933).

Lithium Silicate (Li<sub>2</sub>SiO<sub>3</sub>)

LIQUID

Lithium Silicate (Li<sub>2</sub>SiO<sub>3</sub>)

Li<sub>2</sub>O<sub>3</sub>Si<sub>4</sub>(l)

S°(298.15 K) = [96.064] J·K<sup>-1</sup>·mol<sup>-1</sup>  
 T<sub>fus</sub> = 1474 ± 1 K

M<sub>r</sub> = 89.9657  
 Δ<sub>f</sub>H°(298.15 K) = [-1625.231] kJ·mol<sup>-1</sup>  
 Δ<sub>liq</sub>H° = 28.033 ± 2.1 kJ·mol<sup>-1</sup>

Enthalpy of Formation

Δ<sub>f</sub>H°(Li<sub>2</sub>SiO<sub>3</sub>, l, 298.15 K) is calculated from Δ<sub>f</sub>H°(Li<sub>2</sub>SiO<sub>3</sub>, cr, 298.15 K) by adding the enthalpy of fusion, Δ<sub>liq</sub>H°, and the difference in enthalpy, H°(1474 K) - H°(298.15 K), between the crystal and liquid.

Tschermobaeff<sup>1</sup> measured the enthalpy of reaction between SiO<sub>2</sub> and Li<sub>2</sub>CO<sub>3</sub> in a bomb calorimeter, using carbon as the auxiliary combustible material. Based on the derived Δ<sub>f</sub>H°(298.15 K) = 24.99 kcal·mol<sup>-1</sup> for the reaction Li<sub>2</sub>CO<sub>3</sub>(cr) + SiO<sub>2</sub>(cr) → Li<sub>2</sub>SiO<sub>3</sub>(g) + CO<sub>2</sub>(g), the enthalpy of formation for Li<sub>2</sub>SiO<sub>3</sub>(g) is evaluated as -389.30 kcal·mol<sup>-1</sup>, which is in fair agreement with the adopted value.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those for Na<sub>2</sub>SiO<sub>3</sub>(l), Na<sub>2</sub>O(l) and Li<sub>2</sub>O(l). A glass transition is assumed at 1000 K; i.e., the heat capacities below 1000 K are taken to be the same as those for Li<sub>2</sub>SiO<sub>3</sub>(cr).

S°(Li<sub>2</sub>SiO<sub>3</sub>, l, 298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting point has been reported as 1474 ± 1 and 1461 K by Fracek<sup>2</sup> and Van Klooster,<sup>3</sup> respectively. The value reported by Kracek is adopted.

Schwartz and Sturm<sup>4</sup> used a cooling-curve method to compare the heats of fusion of Li<sub>2</sub>SiO<sub>3</sub>(cr) and NaCl(cr). From the reported ratio, ε(Li<sub>2</sub>SiO<sub>3</sub>)ε(NaCl) = 0.261/0.402, where ε = heat of fusion in kcal·g<sup>-1</sup> and heat of fusion of NaCl(cr), the value Δ<sub>liq</sub>H° = 6.7 kcal·mol<sup>-1</sup> is derived.

References

- <sup>1</sup>Tschermobaeff, Rev. Met. 21, 729 (1905).
- <sup>2</sup>F. C. Kracek, J. Phys. Chem. 34, 2641 (1930).
- <sup>3</sup>H. S. Van Klooster, Z. Anorg. Chem. 69, 135 (1911).
- <sup>4</sup>R. Schwarz and H. Sturm, Ber. 47, 1730 (1914).

T/K	C <sub>p</sub> <sup>o</sup>	S° - (G° - H°(T))/T	H° - H°(T)	Δ <sub>f</sub> H°	log K <sub>r</sub>
Enthalpy Reference Temperature = T <sub>r</sub> = 298.15 K					
Standard State Pressure = p° = 0.1 MPa					
0					
100					
200					
298.15	100.567	96.064	96.064	-1625.231	269.656
300	101.010	96.688	96.066	-1625.254	267.901
400	118.826	126.398	111.252	-1625.968	197.158
500	127.809	155.924	108.716	-1632.348	134.603
600	134.306	179.818	118.619	-1632.314	126.181
700	139.649	200.930	128.898	-1449.396	105.883
800	144.432	219.897	139.108	-1631.792	141.894
900	148.565	237.151	149.057	-1630.889	105.666
1000	152.302	253.001	158.670	-1629.689	78.338
1000.000	152.302	253.001	158.670	-1628.218	69.384
1000.000	167.360	253.001	158.670	94.331	---
				GLASS <- -> LIQUID	---
				TRANSITION	---
1100	167.360	268.952	167.982	-1625.164	61.659
1200	167.360	283.514	177.012	-1622.201	55.234
1300	167.360	296.910	185.726	-1619.325	49.807
1400	167.360	309.313	194.116	-1616.524	45.163
1474.000	167.360	317.933	200.118	-1613.789	---
1500	167.360	320.860	202.185	-1613.789	41.146
1600	167.360	331.661	209.944	-1611.119	37.636
1700	167.360	341.807	217.405	-1608.160	34.090
1800	167.360	351.373	224.584	-1604.879	30.766
1900	167.360	360.422	231.498	-1601.166	27.799
2000	167.360	369.006	238.160	-1596.429	25.134
2100	167.360	377.172	244.587	-1592.264	22.728
2200	167.360	384.957	250.792	-1588.141	20.546
2300	167.360	392.397	256.788	-1584.060	18.558
2400	167.360	399.519	262.588	-1580.026	16.739
2500	167.360	406.351	268.203	-1576.040	15.069
2600	167.360	412.915	273.643	-1572.104	13.531
2700	167.360	419.232	278.919	-1568.221	12.110
2800	167.360	425.318	284.040	-1564.393	10.792
2900	167.360	431.191	288.013	-1560.623	9.569
3000	167.360	436.865	293.848	-1556.915	8.429
3100	167.360	442.352	298.550	-1553.268	7.364
3200	167.360	447.666	303.127	-1549.688	6.368
3300	167.360	452.816	307.586	-1546.174	5.434
3400	167.360	457.812	311.931	-1542.730	4.557
3500	167.360	462.663	316.169	-1539.358	3.731
3600	167.360	467.378	320.304	-1536.052	2.961
3700	167.360	471.964	324.341	-1532.816	2.244
3800	167.360	476.427	328.285	-1529.646	1.584
3900	167.360	480.774	332.139	-1526.538	0.974
4000	167.360	485.011	335.908	-1523.496	0.414

PREVIOUS: March 1964

CURRENT: June 1967

Lithium Silicate (Li<sub>2</sub>SiO<sub>3</sub>)

Li<sub>2</sub>O<sub>3</sub>Si<sub>4</sub>(l)

Lithium Silicate (Li<sub>2</sub>SiO<sub>3</sub>)

Li<sub>2</sub>O<sub>3</sub>Si<sub>1</sub>(cr,l)

Li<sub>2</sub>O<sub>3</sub>Si<sub>1</sub>(cr,l)

0 to 1474 K crystal  
above 1474 K liquid

Refer to the individual tables for details.

T/K	C <sub>p</sub> <sup>o</sup>	Enthalpy Reference Temperature = T <sub>r</sub> = 298.15 K		Standard State Pressure = p <sup>o</sup> = 0.1 MPa		log K <sub>r</sub>
		J·K <sup>-1</sup> ·mol <sup>-1</sup>	S <sup>o</sup> - [C <sub>p</sub> <sup>o</sup> - R ln(T <sub>r</sub> )/T]	H <sup>o</sup> - H <sup>o</sup> (T <sub>r</sub> )	ΔG <sup>o</sup>	
0	0	INFINITE	0	-14.554	-1638.567	INFINITE
100	27.669	12.276	0	-13.667	-1643.293	844.463
200	72.036	45.798	88.665	-8.573	-1647.428	414.816
298.15	100.567	80.295	0	0	-1649.500	273.085
300	101.010	80.919	80.297	0.186	-1649.524	271.303
400	118.826	112.628	84.499	11.252	-1650.237	199.483
500	127.809	140.155	92.946	23.604	-1656.617	156.315
600	134.306	164.049	102.850	36.720	-1656.584	127.470
700	139.649	185.161	113.290	50.422	-1656.061	106.870
800	144.432	204.128	123.338	64.632	-1653.158	91.427
900	148.565	221.382	133.288	79.235	-1653.958	79.423
1000	152.302	237.232	142.900	94.531	-1652.487	69.828
1100	155.576	251.903	152.151	109.728	-1650.773	61.985
1200	158.574	265.571	161.040	125.437	-1648.837	55.456
1300	161.293	278.371	169.578	141.431	-1646.703	49.938
1400	163.942	290.422	177.783	157.694	-1644.375	45.215
1474.000	165.856	298.915	183.653	169.896	—	—
1474.000	167.360	317.933	183.653	197.979	CRYSTAL → LIQUID TRANSITION	—
1500	167.360	320.860	186.006	202.281	-1613.789	41.146
1600	167.360	331.661	194.775	219.017	-1611.119	37.636
1700	167.360	341.807	203.129	235.753	-1609.160	34.090
1800	167.360	351.373	211.102	252.489	-1604.879	30.766
1900	167.360	360.422	218.725	269.225	-1601.166	27.799
2000	167.360	369.006	226.026	285.961	-1596.429	25.134
2100	167.360	377.172	233.030	302.697	-1592.264	22.728
2200	167.360	384.957	239.761	319.433	-1588.141	20.546
2300	167.360	392.397	246.236	336.169	-1584.060	18.588
2400	167.360	399.519	252.476	352.905	-1580.026	16.739
2500	167.360	406.351	258.495	369.641	-1576.040	15.069
2600	167.360	412.915	264.309	386.377	-1572.104	13.531
2700	167.360	419.232	269.931	403.113	-1568.221	12.110
2800	167.360	425.318	275.372	419.849	-1564.393	10.792
2900	167.360	431.191	280.645	436.585	-1560.623	9.569
3000	167.360	436.865	285.758	453.321	-1556.915	8.429
3100	167.360	442.352	290.721	470.057	-1553.268	7.364
3200	167.360	447.666	295.543	486.793	-1549.688	6.368
3300	167.360	452.816	300.231	503.529	-1546.174	5.434
3400	167.360	457.812	304.793	520.265	-1542.730	4.557
3500	167.360	462.663	309.235	537.001	-1539.358	3.731
3600	167.360	467.378	313.562	553.737	-1536.012	2.801
3700	167.360	471.964	317.782	570.473	-1532.676	1.915
3800	167.360	476.427	321.898	587.209	-1529.350	1.078
3900	167.360	480.774	325.916	603.945	-1526.046	0.284
4000	167.360	485.011	329.841	620.681	-1522.761	-0.468

PREVIOUS:

CURRENT: June 1967

Lithium Silicate (Li<sub>2</sub>SiO<sub>3</sub>)

Li<sub>2</sub>O<sub>3</sub>Si<sub>1</sub>(cr,l)

**Li<sub>2</sub>O<sub>3</sub>Ti<sub>1</sub>(cr)**

**Lithium Titanium Oxide (Li<sub>2</sub>TiO<sub>3</sub>)**

**CRYSTAL(α-β)**

**Lithium Titanium Oxide (Li<sub>2</sub>TiO<sub>3</sub>)**

T/K	Enthalpy Reference Temperature = T <sub>r</sub> = 298.15 K		Standard State Pressure = P° = 0.1 MPa		log K <sub>i</sub>
	C <sub>p</sub> <sup>o</sup>	S° - [C <sub>p</sub> <sup>o</sup> - F(T <sub>r</sub> )/T]	H° - H°(T <sub>r</sub> )	ΔG°	
	J·K <sup>-1</sup> ·mol <sup>-1</sup>	J·K <sup>-1</sup> ·mol <sup>-1</sup>	KJ·mol <sup>-1</sup>	KJ·mol <sup>-1</sup>	
0	0	0	INFINITE	-1660.065	INFINITE
100	31.142	14.129	169.105	-1638.099	855.655
200	82.663	52.886	101.316	-1609.488	420.355
298.15	109.855	91.755	91.755	-1579.767	276.769
300	110.750	92.437	91.757	-1579.203	274.964
400	127.361	126.619	96.309	-1548.635	202.231
500	135.645	156.002	105.388	-1517.421	138.524
600	141.503	181.283	115.979	-1485.520	79.376
700	145.854	203.436	126.924	-1453.710	108.477
800	149.034	223.130	137.741	-1422.030	92.849
900	151.670	240.839	148.229	-1390.488	80.702
1000	153.888	256.936	158.307	-1359.077	70.991
1100	155.812	271.696	167.954	-1327.783	63.051
1200	157.318	285.322	177.174	-1296.471	56.434
1300	158.490	297.665	185.985	-1265.052	50.830
1400	159.384	309.751	194.410	-1233.763	46.032
1485.000	160.344	319.174	201.284	175.067	28.402
1485.000	176.063	326.922	201.284	186.573	41.882
1500	176.565	328.694	202.549	189.218	38.278
1600	179.912	340.196	210.795	207.042	34.664
1700	183.259	351.204	218.733	225.200	31.555
1800	186.606	361.773	226.388	243.693	---
1820.000	187.276	363.839	227.887	247.432	---
1900	189.954	371.952	233.783	262.521	---
2000	193.301	381.781	240.939	281.684	---
2100	196.648	391.293	247.873	301.182	---
2200	199.995	400.518	254.603	321.014	---
2300	203.342	409.482	261.143	341.181	---
2400	206.690	418.207	267.506	361.682	---
2500	210.037	426.712	273.705	382.519	---
2600	213.384	435.015	279.750	403.690	---
2700	216.731	443.131	285.652	425.195	---
2800	220.078	451.074	291.418	447.036	---
2900	223.426	458.855	297.058	469.211	---
3000	226.773	466.486	302.579	491.721	---

$\Delta_f H^\circ(0\text{ K}) = -1660.065\text{ kJ}\cdot\text{mol}^{-1}$   
 $\Delta_f H^\circ(298.15\text{ K}) = -1670.671\text{ kJ}\cdot\text{mol}^{-1}$   
 $\Delta_{\text{cr}} H^\circ = 11.506\text{ kJ}\cdot\text{mol}^{-1}$   
 $\Delta_{\text{liq}} H^\circ = 110.165\text{ kJ}\cdot\text{mol}^{-1}$

**Enthalpy of Formation**  
 $\Delta_f H^\circ(298.15\text{ K})$  was calculated from measurements of solution calorimetry by Todd and Kelley<sup>1</sup> according to the following equation:  
 $\text{TiO}_2(\text{cr}) + \text{Li}_2\text{SO}_4(\text{cr}) + 13.312\text{ H}_2\text{O}(\text{l}) = \text{Li}_2\text{TiO}_3(\text{cr}) + \text{H}_2\text{SO}_4(\text{aq})$   $\Delta_f H^\circ(298.15\text{ K}) = 27.04\text{ kcal}\cdot\text{mol}^{-1}$   $\Delta_f H^\circ(\text{TiO}_2, \text{cr}, 298.15\text{ K})$  value for rutile was obtained from the JANAF tables and the other  $\Delta_f H^\circ(298.15\text{ K})$  values were obtained from.<sup>2</sup>

**Heat Capacity and Entropy**  
 The low temperature heat capacities were taken from King.<sup>3</sup> These low temperature heat capacities were fit to the high temperature enthalpies from Christensen *et al.*<sup>4</sup>  
 $S^\circ(298.15\text{ K}) = 211.9\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  was obtained from King<sup>3</sup> based on the measured heat capacities and the extrapolated  $S^\circ(51\text{ K})$  value.

**Transition Data**  
 Christensen *et al.*<sup>4</sup> reported that lithium metatitanate undergoes a transition from the  $\alpha$  to the  $\beta$  form at 1,485 K with an absorption of 2,750 kcal·mol<sup>-1</sup>.

**Fusion Data**  
 The  $T_{\text{fus}}$  and  $\Delta_{\text{fus}} H^\circ$  were obtained from Christensen *et al.*<sup>4</sup>

**References**  
<sup>1</sup>S. S. Todd and K. K. Kelley, U. S. Bur. RI 5193, (1956).  
<sup>2</sup>U. S. Nat. Bur. Stand. Circ. 500, (1952).  
<sup>3</sup>E. G. King, J. Amer. Chem. Soc. 77, 2150 (1955).  
<sup>4</sup>A. U. Christensen, K. C. Conway and K. K. Kelley, U. S. Bur. Mines RI 5565, (1960).

LIQUID

Lithium Titanium Oxide (Li<sub>2</sub>TiO<sub>3</sub>)

M<sub>r</sub> = 109.7602

Lithium Titanium Oxide (Li<sub>2</sub>TiO<sub>3</sub>)

Li<sub>2</sub>O<sub>3</sub>Ti<sub>4</sub>(l)

S°(298.15 K) = [147.656] J·K<sup>-1</sup>·mol<sup>-1</sup>  
 T<sub>fus</sub> = 1820 K  
 $\Delta_f H^\circ(298.15 \text{ K}) = [-1566.760] \text{ kJ mol}^{-1}$   
 $\Delta_{\text{fus}} H^\circ = 110.165 \text{ kJ mol}^{-1}$

Enthalpy of Formation

$\Delta_f H^\circ(\text{Li}_2\text{TiO}_3, l, 298.15 \text{ K})$  is calculated from that of the crystal by adding the enthalpy of fusion,  $\Delta_{\text{fus}} H^\circ$ , and the difference in enthalpy,  $H^\circ(1820 \text{ K}) - H^\circ(298.15 \text{ K})$ , between the crystal and liquid.

Heat Capacity and Entropy

The heat capacities were reported by Christensen *et al.*<sup>1</sup> The measured heat capacity is extrapolated to an assumed glass transition temperature of 1214 K, below which the heat capacity is taken to be equal to that of the crystal.

S°(Li<sub>2</sub>TiO<sub>3</sub>, l, 298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The T<sub>fus</sub> and  $\Delta_{\text{fus}} H^\circ$  were obtained from Christensen *et al.*<sup>1</sup>

Reference

<sup>1</sup>A. U. Christensen, K. C. Conway and K. K. Kelley, U. S. Bur. Mines RI 5565, (1960).

T/K	C <sub>p</sub> <sup>a</sup>	S°	[C° - f(T, T <sub>g</sub> )]/T	H° - H°(T <sub>g</sub> )	Standard State Pressure = P° = 0.1 MPa	log K <sub>f</sub>
	J·K <sup>-1</sup> ·mol <sup>-1</sup>	J·K <sup>-1</sup> ·mol <sup>-1</sup>		kJ·mol <sup>-1</sup>	Δ <sub>f</sub> H°	Δ <sub>f</sub> G°
0				0.	-1566.760	-1492.523
100	109.855	147.656	147.656		-1566.760	261.484
200	110.750	148.338	147.658	0.204	-1566.775	259.791
300	127.361	152.720	152.209	12.124	-1567.127	191.582
400	135.645	161.289	161.289	25.307	-1573.138	150.588
500	141.503	171.803	171.803	39.182	-1572.795	141.460
600	145.854	182.824	182.824	53.559	-1572.038	123.200
700	149.034	193.642	193.642	68.311	-1571.009	103.643
800	151.670	204.130	204.130	83.349	-1569.852	88.984
900	153.888	214.208	214.208	98.628	-1568.659	77.591
1000	155.812	223.855	223.855	114.117	-1567.511	68.483
1200	157.318	233.075	233.075	129.778	-1570.420	61.037
1214.000	157.569	234.333	234.333	131.982	-1570.420	54.831
1214.000	200.832	343.049	343.049	131.982	GLASS <---> LIQUID	
1300	200.832	356.795	241.984	149.253	TRANSITION	49.580
1400	200.832	371.678	250.723	169.336	-1565.044	45.097
1500	200.832	385.534	259.254	189.420	-1559.172	41.226
1600	200.832	398.495	267.556	209.503	-1553.416	37.851
1700	200.832	410.671	275.620	229.586	-1547.787	34.443
1800	200.832	422.150	283.445	249.669	-1825.924	31.320
1820.000	200.832	424.369	284.965	253.716	---> BETA <---> LIQUID	
1900	200.832	433.008	291.033	269.752	-1819.262	28.536
2000	200.832	443.310	298.392	289.836	-1827.482	26.028
2100	200.832	453.108	305.528	309.919	-1821.974	23.758
2200	200.832	462.451	312.450	330.002	-1816.507	21.701
2300	200.832	471.578	319.167	350.085	-1811.084	19.829
2400	200.832	479.926	325.689	370.168	-1805.706	18.118
2500	200.832	488.124	332.023	390.252	-1800.377	16.548
2600	200.832	496.001	338.180	410.335	-1795.098	15.103
2700	200.832	503.580	344.166	430.418	-1789.872	13.770
2800	200.832	510.884	349.991	450.501	-1784.701	12.535
2900	200.832	517.931	355.661	470.584	-1779.588	11.388
3000	200.832	524.740	361.184	490.668	-1774.536	10.321
3100	200.832	531.325	366.567	510.751	-1769.547	9.326
3200	200.832	537.701	371.816	530.834	-1764.623	8.395
3300	200.832	543.881	376.937	550.917	-1759.766	7.524
3400	200.832	549.877	381.935	571.000	-1754.979	6.706
3500	200.832	555.698	386.817	591.084	-1750.265	5.936
3600	200.832	561.356	391.587	611.167	-1745.624	5.212
3700	200.832	566.859	396.250	631.250	-1741.057	4.418
3800	200.832	572.214	400.811	651.333	-1736.561	3.620
3900	200.832	577.431	405.273	671.416	-1732.130	2.865
4000	200.832	582.516	409.641	691.500	-1727.765	2.150

PREVIOUS: June 1961

CURRENT: March 1964

Lithium Titanium Oxide (Li<sub>2</sub>TiO<sub>3</sub>)

Li<sub>2</sub>O<sub>3</sub>Ti<sub>4</sub>(l)



Lithium Titanium Oxide (Li<sub>2</sub>TiO<sub>3</sub>)

CRYSTAL(α-β)-LIQUID

M<sub>r</sub> = 109.7602 Lithium Titanium Oxide (Li<sub>2</sub>TiO<sub>3</sub>)

Li<sub>2</sub>O<sub>3</sub>Ti<sub>1</sub>(cr,l)

0 to 1485 K crystal, alpha  
1485 to 1820 K crystal, beta  
above 1820 K liquid

Refer to the individual tables for details.

T/K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> - (G <sup>o</sup> - H <sup>o</sup> (T))/T	H <sup>o</sup> - H <sup>o</sup> (T)	A <sub>p</sub> H <sup>o</sup>	log K <sub>r</sub>
0	0	0	INFINITE	INFINITE	INFINITE
100	31.142	14.129	169.105	-16.493	-1660.065
200	82.663	52.886	101.316	-15.498	-1638.099
298.15	109.855	91.755	91.755	-9.686	-1609.488
300	110.750	92.437	91.757	0	-1579.767
400	127.361	126.619	96.309	0.204	-1579.203
500	135.645	156.002	105.388	12.124	-1548.635
600	141.503	181.283	115.979	25.307	-1517.421
700	145.854	203.436	126.924	39.182	-1485.520
800	149.034	223.130	137.741	53.559	-1453.710
900	151.670	240.839	148.229	68.311	-1422.030
1000	153.888	256.936	158.307	83.349	-1390.488
1100	155.812	271.696	167.954	98.628	-1359.077
1200	157.318	285.322	177.174	114.117	-1327.783
1300	158.490	297.965	185.965	129.778	-1296.471
1400	159.494	309.751	194.410	145.574	-1265.032
1485.000	160.344	319.174	201.284	161.478	-1233.763
1485.000	176.063	326.922	201.284	175.067	ALPHA <- -> BETA TRANSITION
1500	176.565	328.694	202.549	186.573	TRANSITION
1600	179.912	340.196	210.795	189.218	-1202.712
1700	183.259	351.204	218.733	207.042	-1172.500
1800	186.606	361.773	226.388	223.200	-1141.666
1820.000	187.276	363.839	227.887	243.693	-1108.485
1820.000	200.832	424.369	227.887	247.432	BETA <- -> LIQUID TRANSITION
1900	200.832	433.008	236.343	357.597	TRANSITION
2000	200.832	443.310	246.436	371.664	-1819.262
2100	200.832	453.108	256.046	393.747	-1827.482
2200	200.832	462.451	265.218	413.830	-1821.974
2300	200.832	471.378	273.989	433.913	-1816.507
2400	200.832	479.926	282.392	453.996	-1811.084
2500	200.832	488.124	290.459	474.080	-1805.706
2600	200.832	496.001	298.214	494.163	-1800.377
2700	200.832	503.580	305.681	514.246	-1795.098
2800	200.832	510.884	312.880	534.329	-1789.872
2900	200.832	517.931	319.830	554.412	-1784.701
3000	200.832	524.740	326.547	574.496	-1779.588
3100	200.832	531.325	333.047	594.579	-1774.536
3200	200.832	537.701	339.344	614.662	-1769.547
3300	200.832	543.881	345.449	634.745	-1764.623
3400	200.832	549.877	351.373	654.828	-1759.766
3500	200.832	555.698	357.128	674.912	-1754.979
3600	200.832	561.356	362.723	694.995	-1750.265
3700	200.832	566.859	368.166	715.078	-1745.624
3800	200.832	572.214	373.466	735.161	-1741.057
3900	200.832	577.431	378.629	755.244	-1736.561
4000	200.832	582.516	383.663	775.328	-1732.132
				795.411	-1694.635

PREVIOUS:

CURRENT March 1964

Lithium Titanium Oxide (Li<sub>2</sub>TiO<sub>3</sub>)

Li<sub>2</sub>O<sub>3</sub>Ti<sub>1</sub>(cr,l)

## CRYSTAL(α)

Lithium Sulfate (α-Li<sub>2</sub>SO<sub>4</sub>)

$$S^{\circ}(298.15 \text{ K}) = 113.947 \pm 0.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$T_m(\alpha \rightarrow \beta) = 848 \pm 1 \text{ K}$$

## Enthalpy of Formation

The enthalpy of solution of Li<sub>2</sub>SO<sub>4</sub>(cr, α) has been measured by Ueda,<sup>1</sup> Thomsen,<sup>2</sup> Pickering,<sup>3</sup> Romanova and Samoilov<sup>4</sup> and Tsvetkov and Rabinovich.<sup>5</sup> Adopting the results from<sup>1,4,5</sup> we have  $\Delta_{\text{sol}}H^{\circ}(298.15 \text{ K}) = -7.300 \pm 0.1 \text{ kcal}\cdot\text{mol}^{-1}$  for the enthalpy of solution at infinite dilution. We have used data from Thompson *et al.*<sup>6</sup> to correct the enthalpy of solution data to infinite dilution. When this result is combined with enthalpies of formation of the infinitely dilute ions from CODATA<sup>7</sup> we obtain  $\Delta_f H^{\circ}(\text{Li}_2\text{SO}_4, \text{aq}, \infty, 298.15 \text{ K}) = 350.504 \pm 0.2 \text{ kcal}\cdot\text{mol}^{-1}$  and  $\Delta_f H^{\circ}(\text{Li}_2\text{SO}_4, \text{cr}, 298.15 \text{ K}) = -343.20 \pm 0.3 \text{ kcal}\cdot\text{mol}^{-1}$ .

Lithium sulfate was studied by hydrochloric acid solution calorimetry by Barany and Adams<sup>8</sup> who obtained  $\Delta_f H^{\circ}(298.15 \text{ K}) = -16.020 \pm 0.120 \text{ kcal}\cdot\text{mol}^{-1}$  for the reaction  $2 \text{LiCl}(\text{cr}) + \text{H}_2\text{SO}_4 \cdot 7.068 \text{ H}_2\text{O}(\text{l}) + 18.394 \text{ H}_2\text{O}(\text{l}) = \text{Li}_2\text{SO}_4(\text{cr}) + 2 \text{HCl}\cdot 12.731 \text{ H}_2\text{O}(\text{l})$ . When this result is combined with auxiliary data from,<sup>9,10</sup> we obtain  $\Delta_f H^{\circ}(\text{Li}_2\text{SO}_4, \text{cr}, 298.15 \text{ K}) = -343.30 \pm 0.1 \text{ kcal}\cdot\text{mol}^{-1}$ . Auxiliary data used in the analysis are (in kcal·mol<sup>-1</sup>)  $\Delta_f H^{\circ}(\text{H}_2\text{SO}_4, 7.068 \text{ H}_2\text{O}, 298.15 \text{ K}) = -209.566 \pm 0.10$  and  $\Delta_f H^{\circ}(\text{HCl}\cdot 12.731 \text{ H}_2\text{O}, 298.15 \text{ K}) = 38.792 \pm 0.010$ .

Ueda<sup>1</sup> measured the emf of the cell Li(amalgam, 0.035%)|Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O (sat. soln.)|Hg<sub>2</sub>SO<sub>4</sub>|Hg at 298 K as  $E_{\text{cell}} = 2.67489$  volts. Kelley<sup>11</sup> used this value along with other data to determine  $\Delta_f H^{\circ}(298.15 \text{ K})$  for Li<sub>2</sub>SO<sub>4</sub>(cr). Adopting results given in Kelley,<sup>11</sup> we calculate  $\Delta_f H^{\circ}(298.15 \text{ K}) = -165.780 \text{ kcal}\cdot\text{mol}^{-1}$  for the reaction  $2 \text{Li}(\text{cr}) + \text{Hg}_2\text{SO}_4(\text{cr}) = 2 \text{Hg}(\text{l}) + \text{Li}_2\text{SO}_4(\text{cr})$ . Taking  $\Delta_f G^{\circ}(\text{Hg}_2\text{SO}_4, \text{cr}, 298.15 \text{ K}) = 149.658 \text{ kcal}\cdot\text{mol}^{-1}$  and reference entropies from,<sup>7</sup> we calculate  $\Delta_f G^{\circ}(\text{Li}_2\text{SO}_4, \text{cr}, 298.15 \text{ K}) = -315.438$  and  $\Delta_f H^{\circ}(\text{Li}_2\text{SO}_4, \text{cr}, 298.15 \text{ K}) = -343.0 \pm 0.5 \text{ kcal}\cdot\text{mol}^{-1}$ .

We adopt a value for the enthalpy of reaction based on the solution work of Barany and Adams.<sup>8</sup>

## Heat Capacity and Entropy

Low temperature heat capacities of Li<sub>2</sub>SO<sub>4</sub>(cr, α) have been measured by Paukov<sup>11</sup> in an adiabatic calorimeter from 12.00–311.11 K. We have smoothed the experimental  $C_p^{\circ}$  data by fitting to orthogonal polynomials over selected temperature intervals. Our adopted value of  $S^{\circ}(298.15 \text{ K}) = 27.234 \pm 0.10 \text{ kcal}\cdot\text{mol}^{-1}$  is based on  $S^{\circ}(14 \text{ K}) = 0.051 \text{ kcal}\cdot\text{mol}^{-1}$  and  $H^{\circ}(14.0) = 0.540 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  derived from a Debye  $T^3$  law extrapolation.

Heat capacity data measured by adiabatic calorimetry have been reported by Shimidi,<sup>12</sup> (298.5–774.3) and by Sjöblom,<sup>13</sup> (430–845 K). In addition, drop calorimetric enthalpy measurements have been performed by Demiclou *et al.*,<sup>14</sup> (400–848 K), by Clark,<sup>15</sup> (488.0–848.7 K) and by Voskresenskaya and Banashek,<sup>16</sup> (360–859 K). The data of Clark, is systematically low by 15% while the data from Sjöblom is too high by 10%. There is good agreement among the other three studies.<sup>12,14,15</sup> We adopt heat capacities above 300 K based on a smooth fit to the combined data from,<sup>11,12,14,15</sup>

## Transition Data

Li<sub>2</sub>SO<sub>4</sub>(cr, α) is the low-temperature form of lithium sulfate (sometimes denoted Li<sub>2</sub>SO<sub>4</sub> II). The crystals are monoclinic (space group C<sub>2h</sub>, P2<sub>1</sub>/c). The transformation to the high-temperature β phase (cubic form) occurs at  $848 \pm 1 \text{ K}$ .<sup>14,15</sup> The enthalpy of transition is determined by taking the difference between the adopted enthalpy curves of α and β Li<sub>2</sub>SO<sub>4</sub> extrapolated to 848 K (see the discussion on the Li<sub>2</sub>SO<sub>4</sub>(cr, β) table).

## References

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- JANAF Thermochemical Tables: Li<sub>2</sub>SO<sub>4</sub>(cr, β), 12-31-78.

PREVIOUS

CURRENT December 1978

Lithium Sulfate, Alpha (Li<sub>2</sub>SO<sub>4</sub>)Li<sub>2</sub>O<sub>4</sub>S<sub>1</sub>(cr)

T/K	Enthalpy Reference Temperature = T, - 298.15 K		Standard State Pressure = P° = 0.1 MPa		log K <sub>r</sub>
	C <sub>p</sub> <sup>o</sup>	S° - [C <sub>p</sub> ° - H <sub>f</sub> °(T)]/T	H <sub>f</sub> ° - H <sub>f</sub> °(T)	Δ <sub>f</sub> H <sub>f</sub> °	
0	0	INFINITE	-18.636	-1423.980	INFINITE
100	43.869	28.932	-16.769	-1395.114	728.733
200	86.872	73.028	-10.159	-1358.693	354.854
298.15	117.608	113.947	0	-1321.111	231.453
300	118.026	113.949	0.218	-1320.395	229.901
400	139.244	118.850	13.131	-1281.517	167.349
500	154.473	124.409	27.827	-1241.336	129.682
600	168.469	131.812	43.975	-1200.315	104.497
700	182.360	140.827	61.518	-1159.466	86.370
800	196.062	150.669	80.437	-1118.979	73.062
848.000	202.732	171.544	90.008	ALPHA < -> BETA	
900	209.702	178.033	100.732	-1077.896	62.559
1000	223.384	190.373	123.387	-1032.517	53.933
1100	237.051	202.502	145.408	-987.910	46.912
1200	250.705	214.406	169.796	-944.121	41.097

Lithium Sulfate, Alpha (Li<sub>2</sub>SO<sub>4</sub>)Li<sub>2</sub>O<sub>4</sub>S<sub>1</sub>(cr)

$\text{Li}_2\text{O}_4\text{S}_1(\text{cr})$

Lithium Sulfate, Beta ( $\text{Li}_2\text{SO}_4$ )

CRYSTAL( $\beta$ )

Lithium Sulfate ( $\beta$ - $\text{Li}_2\text{SO}_4$ )

$M_r = 109.9396$

$\Delta H^\circ(298.15 \text{ K}) = [-1425.373] \text{ kJ}\cdot\text{mol}^{-1}$   
 $\Delta_{\text{tr}}H^\circ(\alpha \rightarrow \beta) = -28.451 \pm 0.8 \text{ kJ}\cdot\text{mol}^{-1}$   
 $\Delta_{\text{tr}}H^\circ(\beta \rightarrow \text{l}) = 8.577 \pm 0.8 \text{ kJ}\cdot\text{mol}^{-1}$

$S^\circ(298.15 \text{ K}) = [113.802] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$   
 $T_m(\alpha \rightarrow \beta) = 848 \pm 1 \text{ K}$   
 $T_m(\beta \rightarrow \text{l}) = 1132 \pm 1 \text{ K}$

**Enthalpy of Formation**

$\Delta_f H^\circ(\text{Li}_2\text{SO}_4, \text{cr}, \beta, 298.15 \text{ K})$  is calculated from  $\Delta_f H^\circ(\text{Li}_2\text{SO}_4, \text{cr}, \alpha, 298.15 \text{ K})$  by adding the enthalpy of transition ( $\alpha \rightarrow \beta$ ),  $\Delta_{\text{tr}}H^\circ$ , and the difference in enthalpy,  $H^\circ(848 \text{ K}) - H^\circ(298.15 \text{ K})$ , between the alpha and beta crystalline forms.<sup>1</sup>

**Heat Capacity and Entropy**

High temperature enthalpy measurements by drop calorimetry were carried out by Denielou *et al.*<sup>2</sup> (860–1110 K), by Clark,<sup>3</sup> (874–1103 K), and by Voskresenskaya and Banashek,<sup>4</sup> (859–1133 K). In addition, heat capacities have been measured in an adiabatic calorimeter by Sjolom,<sup>5</sup> (873–1073 K). All of the data indicate that  $C_p^\circ$  is nearly constant over the temperature interval 848–1132 K. The data of Clark<sup>3</sup> is systematically low by 15%, while the other studies<sup>2,4,5</sup> are in substantial agreement. We have adopted enthalpies from Denielou *et al.*<sup>2</sup> for our curve fits, but have neglected points near  $T_m$  and  $T_{\text{tr}}$  where the data shows pronounced curvature. This leads to a constant heat capacity of  $51.0 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  over the range 909–1119 K. Our adopted enthalpies are 1.5% higher than those from Denielou *et al.*<sup>2</sup> at 848 K and 0.5% higher at 1132 K. We have extrapolated a constant heat capacity below  $T_m$  to 700 K at which point we slowly bend  $C_p^\circ$  until it is only 5% higher than  $C_p^\circ$  for the  $\alpha$ -form at 298.15 K. We also extrapolate a constant heat capacity above  $T_{\text{tr}}$ .

**Transition Data**

The high temperature  $\beta$ -modification of lithium sulfate (sometimes denoted  $\text{Li}_2\text{SO}_4(\text{I})$ ) is of cubic structure, space group  $T_{\text{tr}}$ .<sup>6</sup> The  $\alpha$ -transition at 848 K is somewhat gradual and shows a second order rather than first order behavior. We have treated the transition as a first order transition, taking some of the curvature in the enthalpy data (see above) and lumping it into the heat of transition. Reasonable  $C_p^\circ$  curves are obtained by omitting from the curve fits those enthalpy data in the vicinity of  $T_{\text{tr}}$ .  $T_{\text{tr}} = 848 \text{ K}$  is selected as the peak of the transition  $\Delta_{\text{tr}}H^\circ$  is calculated as the difference in the enthalpy curve fits at  $T_{\text{tr}}$ .

**Fusion Data**

The adopted melting point,  $T_m = 1132 \pm 1 \text{ K}$ , was determined from the work of Denielou *et al.*,<sup>2</sup> (1130  $\pm$  3 K), Voskresenskaya and Banashek,<sup>4</sup> (1133  $\pm$  1 K), and Rea,<sup>7</sup> (1132 K). The heat of fusion,  $\Delta_{\text{tr}}H^\circ = 2.050 \pm 0.2 \text{ kcal}\cdot\text{mol}^{-1}$ , is calculated from the difference between the smoothed relative enthalpy of the liquid and the adopted enthalpy value for the  $\beta$ -crystalline form at  $T_m$ .

**References**

- <sup>1</sup>JANAF Thermochemical Tables:  $\text{Li}_2\text{SO}_4(\text{cr}, \alpha)$ , 12-31-78.
- <sup>2</sup>L. Denielou, Y. Fournier, J. P. Petitot, and C. Tequi, *Rev. Int. Hautes Temp.* **8**, 119 (1971).
- <sup>3</sup>R. P. Clark, *J. Chem. Eng. Data* **20**, 17 (1975).
- <sup>4</sup>N. K. Voskresenskaya and E. I. Banashek, *Izv. Sek. Fiz. Khim. Anal., Akad. Nauk SSSR* **25**, 150 (1954).
- <sup>5</sup>C. A. Sjolom, *High Temp. - High Pressures* **8**, 499 (1976).
- <sup>6</sup>T. Forland and J. Krogh-Moe, *Acta. Chem. Scand.* **11**, 565 (1957).
- <sup>7</sup>R. F. Rea, *J. Amer. Ceram. Soc.* **21**, 98 (1938).

T/K	Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$		Standard State Pressure = $p^\circ = 0.1 \text{ MPa}$		log K <sub>r</sub>
	$C_p^\circ$	$S^\circ - (G^\circ - H^\circ(T_r))/T_r$	$H^\circ - H^\circ(T_r)$	$\Delta G^\circ$	
0	0	0	0	-1425.373	229.519
100	129.15	113.802	0.242	-1310.073	227.979
200	132.214	114.612	15.883	-1309.358	227.979
300	176.565	159.302	15.883	-1425.472	165.952
400	196.648	201.029	34.621	-1428.646	128.691
500	207.526	237.933	54.878	-1424.259	103.850
600	212.547	270.354	75.917	-1418.927	86.168
700	213.384	298.803	97.223	-1413.298	72.958
800	213.384	311.237	107.465	---	---
848.000	213.384	323.936	118.561	-1460.810	62.661
900	213.384	346.418	139.900	-1454.024	54.202
1000	213.384	366.756	161.238	-1447.337	47.313
1100	213.384	372.875	168.066	---	---
1132.000	213.384	385.323	182.576	---	---
1200	213.384	402.402	203.915	-1440.735	41.598
1300	213.384	418.216	223.253	-1434.210	36.785
1400	213.384	432.938	246.592	-1427.749	32.678
1500	213.384	446.709	267.930	-1421.342	29.134
1600	213.384	459.646	289.488	-1414.985	26.048
1700	213.384	471.842	310.607	-1699.147	22.895
1800	213.384	483.379	331.945	-689.240	20.001
1900	213.384	494.325	353.284	-633.776	17.424
2000	213.384			-578.716	15.115

PREVIOUS:

CURRENT: December 1978

Lithium Sulfate, Beta ( $\text{Li}_2\text{SO}_4$ )

$\text{Li}_2\text{O}_4\text{S}_1(\text{cr})$

Lithium Sulfate (Li<sub>2</sub>SO<sub>4</sub>)

$$S^{\circ}(298.15 \text{ K}) = [154.332] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$T_{\text{fus}}(\beta \rightarrow \text{l}) = 1132 \pm 1 \text{ K}$$

## LIQUID

$$M_f = 109.9396$$

$$\Delta H^{\circ}(298.15 \text{ K}) = [-1399.296] \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_{\text{fus}} H^{\circ}(\beta \rightarrow \text{l}) = \pm 0.8 \text{ kJ} \cdot \text{mol}^{-1}$$

## Enthalpy of Formation

$\Delta_f H^{\circ}(\text{Li}_2\text{SO}_4, \text{l}, 298.15 \text{ K})$  is calculated from  $\Delta_f H^{\circ}(\text{Li}_2\text{SO}_4, \beta, 298.15 \text{ K})$  by adding the enthalpy of fusion,  $\Delta_{\text{fus}} H^{\circ}$ , and the difference in enthalpy,  $H^{\circ}(1132 \text{ K}) - H^{\circ}(298.15 \text{ K})$ , between the  $\beta$  crystal and liquid.

## Heat Capacity and Entropy

Enthalpies for Li<sub>2</sub>SO<sub>4</sub>(l) have been measured by Clark,<sup>2</sup> (1145–1179 K), by Voskresenskaya and Banashek,<sup>3</sup> (1133–1270 K), and by Denielou *et al.*,<sup>4</sup> (1138–1530 K). The data of Clark is systematically low by 15% while the other two studies<sup>3,4</sup> are in substantial agreement. We adopt enthalpies based on the work of Denielou *et al.*<sup>4</sup> We adopt a constant heat capacity of 49.00 cal·K<sup>-1</sup>·mol<sup>-1</sup> at temperatures above a hypothetical glass transition at 680 K. Below the glass transition, the heat capacity is taken as that of the alpha phase.  $S^{\circ}(298.15 \text{ K})$  is calculated in a manner analogous to that used for the enthalpy of formation.

## Fusion Data

Refer to the  $\beta$ -crystal table for details.

## Vaporization and Decomposition Data

Li<sub>2</sub>SO<sub>4</sub>(l) can vaporize to the gaseous monomer, Li<sub>2</sub>SO<sub>4</sub>(g), or decompose according to Li<sub>2</sub>SO<sub>4</sub>(l) = Li<sub>2</sub>O(cr) + SO<sub>2</sub>(g) + 1/2 O<sub>2</sub>(g) or according to Li<sub>2</sub>SO<sub>4</sub>(l) = 2 Li(g) + SO<sub>2</sub>(g) + O<sub>2</sub>(g). Ficalora *et al.*<sup>5</sup> did not observe ions from Li<sub>2</sub>O or Li<sub>2</sub>SO<sub>4</sub> in their effusion mass-spectrometric experiments, indicating decomposition occurs to the metal. They determined  $\Delta_{\text{vap}} H^{\circ}(1080 \text{ K}) = 324 \pm 12 \text{ kcal} \cdot \text{mol}^{-1}$ . This is in substantial agreement with JANAF thermodynamic data<sup>6</sup> which indicates  $\Delta_{\text{vap}} H^{\circ}(1080 \text{ K}) = 332.3 \text{ kcal} \cdot \text{mol}^{-1}$ . Effusion and transpiration results of Jagannathan and Wyatt<sup>6</sup> also indicate that decomposition to the oxide is less important than decomposition to the metal.  $T_{\text{decomp}} = \sim 2466 \text{ K}$  is the temperature at which the Gibbs energy change is zero for the reaction Li<sub>2</sub>SO<sub>4</sub>(l) = Li<sub>2</sub>O(l) + SO<sub>2</sub>(g) + 1/2 O<sub>2</sub>(g) and  $T_{\text{decomp}} = 2800 \text{ K}$  for the reaction Li<sub>2</sub>SO<sub>4</sub>(l) = 2 Li(g) + SO<sub>2</sub>(g) + O<sub>2</sub>(g).

## References

- <sup>1</sup>JANAF Thermochemical Tables: Li<sub>2</sub>SO<sub>4</sub>(cr,  $\beta$ ), 12–31–78.
- <sup>2</sup>R. P. Clark, *J. Chem. Eng. Data* **20**, 17 (1975).
- <sup>3</sup>N. K. Voskresenskaya and E. I. Banashek, *Izv. Sekti. Fiz. Khim. Anal., Akad. Nauk SSSR*, **25**, 150 (1974).
- <sup>4</sup>L. Denielou, Y. Fournier, J. P. Petitot, and C. Tequi, *Rev. Int. Hautes Temp.*, **8**, 119 (1971).
- <sup>5</sup>P. J. Ficalora, O. M. Uy, D. W. Muenow, and J. L. Mangrove, *J. Amer. Ceram. Soc.* **51**, 574 (1968).
- <sup>6</sup>G. V. Jagannathan and P. A. H. Wyatt, *J. Chem. Res. (M)* 2744 (1978).

Lithium Sulfate (Li<sub>2</sub>SO<sub>4</sub>)

T/K	C <sub>p</sub> <sup>a</sup>	S <sup>b</sup>	-(G <sup>c</sup> -H <sup>c</sup> (T))/T	H <sup>c</sup> -H <sup>c</sup> (T)	$\Delta_f H^{\circ}$	log K <sub>r</sub>
0				0.	-1399.296	-1296.080
100	117.608	154.332	154.332	0.	-1399.320	227.068
200	118.026	155.061	154.334	0.218	-1392.437	225.556
300	139.244	192.064	159.253	1.313	-1260.147	164.617
400	154.473	224.794	169.139	27.827	-1409.362	127.918
500	168.469	254.196	180.904	43.975	-1409.085	103.379
600	179.619	275.966	190.820	57.899	GLASS $\leftarrow$ LIQUID	
680 000	205.016	275.966	190.820	57.899	TRANSITION	
700	205.016	281.909	193.338	61.999	-1406.767	85.864
800	205.016	309.285	206.159	82.501	-1401.943	72.764
900	205.016	333.432	218.985	103.002	-1450.291	62.547
1000	205.016	355.033	231.579	123.504	-1444.342	54.146
1100	205.016	374.573	243.659	144.006	-1438.492	47.301
1132 000	205.016	380.452	247.443	150.566	---	---
1200	205.016	392.412	255.322	164.507	-1432.777	41.620
1300	205.016	408.822	266.507	185.009	-1427.039	36.832
1400	205.016	424.015	277.222	205.510	-1421.414	32.744
1500	205.016	438.160	287.485	226.012	-1415.844	29.216
1600	205.016	451.391	297.370	246.514	-1410.324	26.140
1700	205.016	463.820	306.752	267.015	-1404.853	22.996
1800	205.016	475.538	315.490	287.517	-1399.437	20.108
1900	205.016	486.623	324.508	308.018	-1394.071	17.534
2000	205.016	497.159	332.879	328.520	-1388.761	15.227
2100	205.016	507.142	340.941	349.022	-1383.503	13.149
2200	205.016	516.679	348.714	369.523	-1378.295	11.266
2300	205.016	525.792	356.216	390.025	-1373.140	9.555
2400	205.016	534.518	363.465	410.526	-1368.115	7.992
2500	205.016	542.887	370.476	431.028	-1363.210	6.560
2600	205.016	550.928	377.263	451.530	-1358.422	5.243
2700	205.016	558.665	383.839	472.031	-1353.748	4.029
2800	205.016	566.121	390.217	492.533	-1349.189	2.906
2900	205.016	573.315	396.407	513.034	-1344.736	1.864
3000	205.016	580.266	402.420	533.536	-1340.381	0.895

PREVIOUS:

CURRENT: December 1978

Lithium Sulfate (Li<sub>2</sub>SO<sub>4</sub>)Li<sub>2</sub>O<sub>4</sub>S<sub>4</sub>(l)

Lithium Sulfate (Li<sub>2</sub>SO<sub>4</sub>) *M<sub>r</sub>* = 109.9396 Lithium Sulfate (Li<sub>2</sub>SO<sub>4</sub>) Li<sub>2</sub>O<sub>2</sub>S<sub>1</sub>(cr,l)

T/K	C <sub>p</sub> <sup>o</sup>	Enthalpy Reference Temperature = T <sub>r</sub> = 298.15 K		Standard State Pressure = P <sup>o</sup> = 0.1 MPa		log K <sub>t</sub>
		S <sup>o</sup> - [G <sup>o</sup> - H <sup>o</sup> (T <sub>r</sub> )]/T	H <sup>o</sup> - H <sup>o</sup> (T <sub>r</sub> )	ΔH <sup>o</sup>	ΔG <sup>o</sup>	
0	0	INFINITE	-18.636	-1423.980	-1423.980	INFINITE
100	43.869	196.627	-16.769	-1429.603	-1395.114	728.733
200	86.872	23.028	-10.159	-1434.139	-1358.693	354.854
298.15	117.608	113.947	0	-1436.367	-1321.111	231.453
300	118.026	114.676	0.218	-1436.391	-1320.395	229.901
400	139.244	151.679	13.131	-1439.218	-1281.517	167.349
500	154.473	184.409	27.827	-1446.434	-1241.336	129.682
600	168.469	213.812	43.975	-1446.156	-1200.315	104.497
700	182.360	240.827	61.518	-1444.320	-1159.466	86.520
800	196.062	266.069	80.437	-1441.078	-1118.979	73.062
848.000	202.732	277.686	90.008	—	—	—
848.000	213.384	311.237	118.459	—	—	—
900	213.384	323.936	129.555	-1460.810	-1079.654	62.661
1000	213.384	346.418	150.894	-1454.024	-1037.668	54.202
1100	213.384	366.756	172.232	-1447.337	-996.357	47.313
1132.000	213.384	372.875	179.060	—	—	—
1132.000	205.016	380.452	187.638	—	—	—
1200	205.016	392.412	201.579	-1432.727	-956.149	41.620
1300	205.016	408.822	222.080	-1427.039	-916.665	36.832
1400	205.016	424.015	242.582	-1421.414	-877.617	32.744
1500	205.016	438.159	263.084	-1415.844	-838.970	29.216
1600	205.016	451.391	283.585	-1410.324	-800.691	26.140
1700	205.016	463.820	304.087	-1695.323	-748.405	22.996
1800	205.016	475.538	324.588	-1688.391	-692.905	20.108
1900	205.016	486.623	345.090	-1681.521	-637.788	17.534
2000	205.016	497.139	365.592	-1674.713	-583.031	15.227
2100	205.016	507.147	386.093	-1667.968	-528.613	13.149
2200	205.016	516.670	406.595	-1661.285	-474.513	11.266
2300	205.016	525.792	427.096	-1654.667	-420.718	9.555
2400	205.016	534.518	447.598	-1648.115	-367.210	7.992
2500	205.016	542.887	468.100	-1641.630	-313.972	6.560
2600	205.016	550.928	488.601	-1635.212	-260.993	5.243
2700	205.016	558.665	509.103	-1628.865	-208.258	4.029
2800	205.016	566.121	529.604	-1622.589	-155.758	2.906
2900	205.016	573.315	550.106	-1616.386	-103.482	1.864
3000	205.016	580.266	570.608	-1610.259	-51.417	0.895

0 to 848 K crystal, alpha  
848 to 1132 K crystal, beta  
above 1132 K liquid

Refer to the individual tables for details.

CRYSTAL(α-β)-LIQUID

Lithium Sulfate (Li<sub>2</sub>SO<sub>4</sub>)

PREVIOUS CURRENT: December 1978

Lithium Sulfate (Li<sub>2</sub>SO<sub>4</sub>) Li<sub>2</sub>O<sub>2</sub>S<sub>1</sub>(cr,l)

Lithium Sulfate (Li<sub>2</sub>SO<sub>4</sub>)

IDEAL GAS

$M_r = 109.9396$

Li<sub>2</sub>O<sub>4</sub>S<sub>1</sub>(g)

$S^\circ(298.15\text{ K}) = [322.820 \pm 41.8] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

$\Delta_f H^\circ(0\text{ K}) = [-1030.445 \pm 83.7] \text{ kJ}\cdot\text{mol}^{-1}$   
 $\Delta_f H^\circ(298.15\text{ K}) = [-1041.816 \pm 83.7] \text{ kJ}\cdot\text{mol}^{-1}$

Vibrational Frequencies, Symmetries, and Degeneracies	$\nu, \text{cm}^{-1}$	$B_1$	$B_2$	$E$
$A_1$	[1020](1)	[460](1)		[1115](2)
	[500](1)			[61](2)
	[380](1)			[410](2)
				[100](2)

Ground State Quantum Weight: [1]

Point Group: [D<sub>2h</sub>]

Bond Distances: S-O = [1.48] Å

Bond Angles: O-S-O = [109.47]°

Product of the Moments of Inertia:  $I_A I_B I_C = [1.210866 \times 10^{-113}] \text{ g}^3\cdot\text{cm}^6$

Enthalpy of Formation

Vaporization experiments on Li<sub>2</sub>SO<sub>4</sub> have been carried out by Ficalora *et al.*<sup>1</sup> by Vasilev and Dmitrievskaya,<sup>2</sup> (73–1223 K), and by Jagannathan and Wyatt,<sup>3</sup> (1227–1371 K). Ficalora *et al.*<sup>1</sup> did not observe the Li<sub>2</sub>SO<sub>4</sub> ion nor ions from Li<sub>2</sub>O in their Knudsen effusion mass-spectrometric experiments. Decomposition to Li(g) was the dominant process observed. Vasilev and Dmitrievskaya<sup>2</sup> carried out Langmuir method experiments on solid and liquid lithium sulfate. Their experimental pressures are less than JANAF calculated dissociation pressures from the two reactions Li<sub>2</sub>SO<sub>4</sub>(l) = Li<sub>2</sub>O(cr) + SO<sub>2</sub>(g) + 1/2 O<sub>2</sub>(g) and Li<sub>2</sub>SO<sub>4</sub>(l) = 2 Li(g) + SO<sub>2</sub>(g) + O<sub>2</sub>(g). We have discounted their results. Jagannathan and Wyatt<sup>3</sup> carried out Knudsen effusion weight-loss experiments and transpiration experiments (in N<sub>2</sub>) on molten lithium sulfate. Their transpiration experiments identified high lithium concentrations in the vapor, so that Li<sub>2</sub>O(cr) formation cannot be the major reaction. The effusion experiments yield apparent Li<sub>2</sub>SO<sub>4</sub>(g) pressures of the same order of magnitude as our calculated decomposition pressures to Li<sub>2</sub>O(cr). The data from  $\Delta_f H^\circ$  leads to  $\Delta_f H^\circ(1300\text{ K}) = 58 \pm 20 \text{ kcal mol}^{-1}$  for molecular vaporization. When this result is combined with auxiliary JANAF data,<sup>4</sup> we obtain  $\Delta_f H^\circ(\text{Li}_2\text{SO}_4, \text{g}, 298.15\text{ K}) = -266 \pm 20 \text{ kcal mol}^{-1}$ .

From trends in the enthalpies and entropies of sublimation for the other alkali sulfates<sup>5</sup> we would estimate  $\Delta_f H^\circ(1200\text{ K}) = 75 \pm 15 \text{ kcal mol}^{-1}$  and  $\Delta_f S^\circ(1200\text{ K}) = 35 \pm 5 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for Li<sub>2</sub>SO<sub>4</sub>(l) = Li<sub>2</sub>SO<sub>4</sub>(g). This estimate leads to  $\Delta_f H^\circ(\text{Li}_2\text{SO}_4, \text{g}, 298.15\text{ K}) = -249 \pm 28 \text{ kcal mol}^{-1}$ . We adopt this estimate for this tabulation.

Heat Capacity and Entropy

The adopted structure (D<sub>2h</sub> symmetry) is based on the similar symmetry assigned to Cs<sub>2</sub>SO<sub>4</sub>(g) and K<sub>2</sub>SO<sub>4</sub>(g) in the high-temperature electron diffraction studies of Ugarov *et al.*<sup>6</sup> and Spiridonov and Lutoshkin.<sup>6</sup> The internuclear distance of 1.48 Å for S-O is taken from data on other sulfates<sup>7</sup> while Li-O = 1.90 Å is an estimate based on trends among lithium and sodium compounds. The Li-O distance of 1.96 Å found by Alcock *et al.*<sup>8</sup> seems a bit long. The principal moments of inertia are  $I_A = 15.5185 \times 10^{-39} \text{ g cm}^2$  and  $I_B = I_C = 27.9333 \times 10^{-39} \text{ g cm}^2$ .

Estimates of the eleven fundamental frequencies of Li<sub>2</sub>SO<sub>4</sub> are based on comparisons with Na<sub>2</sub>SO<sub>4</sub>(g) and K<sub>2</sub>SO<sub>4</sub>(g),<sup>7</sup> data on crystalline Li<sub>2</sub>SO<sub>4</sub>,<sup>9</sup> and on a normal coordinate analysis of Devlin.<sup>10</sup> Uncertainties in the estimates of the molecular constants and gas-phase frequencies may contribute 10 cal·K<sup>-1</sup>·mol<sup>-1</sup> to S<sup>o</sup>(298.15 K).

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T/K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup>	H <sup>o</sup> - H <sup>o</sup> (T)	ΔH <sup>o</sup>	log K <sub>1</sub>
0	0	0	INFINITE	-1030.445	INFINITE
100	51.737	242.404	-19.652	-1030.445	533.133
200	79.551	286.652	-18.903	-1030.445	562.654
250	91.859	305.764	-4.670	-1030.445	208.367
298.15	101.804	322.820	0	-1041.816	173.240
300	102.151	323.451	0.189	-988.835	172.114
350	110.669	339.858	5.516	-1043.869	988.506
400	117.688	355.110	11.231	-1046.568	146.183
450	123.463	369.316	17.264	-1048.340	126.700
500	128.218	382.578	23.560	-1056.150	111.504
600	135.407	405.607	36.763	-1058.817	99.260
700	140.417	427.903	50.569	-1062.718	928.688
800	143.997	446.899	64.799	-1062.165	67.688
900	146.631	464.019	79.337	-1116.077	884.730
1000	148.389	479.574	94.102	-1116.264	40.994
1100	150.099	493.810	109.040	-1115.979	43.515
1200	151.278	506.922	124.111	-1115.644	38.215
1300	152.216	519.070	139.287	-1115.281	33.799
1400	152.972	530.379	154.548	-1114.897	30.064
1500	153.591	540.954	169.877	-1114.499	26.864
1600	154.102	550.884	185.262	-1114.095	24.091
1700	154.530	560.239	200.695	-1404.164	21.666
1800	154.893	569.083	216.166	-1402.261	19.086
1900	155.199	577.466	231.671	-1400.388	16.691
2000	155.463	585.433	247.205	-1398.549	14.345
2100	155.692	593.024	262.763	-1396.747	12.627
2200	155.891	600.271	278.340	-1394.987	10.888
2300	156.065	607.205	293.927	-1393.273	9.310
2400	156.218	613.850	309.554	-1391.607	7.871
2500	156.354	620.230	325.183	-1389.995	6.552
2600	156.474	626.365	340.825	-1388.439	5.342
2700	156.582	632.272	356.477	-1386.939	4.226
2800	156.678	637.969	372.141	-1385.501	3.194
2900	156.765	643.468	387.814	-1384.128	2.236
3000	156.843	648.784	403.493	-1382.826	1.345
3100	156.915	653.928	419.181	-1381.586	0.514
3200	156.979	658.911	434.876	-1380.422	0.262
3300	157.038	663.742	450.577	-1379.331	0.989
3400	157.092	668.431	466.283	-1378.312	1.672
3500	157.141	672.986	481.995	-1377.367	2.314
3600	157.186	677.413	497.711	-1376.508	2.919
3700	157.228	681.721	513.425	-1375.725	3.489
3800	157.266	685.914	529.137	-1375.017	4.029
3900	157.302	690.000	544.885	-1374.374	4.540
4000	157.335	693.983	560.617	-1373.798	5.025
4100	157.366	697.868	576.352	-1373.254	5.485
4200	157.394	701.660	592.090	-1372.736	5.922
4300	157.421	705.364	607.831	-1372.241	6.339
4400	157.445	708.984	623.574	-1371.765	6.736
4500	157.468	712.522	639.320	-1371.313	7.115
4600	157.490	715.983	655.068	-1370.884	7.477
4700	157.510	719.371	670.818	-1370.476	7.824
4800	157.529	722.687	686.570	-1370.092	8.155
4900	157.547	725.935	702.324	-1369.731	8.473
5000	157.564	729.118	718.079	-1369.394	8.778
5100	157.580	732.239	733.837	-1369.082	9.071
5200	157.595	735.299	749.595	-1368.793	9.353
5300	157.609	738.301	765.356	-1368.528	9.624
5400	157.622	741.247	781.117	-1368.287	9.885
5500	157.635	744.139	796.880	-1368.062	10.138
5600	157.647	746.980	812.644	-1367.852	10.378
5700	157.658	749.770	828.409	-1367.657	10.612
5800	157.669	752.512	844.176	-1367.476	10.838
5900	157.679	755.207	859.943	-1367.309	11.057
6000	157.689	757.858	875.712	-1367.156	11.268

PREVIOUS December 1978 (1 atm)

CURRENT December 1978 (1 bar)

Lithium Sulfate (Li<sub>2</sub>SO<sub>4</sub>)

Li<sub>2</sub>O<sub>4</sub>S<sub>1</sub>(g)

Lithium Silicate (Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>)

CRYSTAL (I-II)

Lithium Silicate (Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>)

Li<sub>2</sub>O<sub>3</sub>Si<sub>2</sub>(cr)

$\Delta_f H^\circ(298.15 \text{ K}) = [125.520] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$   
 $T_m = 1209 \text{ K}$   
 $T_{fus} = 1307 \pm 1 \text{ K}$   
 $\Delta_f H^\circ(0 \text{ K}) = \text{Unknown}$   
 $\Delta_f H^\circ(298.15 \text{ K}) = -2560.90 \pm 4.2 \text{ kJ} \cdot \text{mol}^{-1}$   
 $\Delta_{sub} H^\circ = 0.941 \text{ kJ} \cdot \text{mol}^{-1}$   
 $\Delta_{sub} H^\circ = [53.806] \text{ kJ} \cdot \text{mol}^{-1}$

Enthalpy of Formation

The enthalpies of solution of LiCl(cr), Li<sub>2</sub>SO<sub>4</sub>(cr), SiO<sub>2</sub>(quartz) and Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(cr) in 20 per cent hydrofluoric acid at 74.7°C were measured by Kracek.<sup>1</sup> The authors derived two values of  $\Delta_{sub} H^\circ$  of Li<sub>2</sub>O(cr) from those of LiCl(cr) and Li<sub>2</sub>SO<sub>4</sub>(cr), presumably employing auxiliary data from.<sup>2</sup> We recalculate  $\Delta_{sub} H^\circ$  of Li<sub>2</sub>O(cr) as -58.74 (chloride scheme, originally -59.36) and -59.83 kcal mol<sup>-1</sup> (sulfate scheme, originally -60.86), using recent  $\Delta_f H^\circ(298.15 \text{ K})$  values for LiCl(cr), Li<sub>2</sub>SO<sub>4</sub>(cr), HCl(aq), H<sub>2</sub>SO<sub>4</sub>(aq), and Li<sub>2</sub>O(cr). The corresponding enthalpy changes,  $\Delta_f H^\circ(298.15 \text{ K})$ , for the reaction Li<sub>2</sub>O(cr) + 2SiO<sub>2</sub>(quartz) = Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(cr) are derived as -33.21 and -34.30 kcal mol<sup>-1</sup>. Adopting the weighted average  $\Delta_f H^\circ(298.15 \text{ K}) = -33.57 \text{ kcal} \cdot \text{mol}^{-1}$  with  $\Delta_f H^\circ(\text{Li}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -143.1 \text{ kcal} \cdot \text{mol}^{-1}$  and  $\Delta_f H^\circ(\text{SiO}_2, \text{quartz}, 298.15 \text{ K}) = -217.7 \text{ kcal} \cdot \text{mol}^{-1}$ , we obtain  $\Delta_f H^\circ(298.15 \text{ K}) = -612.07 \text{ kcal} \cdot \text{mol}^{-1}$  for Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(cr). This value is independent of future changes in  $\Delta_f H^\circ(298.15 \text{ K})$  of Li<sub>2</sub>O(cr) but the values of  $\Delta_{sub} H^\circ$  and  $\Delta_f H^\circ$  are not independent.

The enthalpies of solution of LiOH(cr) and Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(cr) in 20 per cent HF(aq) at 50°C were measured by Hatton *et al.*<sup>3</sup> By use of a reaction scheme similar to that described on the Li<sub>2</sub>SiO<sub>3</sub>(cr) table, the enthalpy change at 298.15 K for the reaction 2LiOH(cr) + 2SiO<sub>2</sub>(cr) → Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(cr) + H<sub>2</sub>O(l) was calculated to be -13.44 kcal mol<sup>-1</sup>. Incorporating this value with  $\Delta_f H^\circ(298.15 \text{ K}) = -115.84$ , -217.7 and -68.315 kcal mol<sup>-1</sup> for LiOH(cr), SiO<sub>2</sub>(cr), and H<sub>2</sub>O(l), respectively, we obtain  $\Delta_f H^\circ(\text{Li}_2\text{Si}_2\text{O}_5, \text{cr}, 298.15 \text{ K}) = -612.20 \pm 2.0 \text{ kcal} \cdot \text{mol}^{-1}$ , which is in excellent agreement with the adopted value.

Heat Capacity and Entropy

Both heat capacities and  $S^\circ(298.15 \text{ K})$  are estimated by comparison with those for Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(cr), Na<sub>2</sub>O(cr) and Li<sub>2</sub>O(cr).

Transition Data

The transition temperature,  $T_m = 1209 \text{ K}$ , is taken from Kracek.<sup>4</sup> The author estimated an enthalpy of transition of 1 to 2 cal·K<sup>-1</sup>·mol<sup>-1</sup> based on the arrest in the cooling and heating curves. The value of  $\Delta_{tr} H^\circ$  is calculated assuming the enthalpy of transition at 1209 K is 1.5 cal·K<sup>-1</sup>·mol<sup>-1</sup>.

Fusion Data

Incongruent melting of Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(cr) at 1033°C has been reported by Kracek<sup>5</sup> and Kracek.<sup>4</sup> The liquidus temperature of 1034°C at the composition 19.92 per cent Li<sub>2</sub>O and 80.08 per cent SiO<sub>2</sub> is reported by Kracek,<sup>4</sup> is adopted as  $T_m$ . The enthalpy of melting is evaluated such that  $\Delta_{tr} H^\circ(298.15 \text{ K}) + \Delta_{sub} H^\circ(298.15 \text{ K}) = 11.43 \text{ kcal} \cdot \text{mol}^{-1}$ , where the value 11.43 kcal·mol<sup>-1</sup> is the difference between  $\Delta_f H^\circ(298.15 \text{ K})$  for Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(cr) and Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(l). The latter were determined by solution calorimetry by Kracek (refer to the Enthalpy of Formation sections in crystal and liquid tables).

References

- <sup>1</sup>R. C. Kracek, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 69 (1953).
- <sup>2</sup>U. S. Nat. Bur. Stand. Circ. 500, (1952).
- <sup>3</sup>W. E. Hatton, G. C. Sinke, D. L. Hildenbrand, and D. R. Stull, The Dow Chemical Co., Midland, Michigan, (1959).
- <sup>4</sup>F. C. Kracek, J. Amer. Chem. Soc. 61, 2863 (1939).
- <sup>5</sup>F. C. Kracek, J. Phys. Chem. 34, 2641 (1930).

T/K	C <sub>p</sub> <sup>o</sup>	Enthalpy Reference Temperature = T, = 298.15 K		Standard State Pressure = P <sup>o</sup> = 0.1 MPa		log K <sub>i</sub>
		S <sup>o</sup> - [G <sup>o</sup> - F(T)]/T	H <sup>o</sup> - H <sup>o</sup> (T)	Δ <sub>f</sub> H <sup>o</sup>	Δ <sub>f</sub> G <sup>o</sup>	
0						
100						
200						
298.15	138.072	125.520	0	-2560.901	-2416.848	423.422
300	136.909	125.523	0.256	-2560.946	-2415.954	420.655
400	174.891	131.457	16.098	-2561.976	-2367.401	509.151
500	192.673	143.694	34.516	-2567.627	-2318.171	642.178
600	205.685	158.287	54.466	-2566.295	-2268.388	797.481
700	214.890	173.613	75.507	-2564.136	-2218.898	965.576
800	222.589	188.951	97.387	-2561.408	-2169.759	1141.671
900	229.492	203.978	120.000	-2558.215	-2120.990	1323.099
1000	235.350	218.552	143.248	-2554.617	-2072.599	1508.261
1100	240.617	232.618	167.052	-2550.660	-2024.585	1694.140
1200	245.182	246.164	191.347	-2546.385	-1976.947	1880.054
1209.000	245.539	247.358	193.556			
1209.000	245.539	247.358	194.497			
1300	248.195	259.253	216.960	-2540.956	-1929.746	2175.38
1307.000	248.417	260.150	218.698			
1400	251.207	271.841	241.929	-2536.318	-1882.902	2502.52
1500	254.868	283.949	267.239	-2531.474	-1836.398	3039.49
1600	257.734	295.606	292.876	-2526.436	-1790.223	3844.45
1700	259.617	306.839	318.747	-2521.119	-1729.121	5312.9
1800	261.082	317.672	344.786	-2515.970	-1659.740	7816.64
1900	262.075	328.129	370.946	-2510.956	-1590.756	10816.33
2000	262.755	338.230	397.190	-2506.030	-1522.153	14816.755
2100	263.078	347.995	423.477	-2501.283	-1453.912	19816.164
2200	263.174	357.441	449.785	-2496.685	-1386.012	25816.908
2300	263.341	366.581	476.111	-2489.131	-1318.430	32816.433
2400	263.480	375.447	502.452	-2481.964	-1251.174	40816.231
2500	263.592	384.038	528.806	-2475.934	-1184.202	49816.243

PREVIOUS

CURRENT June 1967

Lithium Silicate (Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>)

Li<sub>2</sub>O<sub>3</sub>Si<sub>2</sub>(cr)

Lithium Silicate ( $\text{Li}_2\text{Si}_2\text{O}_5$ )

## LIQUID

 $M_r = 150.0500$  $\text{Li}_2\text{O}_3\text{Si}_2(\text{l})$ 

$$S^\circ(298.15 \text{ K}) = [160.243] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$T_{\text{fus}} = 1307 \pm 1 \text{ K}$$

$$\Delta H_f^\circ(298.15 \text{ K}) = [-2513.068] \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{fus}}H^\circ = [53.806] \text{ kJ}\cdot\text{mol}^{-1}$$

## Enthalpy of Formation

The enthalpies of solution of  $\text{LiCl}(\text{cr})$ ,  $\text{Li}_2\text{SO}_4(\text{cr})$ ,  $\text{SiO}_2(\text{quartz})$  and  $\text{Li}_2\text{Si}_2\text{O}_5(\text{gl})$  in 20 per cent hydrofluoric acid at 74 °C were measured by Kracek.<sup>1</sup> Following the same procedure as described in  $\text{Li}_2\text{Si}_2\text{O}_5(\text{cr})$  table, we derived the enthalpy changes,  $\Delta H_f^\circ(298.15 \text{ K})$ , for the reaction  $\text{Li}_2\text{O}(\text{cr}) + 2\text{SiO}_2(\text{quartz}) = \text{Li}_2\text{Si}_2\text{O}_5(\text{gl})$  as  $-21.78$  and  $-22.87$  kcal mol<sup>-1</sup>. Adopting the weighted average  $\Delta H_f^\circ(298.15 \text{ K}) = -22.14$  kcal mol<sup>-1</sup> with  $\Delta H_f^\circ(\text{Li}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -143.1$  kcal mol<sup>-1</sup> and  $\Delta H_f^\circ(\text{SiO}_2, \text{quartz}, 298.15 \text{ K}) = -217.7$  kcal mol<sup>-1</sup>, we obtain  $\Delta H_f^\circ(298.15 \text{ K}) = -600.640$  kcal mol<sup>-1</sup> for  $\text{Li}_2\text{Si}_2\text{O}_5(\text{gl})$ . This  $\Delta H_f^\circ(\text{Li}_2\text{Si}_2\text{O}_5, \text{gl}, 298.15 \text{ K})$  value is independent of future changes in  $\Delta H_f^\circ(298.15 \text{ K})$  of  $\text{Li}_2\text{O}(\text{cr})$  but the values of  $\Delta_{\text{fus}}H^\circ$  and  $\Delta_fH^\circ$  are not independent.

## Heat Capacity and Entropy

The heat capacity is estimated by comparison with those for  $\text{Na}_2\text{Si}_2\text{O}_5(\text{l})$ ,  $\text{Na}_2\text{SiO}_4(\text{l})$  and  $\text{Li}_2\text{SiO}_4(\text{l})$ . A glass transition temperature at 800 K is assumed, i.e. the heat capacities below 800 K are taken from those for  $\text{Li}_2\text{Si}_2\text{O}_5(\text{cr})$  and above 800 K are assumed to be constant.

$S^\circ(\text{Li}_2\text{Si}_2\text{O}_5, \text{l}, 298.15 \text{ K})$  is calculated from  $S^\circ(\text{Li}_2\text{Si}_2\text{O}_5, \text{cr}, 298.15 \text{ K})$  by adding the entropy of fusion,  $\Delta_{\text{fus}}S^\circ(1307 \text{ K})$ , and the difference in entropy,  $S^\circ(1307 \text{ K}) - S^\circ(298.15 \text{ K})$ , between the crystal and liquid.

## Fusion Data

Refer to the crystal table for details.

## References

<sup>1</sup>F. C. Kracek, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 69, (1953).

T/K	$C_p^\circ$	$S^\circ$	$-[G^\circ - H^\circ(T)]/T$	$H^\circ - H^\circ(T)$	$\Delta_fH^\circ$	$\Delta_fG^\circ$	log K <sub>f</sub>
Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$							
Standard State Pressure = $p^\circ = 0.1 \text{ MPa}$							
kJ·mol <sup>-1</sup>							
0				0.	-2513.068	-2379.367	416.855
100	138.072	160.243	160.243	0.256	-2513.113	-2378.537	414.140
200	138.909	161.099	160.245	0.256	-2513.143	-2378.537	414.140
298.15	174.891	206.424	166.179	16.098	-2514.143	-2333.457	304.718
300	192.673	247.448	178.417	34.516	-2519.794	-2287.699	238.994
400	205.685	283.785	193.009	54.466	-2518.462	-2241.388	195.130
500	214.890	316.202	208.335	75.507	-2516.303	-2195.371	163.821
600	222.589	345.416	223.674	97.393	-2513.569	-2149.704	140.361
800.000	222.589	345.416	223.674	97.393	GLASS <---> LIQUID	TRANSITION	
800.000	251.040	374.984	238.876	122.497	-2507.885	-2104.565	122.146
900	251.040	401.434	253.833	147.601	-2502.430	-2060.046	107.606
1000	251.040	425.361	268.356	172.705	-2497.173	-2016.063	95.735
1100	251.040	447.704	282.363	197.809	-2492.090	-1972.552	83.865
1200	251.040	467.298	295.826	222.913	-2487.169	-1929.438	72.527
1307.000	251.040	468.646	296.748	224.671	GLASS <---> LIQUID	TRANSITION	
1400	251.040	485.902	308.747	248.017	-2482.396	-1886.737	70.395
1500	251.040	503.222	321.141	273.121	-2477.759	-1844.353	64.226
1600	251.040	519.424	333.033	298.225	-2473.253	-1802.273	58.838
1700	251.040	534.643	344.449	323.329	-2468.904	-1761.276	53.624
1800	251.040	548.992	355.418	348.433	-2464.689	-1720.849	48.746
1900	251.040	562.565	365.966	373.537	-2460.578	-1681.414	44.304
2000	251.040	575.442	376.121	398.641	-2456.545	-1642.425	40.485
2100	251.040	587.690	385.906	423.745	-2452.578	-1603.959	36.955
2200	251.040	599.368	395.346	448.849	-2448.669	-1565.994	33.752
2300	251.040	610.527	404.461	473.953	-2444.817	-1528.526	30.833
2400	251.040	621.212	413.271	499.057	-2441.012	-1491.549	28.166
2500	251.040	631.460	421.795	524.161	-2437.353	-1455.063	25.715
2600	251.040	641.306	430.050	549.265	-2433.837	-1419.163	23.458
2700	251.040	650.780	438.050	574.369	-2430.453	-1383.847	21.372
2800	251.040	659.910	445.812	599.473	-2427.201	-1349.111	19.439
2900	251.040	668.719	453.347	624.577	-2424.071	-1314.952	17.643
3000	251.040	677.230	460.669	649.681	-2421.053	-1281.363	15.970

PREVIOUS:

CURRENT: June 1967

Lithium Silicate ( $\text{Li}_2\text{Si}_2\text{O}_5$ ) $\text{Li}_2\text{O}_3\text{Si}_2(\text{l})$



Lithium Silicate (Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>)

M<sub>r</sub> = 150.0500 Lithium Silicate (Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>)

Li<sub>2</sub>O<sub>3</sub>Si<sub>2</sub>(cr,l)

0 to 1209 K crystal, I  
1209 to 1307 K crystal, II  
above 1307 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T <sub>r</sub> = 298.15 K		Standard State Pressure = p° = 0.1 MPa			
T/K	C <sub>p</sub> <sup>o</sup> J·K <sup>-1</sup> ·mol <sup>-1</sup>	S <sup>o</sup> - [G° - H°(T <sub>r</sub> )]/T J·K <sup>-1</sup> ·mol <sup>-1</sup>	H° - H°(T <sub>r</sub> ) kJ·mol <sup>-1</sup>	Δ <sub>f</sub> G° kJ·mol <sup>-1</sup>	log K <sub>f</sub>
0			0.		
100					
200					
298.15	138.072	125.520	125.520	-2560.901	-2416.848
300	138.909	126.377	125.523	-2560.946	-2415.954
400	174.891	171.701	131.457	-2561.976	-2367.401
500	192.673	212.726	143.694	-2567.627	-2318.171
600	205.685	249.062	158.287	-2566.295	-2268.388
700	214.890	281.479	173.613	-2564.136	-2218.898
800	222.589	310.685	188.951	-2561.408	-2169.759
900	229.492	337.312	203.978	-2558.215	-2120.990
1000	235.350	361.800	218.552	-2554.617	-2072.599
1100	240.617	384.483	232.618	-2550.660	-2024.585
1200	245.182	405.621	246.164	-2546.385	-1976.947
1209.000	245.559	407.454	247.358		
1209.000	245.559	408.233	247.358		
1300	248.195	426.145	259.253	-2540.956	-1979.746
1307.000	248.417	427.478	260.150		
1307.000	251.040	468.646	260.150		
1400	251.040	485.902	274.580	-2482.396	-1886.737
1500	251.040	503.222	289.252	-2477.759	-1844.353
1600	251.040	519.424	303.137	-2473.253	-1802.273
1700	251.040	534.643	316.312	-2469.704	-1761.226
1800	251.040	548.992	328.844	-2467.267	-1721.849
1900	251.040	562.565	340.791	-2465.841	-1684.814
2000	251.040	575.442	352.204	-2465.425	-1650.102
2100	251.040	587.690	363.129	-2465.217	-1627.694
2200	251.040	599.368	373.603	-2465.253	-1615.569
2300	251.040	610.527	383.664	-2465.566	-1603.717
2400	251.040	621.212	393.341	-2466.091	-1592.119
2500	251.040	631.460	402.662	-2466.811	-1580.763
2600	251.040	641.306	411.652	-2467.699	-1570.635
2700	251.040	650.780	420.334	-2468.700	-1561.724
2800	251.040	659.910	428.739	-2469.865	-1554.020
2900	251.040	668.719	436.853	-2471.141	-1547.515
3000	251.040	677.230	444.725	-2472.515	-1542.194
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Lithium Nitride (Li<sub>3</sub>N)

## CRYSTAL

 $M_r = 34.8297$ Li<sub>3</sub>N<sub>1</sub>(cr)

$S^\circ(298.15 \text{ K}) = 62.593 \pm 0.13 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$   
 $T_m = 1086 \text{ K}$   
 $\Delta_f H^\circ(0 \text{ K}) = -157.57 \pm 1.3 \text{ kJ}\cdot\text{mol}^{-1}$   
 $\Delta_f H^\circ(298.15 \text{ K}) = -164.56 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$

## Enthalpy of Formation

The adopted enthalpy of formation for Li<sub>3</sub>N(cr) is derived from the solution calorimetric study of O'Hare and Johnson.<sup>1</sup> The reported values have been revised by Osborne and Flotow<sup>2</sup> to correct for the current atomic weight of lithium to give  $\Delta_f H^\circ(298.15 \text{ K}) = -39.33 \pm 0.26 \text{ kcal}\cdot\text{mol}^{-1}$ . This uncertainty is derived from the experimental studies.

Previous studies on the measurement of the enthalpy of reaction of lithium with nitrogen<sup>4</sup> and the enthalpy of solution of Li<sub>3</sub>N in water<sup>3</sup> are currently thought to be less reliable.<sup>1</sup> Both these studies<sup>3,4</sup> yielded  $\Delta_f H^\circ(298.15 \text{ K})$  values of approximately 47 kcal/circal·mol<sup>-1</sup>. Yonco *et al.*<sup>5</sup> studied the solubility of nitrogen in liquid lithium (468–714 K) and the equilibrium pressure of nitrogen over solid Li<sub>3</sub>N (933–1051 K). A 2nd and 3rd law analysis of their reported  $\Delta_f G^\circ(T)$  values supports our adopted  $S^\circ(298.15 \text{ K})$  value, to within 0.1 cal·K<sup>-1</sup>·mol<sup>-1</sup>, but suggests a 3rd law  $\Delta_f H^\circ(298.15 \text{ K})$  value which is more positive by roughly 1.5 kcal·mol<sup>-1</sup> than our adopted value. Enthalpy measurements (823–973 K) of Bonomi *et al.*<sup>6</sup> gave  $\Delta_f G^\circ(T)$  values which are also more positive than our adopted values by roughly 2 kcal·mol<sup>-1</sup> at 900 K. These are suspect since Li<sub>3</sub>N<sub>2</sub>Cl<sub>2</sub> may be involved in the reaction.<sup>6</sup> A 2nd and 3rd law analysis of this latter data suggests a  $S^\circ(298.15 \text{ K})$  value which is 1.8 cal·K<sup>-1</sup>·mol<sup>-1</sup> smaller than our adopted value and a 3rd law  $\Delta_f H^\circ(298.15 \text{ K})$  value which is more positive by 2 kcal·mol<sup>-1</sup> than our adopted value. The  $S^\circ(298.15 \text{ K})$  discrepancy is very difficult to reconcile without an unreasonable change in the heat capacity values.

## Heat Capacity and Entropy

The thermal functions adopted are those tabulated by Osborne and Flotow.<sup>2</sup> These authors determined the heat capacity of a well characterized sample of Li<sub>3</sub>N between 5 and 350 K. They used the results of Satoh,<sup>7</sup> ice calorimetric data from 273 to 773 K, to extend the heat capacity results to 773 K and then extrapolate to 1086 K, the melting point of Li<sub>3</sub>N.<sup>15</sup>

As a check, the low temperature experimental heat capacity values are smoothed by fitting the data with orthogonal polynomials over selected overlapping temperature intervals. This fitting procedure gave an  $S^\circ(298.15 \text{ K})$  identical to that reported by Osborne and Flotow.<sup>2</sup> The ice calorimetric data of Satoh<sup>7</sup> are not extensive enough to reliably define the entire heat capacity dependence from 350 to 1086 K, however the three data points at 373 K, 578 K, and 773 K are sufficient to define a reasonable temperature dependence.

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T/K	Enthalpy Reference Temperature = T <sub>r</sub> = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K <sub>r</sub>
	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> - (G° - H°(T <sub>r</sub> ))/T <sub>r</sub>	H° - H°(T <sub>r</sub> )	Δ <sub>f</sub> H°	
0	0	INFINITE	-11.212	-157.567	INFINITE
100	22.204	10.114	-10.488	-150.597	76.664
200	55.417	36.403	-6.503	-140.160	36.606
298.15	75.266	62.593	0	-164.537	22.537
300	75.544	63.059	0.139	-164.581	22.359
400	87.100	86.504	8.316	-116.192	15.173
500	96.940	107.004	17.521	-102.781	10.737
600	106.430	125.522	27.693	-88.148	7.674
700	115.580	142.620	38.706	-73.556	5.489
800	124.380	158.632	50.707	-59.146	3.862
900	132.840	173.773	63.661	-45.008	2.612
1000	140.950	188.192	77.353	-31.203	1.650
1100	148.693	201.995	91.841	-17.779	0.844
1200	156.108	215.253	107.084	-4.769	0.208
1300	163.177	228.030	123.051	7.799	-0.313

PREVIOUS: September 1966

CURRENT: March 1978

Lithium Nitride (Li<sub>3</sub>N)Li<sub>3</sub>N<sub>1</sub>(cr)

## Lithium

## Continued from page 1497

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## Continuation of discussions of selected Li species

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