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Thermodynamic Properties of Two Lithium Silicates (Li_2SiO_3 and $Li_2Si_2O_5$)

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8187

Thermodynamic Properties of Two Lithium Silicates (Li_2SiO_3 and $Li_2Si_2O_5$)

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THERMODYNAMIC PROPERTIES OF TWO LITHIUM SILICATES (Li_2SiO_3 AND $Li_2Si_2O_5$)

by

K. O. Bennington,[1] M. J. Ferrante,[1] and J. M. Stuve[1]

ABSTRACT

Thermodynamic properties were determined by the Federal Bureau of Mines for lithium metasilicate (Li_2SiO_3) and lithium disilicate ($Li_2Si_2O_5$). Their enthalpies of formation were investigated by hydrofluoric acid solution calorimetry. The standard values are

$$\Delta Hf^\circ_{298} = -393.8 \pm 0.8 \text{ kcal/mole for } Li_2SiO_3,$$

and

$$\Delta Hf^\circ_{298} = -611.8 \pm 1.0 \text{ kcal/mole for } Li_2Si_2O_5.$$

Enthalpy increments above 298 K were measured by copper-block drop calorimetry from 298 to 1,404 K for Li_2SiO_3, and from 298 to 1,281 K for $Li_2Si_2O_5$. Low-temperature heat capacities were determined adiabatically from 6 to 305 K for $Li_2Si_2O_5$ only. The derived standard entropy is S°_{298} = 29.20 ± 0.10 cal/deg-mole.

The various experimental data were combined with other data from the literature, and resulting properties of ΔHf°, ΔGf°, and log Kf were tabulated as a function of temperature.

INTRODUCTION

This investigation of the thermodynamic properties of synthetic lithium metasilicates and dissilicates is one of a series on lithium minerals. The enthalpies of formation, low-temperature heat capacities, and high-temperature enthalpies of minerals in the Li_2O-Al_2O_3-SiO_3 system (13-14),[2] eucryptite ($LiAlSiO_4$), and spodumene ($LiAlSi_2O_6$) have been reported by this laboratory (1, 12). Reports on data for natural petalite ($LiAlSi_4O_{10}$) and lepidolite ($KLi_2AlSi_4O_{10}(OH,F)_2$) are planned.

There are no values reported in the literature for the low-temperature heat capacity of lithium disilicate or for the high-temperature enthalpy for either of the two lithium compounds. Values for the heats of formation

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[1] Research chemist.

[2] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

determined by Kracek (2) were listed in an annual report of the Geophysical Laboratory.

The two synthetic lithium silicates used in this study also appear in the Na_2O-Li_2O-SiO_2 system (10). The information gained from this investigation contributes to the knowledge of equilibrium at low temperature and has applications in the fields of extractive metallurgy, ceramics, and geochemistry.

MATERIALS

Lithium Metasilicate (Li_2SiO_3)

Lithium metasilicate was prepared by heating a stoichoimetric mixture of the reagent-grade compounds lithium carbonate and silicic acid. The mixture was heated in a nickel crucible for 8 days at 700° C, for 3 days at 800° C, and for 4 days at 900° C. Finally, the material was heated in a platinum crucible for 8 days at 1,100° C. The product was ground and screened after each heating, and analyses and composition adjustments were made. Final analysis gave 66.76 pct SiO_2 and 33.11 pct Li_2O, compared with the theoretical 66.79 pct SiO_2 and 33.21 pct Li_2O. The X-ray diffraction pattern agreed with that in the ASTM card catalog. No calorimetric corrections were made for the slight compositional deficiencies.

Lithium Disilicate ($Li_2Si_2O_5$)

The disilicate was synthesized in a manner similar to that used for the metasilicate. The proper mixture was heated in a nickel crucible for 5 days from 800° to 900° C, and for 9 days at 970° C. Finally, the mixture was heated in a platinum container for 36 hours at 1,000° C. The preparation was ground, screened, mixed, and analyzed several times during the preparation procedure. Adjustments in composition were made as necessary. Analysis for the final sample showed 80.00 pct SiO_2 and 19.95 pct Li_2O, compared with the theoretical 80.09 pct SiO_2 and 19.91 pct Li_2O. The X-ray diffraction pattern was the same as the one given in the ASTM file. The sample was considered pure for calorimetric purposes.

Other Substances

The quartz used in the investigation was from a single, clear crystal.[3] The material, reduced by grinding in an agate mortar to a particle size ranging between 10 and 20 micrometers, was segregated for use by water sedimentation. Aluminum and titanium were found spectroscopically to be present but in amounts too small for compositional corrections. The sample for each solution determination was heated through the α-β transition immediately prior to use.

The remaining materials--hydrochloric acid solutions, hydrofluoric-hydrochloric acid solvent, and lithium chloride--were of reagent-grade quality. The acids required no special treatment other than dilution with distilled

[3] The quartz specimen was provided by Edwin Roedder, U.S.Geological Survey, Washington, D. C.

water to the proper strength. The lithium chloride was heated to 450° C to constant weight before use.

ENTHALPIES OF FORMATION

The enthalpies of formation were determined by hydrofluoric acid calorimetry. The apparatus used was one described earlier (9, 17), with a few alterations. The platinum-rhodium solution vessel was suspended within a new outer housing made of very heavy copper. The copper housing, in turn, was suspended in a Transite-covered[4] water bath by heavy copper tubes attached to a Micarta lid. The escape of water vapor from the bath (operated at 73.7° C) was satisfactorily retarded by a covering of copper sheet on the underside of the bath cover. Openings in the bath cover were also copper-surfaced to promote condensation and return of water to the bath. The bath was controlled to within 0.005° C. The thermal leakage modulus for this calorimeter is 0.0029 min^{-1}.

Measurements of temperature and energy utilized a Guildline Nanopot potentiometer in conjunction with a Keithley 147 Nanovolt null detector. During calibration the period of electrical energy input was measured with an electronic counter-timer.

The solution medium was 950.0 grams of an acid mixture composed of 20.0 wt-pct hydrofluoric acid and 5.0 wt-pct hydrochloric acid. The quantities of reacting substances were stoichiometric with 0.742 gram of quartz. Substances to be dissolved were placed in Teflon tape capsules which, when sealed with paraffin, would spring open at the reaction vessel temperature and disperse the sample. The solution process consisted of dropping the capsule and its contents from room temperature (near 25° C) into the solution calorimeter which was operated at 73.7° C. Corrections were made for the heat effects of the paraffin and Teflon as well as for gold weights contained as sinkers with the samples.

The precision uncertainty assigned to the mean of solution heat values is twice the standard deviation of the mean. When two or more separate heat values are combined, the uncertainty is taken as the square root of the sum of the squares of the individual uncertainties.

All heat results here and in other parts of this investigation are expressed in terms of the thermochemical calorie (1 calorie = 4.1840 joules). Weighings are corrected to vacuum, and molecular weights conform to the 1973 Table of Atomic Weights (7).

Lithium Metasilicate (Li_2SiO_3)

The reaction scheme for obtaining the enthalpy of formation of lithium metasilicate is given in table 1. The reactions are written in an abbreviated form sufficient to show that rigid stoichiometry was maintained. Table 1 also

[4]Reference to specific manufacturers, brands of equipment, and trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

contains the heat values and uncertainties for the individual reaction steps. The symbols s, l, and sol denote substances that are crystalline, liquid, and in solution.

TABLE 1. - Reaction scheme for lithium metasilicate (Li_2SiO_3)

	Reaction	ΔH, kcal	Uncertainty, kcal
(1)	SiO_2(s,25°) + 6HF(sol, 73,7°) = H_2SiF_6(sol,73.7°) + $2H_2O$(sol,73.7°)..........	-34.304	0.042
(2)	2LiCl(s,25°) = $2Li^+$(sol,73.7°) +$2Cl^-$(sol,73.7°).............................	-13.404	.022
(3)	$26.462H_2O$(l,25°) = $26.462H_2O$(sol,73.7°)..........	18.762	.238
(4)	2(HCl·$12.731H_2O$)(l,25°) = $2H^+$(sol,73.7°) + $2Cl^-$(sol,73.7°) + $25.462H_2O$(sol,73.7°)........	20.662	.054
(5)	Li_2SiO_3(s,25°) + 6HF(sol,73.7°) + $2H^+$(sol,73.7°) = $2Li^+$(sol,73.7°) + H_2SiF_6(sol,73.7°) + $3H_2O$(sol,73.7°)...........	-59.362	.017

(6) 2LiCl(s,25°) + SiO_2(s,25°) + $26.462H_2O$(l,25°) = Li_2SiO_3(s,25°) + 2(HCl·$12,731H_2O$)(l,25°)

$$\Delta H_6 = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5$$

$$\Delta H_6 = 9.75 \pm 0.40 \text{ kcal}$$

Reactions 1, 2, and 3 were determined consecutively in 950.0 grams of a solution containing 20.0 wt-pct hydrofluoric acid and 5.0 wt-pct hydrocloric acid. Reactions 4 and 5 were determined consecutively in a change of solvent.

The experimental heats of solution relating to lithium metasilicate are given in table 2, together with mean values and precision uncertainties.

TABLE 2. - Experimental heats of solution, kcal/mole

H

SiO_2, reaction 1	LiCl(s), reaction 2	H_2O(l), reaction 3	HCl·$12.731H_2O$(l), reaction 4	Li_2SiO_3(s), reaction 5
-34.259	-6.707	0.703	10.354	-59.383
-34.329	-6.696	.708	10.272	-59.341
-34.378	-6.709	.719	10.387	-59.340
-34.274	-6.727	.719	10.302	-59.369
-34.239	-6.699	.692	10.299	-59.384
-34.234	-6.695	.715	10.345	-59.355
-34.354	-6.682	-	10.386	-
-34.364	-	-	10.309	-
			10.324	
Mean -34.304	-6.702	0.709	10.331	-59.362
±.042	±.011	±.009	±.027	±.017

The final solution after conducting reactions 1, 2, and 3 was identical to the one obtained after conducting reactions 4 and 5. Thus rigid stoichiometry was maintained and reaction 6 may be obtained by combining the reactions and heats as shown in table 1.

The uncertainty given in table 1 for the heat accompanying reaction 6 contains, in addition to precision uncertainties, uncertainties associated with the measurements, energy calibrations, and sample composition.

The enthalpies of formation at 298.15 K for LiCl(s), SiO_2(quartz), H_2O(l), and $HCl\cdot 12.731H_2O$(l) are needed to calculate the standard enthalpy of formation of Li_2SiO_3(s).

$$Li(s) + 1/2Cl_2(g) = LiCl(s),\ \Delta H^\circ_{298.15} = -97.58 \pm 0.27\ \text{kcal}, \quad (7)$$

$$Si(s) + O_2(g) = SiO_2(\text{quartz}),\ \Delta H^\circ_{298.15} = -217.72 \pm 0.34\ \text{kcal}, \quad (8)$$

$$H_2(g) + 1/2O_2(g) = H_2O(l),\ \Delta H^\circ_{298.15} = -68.315 \pm 0.01\ \text{kcal}, \quad (9)$$

and

$$1/2H_2(g) + 1/2Cl_2(g) + 12.731H_2O(l) = (HCl\cdot 12.731H_2O(l),$$

$$\Delta H^\circ_{298.15} = -38.82 \pm 0.05\ \text{kcal}. \quad (10)$$

The formation enthalpy, ΔH_7, was from the JANAF tables (5); ΔH_8 was from Wise (19); and ΔH_9 and ΔH_{10} were from Wagman (18).

The combination of reactions and enthalpies,

$$\Delta H_6 + 2\Delta H_7 + \Delta H_8 + \Delta H_9 - 2\Delta H_{10},$$

gives

$$\Delta H^\circ_{298.15} = -393.8 \pm 0.8\ \text{kcal/mole}$$

as the standard enthalpy of formation of lithium metasilicate, according to the reaction

$$2Li(s) + Si(s) + 3/2O_2(g) = Li_2SiO_3(s). \quad (11)$$

The enthalpy of formation of Li_2O(s) at 298.15 K is used to obtain the enthalpy of formation of lithium metasilicate from its component oxides,

$$2Li(s) + 1/2O_2(g) = Li_2O(s),\ \Delta H_{298.15} = -142.90 \pm 0.07\ \text{kcal}. \quad (12)$$

This enthalpy is from Johnson (8). By the combination of reactions and enthalpies

$$\Delta H_6 + 2\Delta H_7 + \Delta H_9 - 2\Delta H_{10} - \Delta H_{12},$$

there is obtained

$$\Delta H^\circ_{298.15} = -33.2 \pm 0.7\ \text{kcal}$$

for the reaction

$$Li_2O(s) + SiO_2(quartz) = Li_2SiO_3(s). \tag{13}$$

Lithium Disilicate ($Li_2Si_2O_5$)

The reaction scheme for obtaining the enthalpy of formation of lithium disilicate is given in table 3. Again, 0.742 gram of quartz was used as the basis for the quantities of the other substances to be dissolved.

TABLE 3. - Reaction scheme for lithium disilicate ($Li_2Si_2O_5$)

Reaction	ΔH, kcal	Uncertainty, kcal
(14) $2SiO_2(s,25°) + 12HF(sol,73.7°) = 2H_2SiF_6(sol,73.7°) - 4H_2O(sol,73.7°)$..........	-68.608	0.084
(15) $2LiCl(s,25°) = 2Li^+(sol, 73.7°) + 2Cl^-(sol,73.7°)$..............................	-13.384	.028
(16) $26.462H_2O(l,25°) = 26.462H_2O(sol,73.7°)$..........	18.894	.106
(17) $2(HCl\cdot 12.731H_2O)(l,25°) = 2H^+(sol,73.7°) + 2Cl^-(sol,73.7°) + 25.462H_2O(sol,73.7°)$........	20.602	.098
(18) $Li_2Si_2O_5(s,25°) + 12HF(sol,73.7°) + 2H^+(sol,73.7°) = 2Li^+(sol,73.7°) + 2H_2SiF_6(sol,73.7°) + 5H_2O(sol,73.7°)$..........	-93.191	.032

(19) $2LiCl(s,25°) + 2SiO_2(s,25°) + 26.462H_2O(l,25°) = Li_2Si_2O_5(s,25°) + 2(HCl\cdot 12.731H_2O)(l,25°)$

$$\Delta H_{19} = \Delta H_{14} + H_{15} + \Delta H_{16} - \Delta H_{17} - \Delta H_{18}$$

$$\Delta H_{19} = 9.49 \pm 0.40 \text{ kcal}$$

Proceeding as before, the substances were dissolved consecutively for reactions 14, 15, and 16. A new batch of acid was used for consecutive reactions 17 and 18.

Reaction 14, the solution of quartz, was identical to reaction 1. The experimental values listed in table 2 for reaction 1 are applicable here. The heat values associated with reactions 15, 16, and 17, although similar to reactions 2, 3, and 4, were redetermined because of concentration differences. These new experimental values and those for reaction 18, the heat of solution of the disilicate shown in table 4, provide the heat for overall calorimetric reaction 19, which amounts to 9.49 ± 0.40 kcal.

TABLE 4. - Experimental heats of solution, kcal/mole

LiCl(s), reaction 15	$H_2O(l)$, reaction 16	$HCl\cdot12.731H_2O(l)$, reaction 17	$Li_2Si_2O_5(s)$, reaction 18
-6.677	0.710	10.269	-93.186
-6.706	.704	10.277	-93.194
-6.708	.722	10.294	-93.178
-6.679	.716	10.396	-93.266
-6.703	.715	10.269	-93.214
-6.676	.720	-	-93.130
-6.685	.714	-	-93.166
-6.680	.713	-	-
-6.715	.718	-	-
-	.713	-	-
Mean -6.692	0.714	10.301	-93.191
±.011	±.004	±.049	±.032

By using supplementary data already cited, the standard enthalpy of formation is given by

$$\Delta H_{19} + 2\Delta H_7 + 2\Delta H_8 + \Delta H_9 - 2\Delta H_{10}$$

for the reaction

$$2Li(s) + 2Si(s) + 5/2O_2(g) = Li_2Si_2O_5(s). \qquad (20)$$

$$\Delta H_{20} = -611.8 \pm 1.0 \text{ kcal at } 298.15 \text{ K.}$$

The enthalpy of formation from Li_2O and SiO_2 is given by

$$\Delta H_{19} + 2\Delta H_7 + \Delta H_9 - 2\Delta H_{10} - \Delta H_{12}$$

for the reaction

$$Li_2O(s) + 2SiO_2(\text{quartz}) = Li_2Si_2O_5(s). \qquad (21)$$

$$\Delta H_{21} = -33.4 \pm 0.7 \text{ kcal at } 298.15 \text{ K.}$$

LOW-TEMPERATURE HEAT CAPACITIES

Adequate low-temperature heat capacities for the lithium metasilicate have been reported by Stull (15). The heat capacities for lithium disilicate were determined from 6 to 305 K as part of this investigation.

The apparatus and method of operation were given in an earlier publication by Stuve (16). The gold-plated copper sample container, with a capacity of 90 ml, held a sample mass of 75.678 grams. Helium gas (1.6 X 10^{-4} moles) was used within the powdered sample mass for better heat exchange. The experimental heat capacities are given in table 5 and shown in figure 1. The uncertainty of the determinations was estimated to be ±1 pct below 25 K, ±0.5 pct from 25 to 50 K, and ±0.2 pct from 50 to 300 K. No unusual behavior was noted over the measured range of temperature.

TABLE 5. - Low-temperature heat capacities (experimental) of $Li_2Si_2O_5$(s)

T, K	Cp, cal/deg mole	T, K	Cp, cal/deg mole
6.04........	0.0087	67.39........	5.330
7.05........	.012	73.72........	6.216
7.84........	.018	81.13........	7.342
8.57........	.023	86.48........	8.153
9.57........	.031	94.63........	9.432
11.07	.044		
		104.16........	10.917
13.07........	.068	114.15........	12.535
15.06........	.093	124.04........	14.119
16.81........	.121	134.30........	15.75
18.68........	.177	145.48........	17.47
20.85........	.268		
		155.84........	19.02
22.20........	.339	166.31........	20.52
24.44........	.470	176.89........	21.96
27.04........	.658	188.06........	23.43
30.26........	.922	200.75........	25.02
33.77........	1.255		
		213.33........	26.54
37.33........	1.622	225.81........	27.93
41.13........	2.028	238.57........	29.25
45.23........	2.490	251.69........	30.58
49.67........	3.009	264.53........	31.79
53.85........	3.525	277.20........	32.90
57.84........	4.003	291.02........	34.03
62.18........	4.600	304.58........	35.07

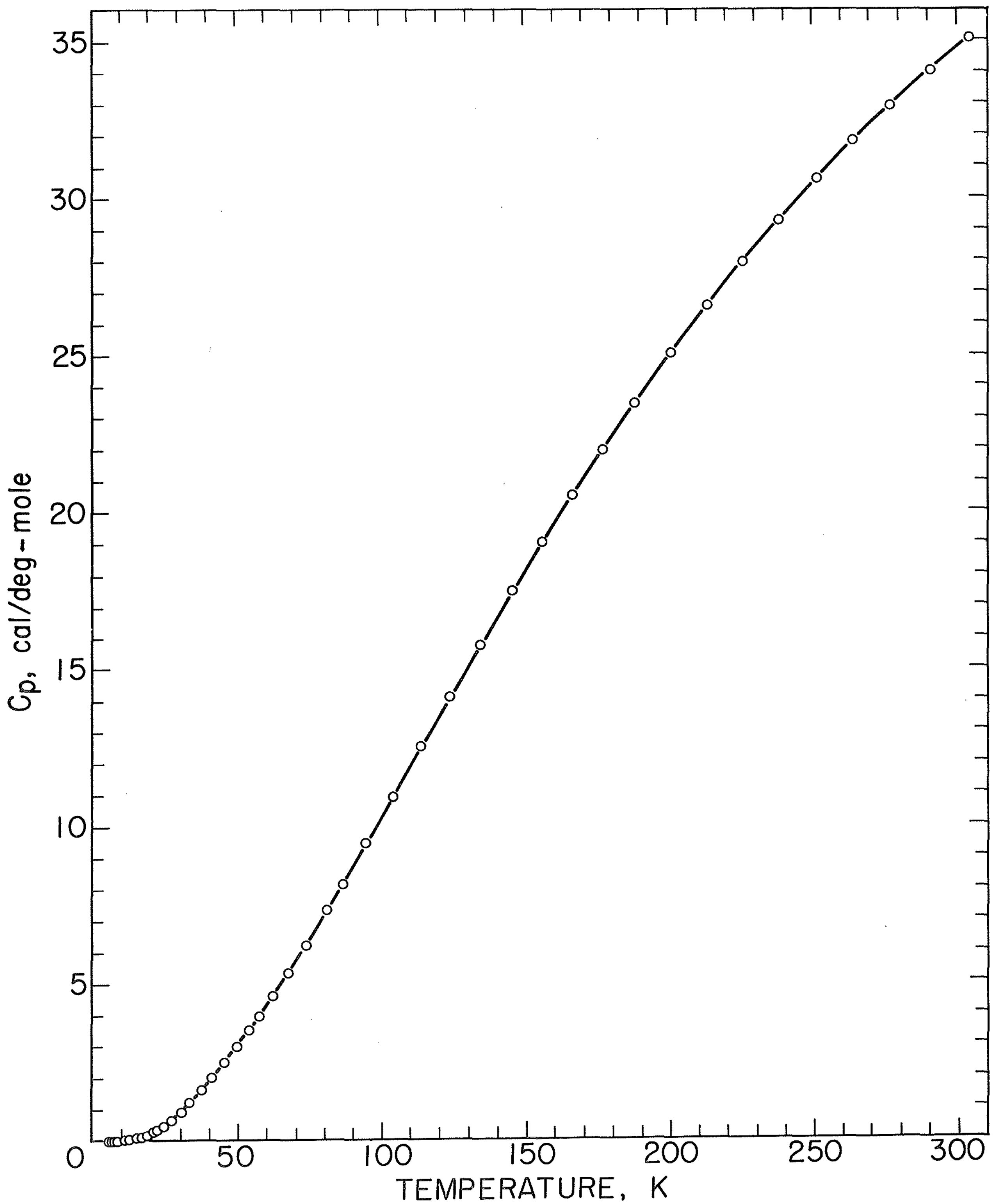

FIGURE 1. - Low-temperature heat capacity of $Li_2Si_2O_5$.

Extrapolation to 0 K was accomplished by plotting Cp/T against T^2 using experimental data at 20.85 K and below. The data were then fitted to polynominal functions with the aid of a digital computer. These functions were used to calculate values of Cp°, S°, $-(G.-H_0^\circ)/T$, and $H^\circ - H_0^\circ$ at regular intervals of temperature. Table 6 lists the calculated low-temperature thermodynamic properties.

TABLE 6. - Low-temperature thermodynamic properties of $Li_2Si_2O_5$(s)

T, K	Cal/deg mole			$H^\circ - H_0^\circ$,
	Cp°	S°	$-(G^\circ - H_0^\circ)/T$	cal/mole
10	0.034	0.012	0.003	0.092
15	.091	.036	.009	.400
20	.231	.078	.021	1.145
25	.507	.157	.040	2.935
30	.901	.282	.068	6.410
35	1.380	.456	.111	12.084
40	1.907	.675	.168	20.286
45	2.461	.931	.238	31.198
50	3.047	1.220	.321	44.956
60	4.309	1.885	.525	81.61
70	5.690	2.652	.773	131.52
80	7.159	3.507	1.061	195.70
90	8.694	4.438	1.383	274.92
100	10.273	5.436	1.739	369.73
110	11.874	6.490	2.122	480.46
120	13.477	7.592	2.532	607.2
130	15.07	8.733	2.964	750.0
140	16.63	9.907	3.418	908.5
150	18.15	11.106	3.890	1,082.4
160	19.62	12.325	4.380	1,271.2
170	21.03	13.557	4.883	1,474.5
180	22.39	14.797	5.399	1,691.6
190	23.69	16.04	5.924	1,922.1
200	24.94	17.29	6.464	2,165.3
210	26.13	18.54	7.013	2,420.7
220	27.27	19.78	7.563	2,687.8
230	28.37	21.02	8.124	2,966.0
240	29.42	22.25	8.688	3,255.0
250	30.42	23.47	9.253	3,554.2
260	31.37	24.68	9.822	3,863.2
270	32.28	25.88	10.393	4,181.5
273.15	32.55	26.26	10.569	4,283.6
280	33.14	27.07	10.968	4,508.6
290	33.95	28.25	11.547	4,844.0
298.15	34.59	29.20	12.017	5,123
300	34.73	29.41	12.120	5,187

HIGH-TEMPERATURE ENTHALPIES

Enthalpy determinations relative to 298.15 K of the two lithium silicates were made with a previously described copper-block drop calorimeter (4). Sample sizes (contained in platinum-rhodium capsules) were 7.1621 grams for Li_2SiO_3, and 6.1300 grams for $Li_2Si_2O_5$. Enthalpies of the empty capsules were determined in separate measurements.

Values of experimental enthalpies are listed in table 7. Figure 2 shows them as the function $(H-H_{298.15})/(T-298.15)$. The uncertainty of the data for both compounds is estimated to be less than 0.5 pct.

TABLE 7. - Enthalpies above 298.15 K (experimental)

T, K	$H^\circ-H^\circ_{298.15}$, kcal/mole	T, K	$H^\circ-H^\circ_{298.15}$, kcal/mole
	Li_2SiO_3		
401.4	2.733	992.9	22.975
401.7	2.743	1,006.4	23.490
504.2	5.827	1,100.2	27.045
602.0	9.008	1,102.4	27.175
707.4	12.580	1,194.2	30.730
807.7	16.145	1,286.5	34.400
907.2	19.790	1,403.5	39.650
	$Li_2Si_2O_5$		
400.0	3.881	1,056.6	37.120
447.3	5.882	1,094.6	39.265
500.8	8.269	1,100.6	39.545
597.5	12.840	1,149.8	42.375
702.3	18.050	1,195.5	45.115
702.8	18.070	1,210.7	45.925
802.4	23.225	1,221.8	46.830
902.3	28.595	1,252.3	48.630
993.5	33.585	1,253.2	48.720
1,001.8	34.070	1,281.0	50.47

Determinations for Li_2SiO_3 were interrupted after the run at 1,403.5 K showed a pressure buildup within the sample container. Because this swelling of containers occurred with two samples, the pressure was believed to be caused by a small amount of water impurity adsorbed on the sample. In any case, the temperature and enthalpy of fusion were not determined for Li_2SiO_3. The melting point reported by Kracek was corrected to 1,475 K to be in agreement with IPRS-68 (3). The present enthalpy data were extrapolated to this temperature. The last experimental enthalpy at 1,403.5 K shows some premelting effect, as seen by the value at this temperature being slightly above the curve in figure 2. No other irregular behavior was noted in the temperature range from 400 to 1,404 K.

The experimental enthalpy data for $Li_2Si_2O_5$ extend to 1,281 K. A reversible, first order transition with a heat adsorption of 0.255 kcal/mole was

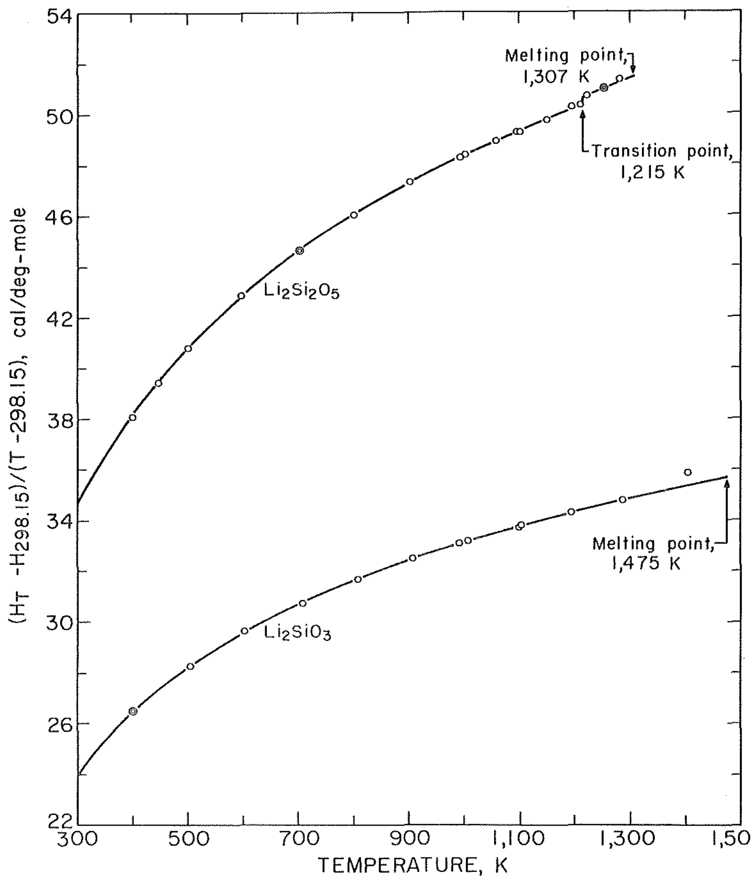

FIGURE 2. - High-temperature enthalpy functions of Li_2SiO_3 and $Li_2Si_2O_5$.

found at 1,215 K. Kracek reported 1,210 K as the temperature of this transition. Kracek also reported the melting point to be 1,307 K. Both temperatures have been corrected to IPTS-68. Our petrographic examination of a specimen quenched from the melt showed it to be a uniform glass.

Enthalpy data for both silicates were fitted to polynomial functions. Care was taken to merge smoothly with the low-temperature data of Stull in the case of Li_2SiO_3 and with the present low-temperature data in the case of $Li_2Si_2O_5$. Values of $Cp°$, $S°-S°_{298}$, $-(G°-H°_{298})/T$, and $H°-H°_{298}$ were then calculated at 50° intervals by means of the functions. These properties are listed in tables 8-9. Values of $S°_{298}$ were added from the work of Stull for Li_2SiO_3 and from table 6 for $Li_2Si_2O_5$. The melting points reported by Kracek were adopted.

Smooth enthalpies from tables 8-9 were fitted to the equation form suggested by Maier and Kelley (11). The equations for kilocalorie per mole, together with ranges of applicability and average deviations from the experimental data, follow·

$$Li_2SiO_3(s):\ 30.687 \times 10^{-3}T + 3.901 \times 10^{-6}T^2 + 8.119 \times 10^2T^{-1} - 12.219$$

(298 to 1,475 K; 0.3 pct)

$$Li_2Si_2O_5(\alpha):\ 42.979 \times 10^{-3}T + 6.906 \times 10^{-6}T^2 + 11.122 \times 10^2T^{-1} - 17.158$$

(298 to 1,215; 0.3 pct)

$$Li_2Si_2O_5(\beta):\ 59.500 \times 10^{-3}T - 25.869$$

(1,215 to 1,307 K; 0.1 pct)

TABLE 8. - High-temperature thermodynamic properties of $Li_2SiO_3(s)$[1]

T, K	Cal/deg-mole			$H°-H°_{298}$
	Cp°	S°	$-(G°-H°_{298})/T$	kcal/mole
298.15	23.88	19.08	19.08	0
300	24.00	19.23	19.08	.044
350	26.64	23.14	19.38	1.315
400	28.56	26.83	20.09	2.697
450	30.07	30.28	21.03	4.164
500	31.31	33.52	22.12	5.699
550	32.35	36.55	23.29	7.291
600	33.24	39.41	24.52	8.932
650	34.03	42.10	25.77	10.615
700	34.72	44.65	27.03	12.335
750	35.35	47.06	28.28	14.085
800	35.92	49.36	29.53	15.865
850	36.44	51.56	30.77	17.675
900	36.93	53.65	31.97	19.510
950	37.38	55.66	33.17	21.370
1,000	37.80	57.59	34.34	23.250
1,050	38.20	59.44	35.49	25.150
1,100	38.58	61.23	36.63	27.065
1,150	38.93	62.95	37.73	29.005
1,200	39.27	64.62	38.82	30.960
1,250	39.59	66.23	39.89	32.930
1,300	(39.88)	(67.78)	(40.92)	(34.920)
1,350	(40.16)	(69.29)	(41.94)	(36.920)
1,400	(40.41)	(70.76)	(42.95)	(38.935)
1,450	(40.64)	(72.18)	(43.93)	(40.960)
1,475[2]	(40.74)	(72.88)	(44.42)	(41.980)

[1]Values in parentheses are extrapolations.
[2]Melting point of Li_2SiO_3.

TABLE 9. - High-temperature thermodynamic properties of $Li_2Si_2O_5$(s)[1]

T, K	Cal/deg-mole			$H°-H°_{298}$, kcal/mole
	Cp°	S°	$-(G°-H°_{298})/T$	
298.15	34.59	29.20	29.20	0
300	34.73	29.41	29.20	.064
350	38.39	35.05	29.63	1.897
400	41.23	40.37	30.65	3.890
450	43.54	45.36	32.00	6.011
500	45.48	50.05	33.58	8.237
550	47.14	54.47	35.28	10.555
600	48.57	58.63	37.06	12.945
650	49.82	62.57	38.87	15.405
700	50.92	66.30	40.69	17.925
750	51.89	69.85	42.52	20.495
800	52.76	73.23	44.34	23.115
850	53.55	76.45	46.13	25.770
900	54.26	79.53	47.90	28.470
950	54.92	82.48	49.64	31.200
1,000	55.54	85.32	51.36	33.960
1,050	56.14	88.04	53.04	36.750
1,100	56.71	90.67	54.69	39.575
1,150	57.29	93.20	56.31	42.425
1,200	57.88	95.65	57.90	45.300
1,215[2]	58.06	96.37	58.37	46.170
1,215	59.50	96.58	58.37	46.425
1,250	59.50	98.27	59.47	48.505
1,300	(59,50)	(100.6)	(61.00)	(51.48)
1,307[3]	(59.50)	(100.9)	(61.19)	(51.90)

[1]Values in parentheses are extrapolations.
[2]Transition point of $Li_2Si_2O_5$; ΔH = 0.255 kcal/mole.
[3]Melting point of $Li_2Si_2O_5$.

ENTHALPY AND GIBBS ENERGY OF FORMATION

The results of the preceding sections have been combined to give the enthalpies of formation and the Gibbs energies of formation as a function of temperature. In addition to the auxiliary data already cited, $H°-H°_{298}$ data for Li(s,l) and Si(s) were taken from Hultgren (6). Similar data for $Li_2O(s)$ and $O_2(g)$ were from the JANAF tables.

Tables 10-11 provide ΔHf°, ΔGf°, and $\log_{10}Kf$ for the reactions

$$2Li(s,l) + Si(s) + 3/2O_2(g) = Li_2SiO_3(s), \quad (22)$$

and

$$2Li(s,l) + 2Si(s) + 5/2O_2(g) = Li_2Si_2O_5(s). \quad (23)$$

TABLE 10. - Formation data for the reaction $2Li(s,l) + Si(s) + 3/2O_2(g) = Li_2SiO_3(s)$

T, K	Kcal		Log K	T, K	Kcal		Log K
	ΔH°	ΔG°			ΔH°	ΔG°	
298.15	-393.8	-372.1	272.76	800	-394.8	-334.2	91.30
300	-393.8	-371.9	270.93	900	-394.3	-326.7	79.33
400	-394.0	-364.6	199.21	1,000	-393.8	-319.2	69.76
453.7[1]	-394.0	-360.7	173.75	1,100	-393.3	-311.7	61.93
453.7	-395.4	-360.7	173.75	1,200	-392.7	-304.3	55.42
500	-395.4	-357.1	156.09	1,300	-392.0	-297.0	49.93
600	-395.3	-349.4	127.27	1,400	-391.3	-289.7	45.22
700	-395.1	-341.8	106.71	1,475[2]	-390.8	-284.3	42.12

[1]Melting point of Li; ΔH = 1.434 kcal/mole.
[2]Melting point of Li_2SiO_3.

TABLE 11. - Formation data for the reaction $2Li(s,l) + 2Si(s) + 5/2O_2(g) = Li_2Si_2O_5(s)$

T, K	Kcal		Log K	T, K	Kcal		Log K
	ΔH°	ΔG°			ΔH°	ΔG°	
298.15	-611.8	-577.1	423.03	900	-611.4	-505.8	122.82
300	-611.8	-576.9	420.27	1,000	-610.6	-494.1	107.99
400	-612.0	-565.2	308.81	1,100	-609.8	-482.5	95.86
453.7[1]	-612.0	-558.9	269.23	1,200	-608.8	-471.0	85.78
453.7	-613.4	-558.9	269.23	1,215[2]	-608.7	-469.3	84.42
500	-613.4	-553.4	241.89	1,215	-608.4	-469.3	84.42
600	-613.2	-541.4	197.20	1,300	-607.5	-459.6	77.27
700	-612.7	-529.5	165.32	1,307[3]	-607.4	-458.8	76.72
800	-612.1	-517.6	141.40				

[1]Melting point of Li; ΔH = 1.434 kcal/mole.
[2]Transition point of $Li_2Si_2O_5$; ΔH = 0.255 kcal/mole.
[3]Melting point of $Li_2Si_2O_5$.

Tables 12-13 give the same properties for the reactions

$$Li_2O(s) + SiO_2(s) = Li_2SiO_3(s), \quad (24)$$

and

$$Li_2O(s) + 2SiO_2(s) = Li_2Si_2O_5(s). \quad (25)$$

TABLE 12. - Formation data for the reaction $Li_2O(s) + SiO_2(s) = Li_2SiO_3(s)$

T, K	Kcal ΔH°	Kcal ΔG°	Log K	T, K	Kcal ΔH°	Kcal ΔG°	Log K
0	-33.2	-33.2	∞	847[1]	-33.2	-33.4	8.62
100	-33.4	-33.4	73.00	847	-33.3	-33.4	8.62
200	-33.2	-33.2	36.28	900	-33.3	-33.4	8.11
298.15	-33.2	-33.2	24.34	1,000	-33.2	-33.4	7.30
300	-33.2	-33.2	24.19	1,100	-33.2	-33.5	6.66
400	-33.1	-33.2	18.14	1,200	-33.1	-33.5	6.10
500	-33.1	-33.3	14.56	1,300	-33.0	-33.5	5.63
600	-33.0	-33.3	12.13	1,400	-33.0	-33.5	5.23
700	-33.0	-33.3	10.40	1,475[2]	-33.0	-33.6	4.98
800	-33.1	-33.4	9.12				

[1] Transition point of SiO_2; ΔH = 0.174 kcal/mole.
[2] Melting point of Li_2SiO_3.

TABLE 13. - Formation data for the reaction $Li_2O(s) + 2SiO_2(s) = Li_2Si_2O_5(s)$

T, K	Kcal ΔH°	Kcal ΔG°	Log K	T, K	Kcal ΔH°	Kcal ΔG°	Log K
0	-33.5	-33.5	∞	847[1]	-33.6	-33.8	8.72
100	-33.5	-33.5	73.21	847	-33.9	-33.8	8.72
200	-33.5	-33.5	36.61	900	-33.8	-33.8	8.21
298.15	-33.5	-33.6	24.63	1,000	-33.6	-33.8	7.39
300	-33.5	-33.6	24.48	1,100	-33.4	-33.9	6.74
400	-33.4	-33.6	18.36	1,200	-33.2	-33.9	6.17
500	-33.4	-33.6	14.69	1,215[2]	-33.2	-33.9	6.10
600	-33.4	-33.7	12.28	1,215	-32.9	-33.9	6.10
700	-33.4	-33.8	10.55	1,300	-32.7	-34.0	5.72
800	-33.5	-33.8	9.23	1,307[3]	-32.6	-34.0	5.69

[1] Transition point of SiO_2; ΔH = 0.174 kcal/mole.
[2] Transition point of $Li_2Si_2O_5$; ΔH = 0.255 kcal/mole.
[3] Melting point of $Li_2Si_2O_5$.

SUMMARY OF RESULTS

No previous experimental high-temperature data have been reported in the literature for either the metasilicate or disilicate. Also, low-temperature heat capacities for lithium disilicate are reported for the first time. Incomplete data for the enthalpies of formation of the two silicates were given by Kracek (2) who used solution calorimetry. He reported -34.45 kcal/mole for reaction 24 and -34.58 kcal/mole for reaction 25. His values are different from those reported here by approximately 1 kcal.

By a combination of experimental data determined in this investigation and selected values from the literature, reliable sets of thermodynamic parameters are now available over extended temperature ranges. These two lithium silicates are shown to be stable relative to their constituent elements or oxides over the range of the data.

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