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Thermodynamic Properties of Petalite ($\text{Li}_2\text{Al}_2\text{Si}_8\text{O}_{20}$)

By K. O. Bennington, J. M. Stuve,
and M. J. Ferrante

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UNITED STATES DEPARTMENT OF THE INTERIOR

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THERMODYNAMIC PROPERTIES OF PETALITE ($\text{Li}_2\text{Al}_2\text{Si}_8\text{O}_{20}$)

by

K. O. Bennington,¹ J. M. Stuve,¹ and M. J. Ferrante¹

ABSTRACT

The thermodynamic properties of petalite ($\text{Li}_2\text{Al}_2\text{Si}_8\text{O}_{20}$) were determined by the Bureau of Mines. The enthalpy of formation was determined by hydrofluoric acid solution calorimetry. The values from the elements and from the oxides are

$$\Delta H_{f,298.15}^\circ = 2,335.8 \pm 3.0 \text{ kcal/mole}$$

and ΔH_{298}° (from oxides) = -50.60 ± 1.20 kcal/mole.

Low-temperature heat capacities were determined by adiabatic calorimetry from 10.69 to 302.11 K. The derived standard entropy is

$$S_{298.15}^\circ = 111.0 \pm 1 \text{ cal/deg-mole.}$$

Enthalpy increments above 298 K were measured by copper block calorimetry from 298 K to 1,193.6 K.

The various experimental data were combined with other data from the literature to calculate the Gibbs energies of formation and equilibrium constants of formation over the temperature range of the measurements. Tables of enthalpies of formation and Gibbs energies of formation are given as a function of temperature from the elements and constituent oxides. The Gibbs energy of formation is

$$\Delta G_{f,298.15}^\circ = 2,203.8 \text{ kcal/mole.}$$

INTRODUCTION

This investigation of the thermodynamic properties of the mineral petalite ($\text{Li}_2\text{Al}_2\text{Si}_8\text{O}_{20}$) is one of a series on lithium compounds. The enthalpies of formation, low-temperature heat capacities, and high-temperature

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enthalpies of compounds in the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system have been reported (28-29),² as have those of eucryptite (LiAlSiO_4) and spodumene ($\text{LiAlSi}_2\text{O}_6$) (1, 26). Closely related work on synthetic lithium silicates, also appearing in the $\text{Na}_2\text{O}-\text{Li}_2\text{O}-\text{SiO}_2$ system (21), has been reported (2) as part of this general study.

These data contribute towards the understanding of equilibrium at low temperature and will aid in outlining the conditions of deposition of the lithium pegmatitic minerals. This investigation was part of the Bureau of Mines research program directed at advancing mineral technology and minimizing energy requirement for extraction of metals and oxides.

MATERIALS

Petalite ($\text{Li}_2\text{Al}_2\text{Si}_8\text{O}_{20}$)

The petalite used in this investigation was obtained from Wards' Natural Science Establishment.³ It was collected near Fort Victoria, Southern Rhodesia. This material was crushed, ground, screened, and washed. The minus 100- plus 200-mesh fraction was used in the low-temperature heat capacity measurements and in the high-temperature enthalpy investigation. The minus 200- plus 400-mesh fraction was used for the heat of solution measurements and the chemical analysis. Spectrographic analysis identified minor impurities that collected in the minus 400-mesh fraction, which was discarded. The X-ray diffraction pattern matched the pattern for petalite given by Powder Diffraction File (PDF) card 14-90.

Silica (SiO_2)

The SiO_2 used was from an exceedingly clear and pure single quartz crystal. The crystal was sawed, crushed, ground to pass a 400-mesh screen, and elutriated in distilled water. The size fraction ranging between 10 and 20 μm was retained for the heat of solution measurements. This fraction was repeatedly leached with hydrochloric acid until the solution remained clear; it was then digested with hydrogen peroxide and dried. Each sample was heated through the alpha-beta transition immediately before solution measurements were made. No impurities were detected spectrographically, and the X-ray diffraction pattern matched that given in the PDF.

$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$

The $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was reagent-grade material that showed spectrographic traces of barium, calcium, and magnesium, and approximately 0.05 wt-pct Na and 0.15 wt-pct Si. No corrections were made for impurities. It was stored over sulfuric acid in a desiccator until stable with 6 moles of water. The final analysis showed 11.20 pct Al, 44.00 pct Cl, and 44.80 pct H_2O , as compared

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

³Reference to specific brand names is made for identification only and does not imply endorsement by the Bureau of Mines.

with the theoretical composition of 11.176 pct Al, 44.053 pct Cl₂, and 44.776 pct H₂O.

Lithium Chloride (LiCl)

The lithium chloride was a reagent-grade product that contained a spectrographically determined impurity of approximately 0.05 pct Na. No correction was made for this impurity. The sample was heated at 420° C to constant weight before use.

Acids

The hydrochloric and hydrofluoric acid solvents used were reagent-grade products that required no special treatment other than dilution with distilled water to the proper strength.

MINERAL ANALYSIS AND FORMULAS

Analysis

The chemical analysis presented in table 1 was made by the analytical laboratory, Albany Research Center. One impurity, approximately 30 ppm titanium, was found spectrographically that does not appear in the chemical analysis. The X-ray analysis indicated a possible trace of alpha-quartz; however, calculations concerning the chemical composition indicated a deficiency of SiO₂. No attempt was made to correct for these two impurities.

TABLE 1. - Analysis of petalite¹

Composition		Ions in extended formula	Formula weight, grams	Substitution site	Site deviation	Adjusted formula	Formula weight (ideal), grams
Oxide	Wt-pct						
SiO ₂	77.11	7.9239	222.5506	Si Al	-0.0581	8.0000	224.688
Al ₂ O ₃	16.64	2.0153	54.3758			2.0000	53.963
Fe ₂ O ₃	2.034	0.0027 2.0180	.1508				
MnO	.023	.0018	.0989	Li	+0.0018	2.0000	13.882
MgO	.23	.0352	.8555		+0.0352		
CaO	.07	.0077	.3086		+0.0077		
Li ₂ O	4.65	1.9215	13.3371				
Na ₂ O	.67	.1334	3.0668		+0.0549		
K ₂ O	.09	.0117 2.113	.4574		+0.0117		
H ₂ O ⁻	.37			O		20.0000	319.988
F ⁻	.29	.0945	1.7953				
O		19.9055	318.4761				
F-wt			615.473				612.521

¹ Adjusted formula (ideal) [(Li_{2.000}) (Al_{2.000}) (Si_{8.000}) (O_{20.000})].

² Includes 0.03 pct Ga₂O₃.

Note.--Total charge = 40.

Formulas

The formula for petalite and the formula weight were calculated from the chemical analysis using the anion-based hydrogen-equivalent method. This method for deriving the number of ions per mineral formula consists of calculating the ratios of hydrogen equivalents of the analyzed constituents and normalizing these values to the ideal sum of anions per unit formula. A detailed description for the calculations for this technique is given by Jackson (14). This procedure was described earlier by Miser (23) and Stevens (32-33) and more recently by Goff (10).

The extended formula was constructed using 20 oxygen anions per formula. The formula usually accepted is $\text{Li}_2\text{Al}_2\text{Si}_8\text{O}_{20}$ and is the ideal formula adopted for this study because the chemical analysis adapts to this stoichiometry with the least adjustment. Other proposed formulas based on the analyses of specimens from other localities are discussed by Deer (6). A detailed study of synthetic petalite and related minerals and solid solutions in the $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ system is presented by Roy (29) and also indicates that the 1:1:8 ratio of oxides is the most probable formula.

It was necessary to make several assumptions in the construction of this formula. Following Jackson (14) and Sommerfeld (31), it is assumed that all of the anion positions in the mineral structure are filled and that the charges in the mineral are balanced. Jackson (14) has pointed out that under these assumptions cation deficiencies may be due to vacant cation positions or analytical errors, and further, that if the type formula for the mineral is correctly chosen, any calculated excess of cations may be due only to analytical error. For the purposes of this study the chemical analysis is considered to be absolutely accurate; consequently, information is shown in sufficient detail and completeness for recalculation.

The number of atoms of the individual elements in the extended formula was used in computing the formula weight, the total of which provides the gram formula weight of the natural mineral. The grouping of ions into particular positions follows the example of Deer (6). The numbers of ions, even though unrealistic, were carried without rounding to maintain internal consistency.

The number of ions in the extended formula does not provide a practical composition; consequently, it was adjusted to the ideal end member molecule. This was done by substituting some of the minor elements into the most likely major element sites and calculating others as excess. The deviations in each structural position represent the difference between the ideal stoichiometry and the sum of ions substituted per structural site.

The adjusted formula weight for each structural position provided the total adjusted formula weight. The construction necessary to develop the adjusted formula and formula weight required that corresponding heat corrections be made. The heat solution corrections for cation substitutions and impurities were made by treating the minor element as substituted into the most likely major element sites, as previously described. The difference in

energy between the quantity of the major element that is deficient or has been displaced by an equal quantity or excess of the proxying element was computed from the respective heat of solution values of their oxides determined under similar conditions. The corrections applied were the net energy differences for the specific number of ions in a particular structure position.

The thermal correction required by the change in gram formula weight was applied by scaling the heat of solution value for the natural mineral to the adjusted gram formula weight. This was done assuming that the vacancy sites are uniformly distributed, that the added ions are completely bonded in the structure, and that the heat of solution of the natural mineral is more suitable than a thermal adjustment based on the separate heats of solution of the deficient or excess oxides.

The values for the thermal corrections and sequence of application of the corrections are given in detail under the reaction description for the mineral, reaction 6, in the petalite reaction scheme. The heat of solution values were determined and calculated for the formula weight of the natural mineral, and the corrections were then applied.

EXPERIMENTAL DETERMINATIONS

Heats of Formation at 298.15 K

The heat of formation of petalite was determined by hydrofluoric acid solution calorimetry. The apparatus used has been described in earlier publications (2, 20, 35). The solvent used was 950 grams of an acid mixture composed of 20 wt-pct hydrofluoric acid and 5 wt-pct hydrochloric acid. The quantities of all reacting substances were stoichiometric with 0.742 g of alpha-quartz which, when substituted into reaction 1, table 2 provides the stoichiometric molar proportions for all succeeding reactions.

Weighed amounts of solid or liquid substances to be dissolved were placed in paraffin-sealed Teflon tape capsules and dropped at the appropriate time, at 25° C, into the calorimeter, which was operated at 73.7° C. Each measurement resulted from a process of converting the pure reacting substance at 25° C plus the solvent at 73.7° C to a solution product at 73.7° C. Corrections were applied for the heat effects of the paraffin, Teflon, and a gold ballast, when used. Electrical calibrations of the calorimeter were made over the temperature range of measurements.

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.

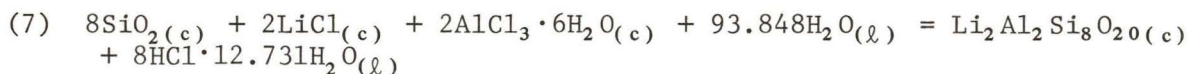
All energy units are expressed in terms of the defined calorie. (1 calorie = 4.1840 joules.) All weighings were corrected to vacuum, and molecular weights are in accordance with the 1973 table of atomic weights (13). Final values are rounded to 10 calories. All calibrations are traceable to the National Bureau of Standards (NBS), and sample temperatures are based on the International Practical Temperature Scale of 1968 (IPTS-68) (3).

The reaction scheme for the solution calorimetric investigation is given in table 2. The symbols c, l, and sol are used to denote substances that are crystalline, liquid, or in solution. The reactions are written in an abbreviated form sufficient to show that stoichiometry was maintained in such a way as to permit cancellation of the reaction products. The table also contains the average measured heat values and their precision uncertainties.

TABLE 2. - Reaction scheme for petalite¹

Reaction	ΔH , kcal	Uncertainty, \pm kcal
(1) $8\text{SiO}_{2(c)} + 48\text{HF}_{(\text{sol})} = 8\text{H}_2\text{SiF}_{6(\text{sol})} + 16\text{H}_2\text{O}_{(\text{sol})} \dots\dots$	-274.432	0.336
(2) $93.848\text{H}_2\text{O}_{(\text{l})} = 93.848\text{H}_2\text{O}_{(\text{sol})} \dots\dots\dots$	+67.383	.281
(3) $2\text{AlCl}_3 \cdot 6\text{H}_2\text{O}_{(c)} = 2\text{Al}^{+3}_{(\text{sol})} + 6\text{Cl}^{-}_{(\text{sol})} + 12\text{H}_2\text{O}_{(\text{sol})} \dots$	-38.260	.158
(4) $2\text{LiCl}_{(c)} = 2\text{Li}^{+}_{(\text{sol})} + 2\text{Cl}^{-}_{(\text{sol})} \dots\dots\dots$	-13.434	.012
(5) $8\text{HCl} \cdot 12.731\text{H}_2\text{O}_{(\text{l})} = 8\text{H}^{+}_{(\text{sol})} + 8\text{Cl}^{-}_{(\text{sol})}$ $+ 101.848\text{H}_2\text{O}_{(\text{sol})} \dots\dots\dots$	+82.600	.208
(6) $\text{Li}_2\text{Al}_2\text{Si}_8\text{O}_{20(c)} + 48\text{HF}_{(\text{sol})} + 8\text{H}^{+}_{(\text{sol})} = 8\text{H}_2\text{SiF}_{6(\text{sol})}$ $+ 2\text{Al}^{+3}_{(\text{sol})} + 2\text{Li}^{+}_{(\text{sol})} + 20\text{H}_2\text{O}_{(\text{sol})} \dots\dots\dots$	² -372.567	.400

$$\Delta H_7 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_5 - \Delta H_6$$



$$\Delta H_7 = 31.224 \pm 0.65 \text{ kcal}$$

¹For reactions 1-6, reactants are at 25° C and reaction products at 73.7° C.

²Corrected value.

Reaction 1, the dissolution of quartz, was identical to a first-reaction value determined previously (2) under identical conditions; consequently, the experimentally determined value, -34.304 ± 0.042 kcal is adopted directly.

Reaction 2, the dilution of water, was redetermined, and the data are presented in table 3 with their uncertainties. The stoichiometric amounts of materials for the preceding reactions were added prior to making measurements for reaction 3.

Reaction 3, the heat of solution of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, was determined in the solution following reaction 2. These experimentally determined heat values and their uncertainties are listed in table 3. Prewighed samples were loaded into unsealed capsules and stored over sulfuric acid preceding use. Containers were quickly and easily sealed, and the weight was checked before they were dropped into the calorimeter.

TABLE 3. - Experimental heats of solution, kcal/mole

H ₂ O, reaction 2	AlCl ₃ ·6H ₂ O, reaction 3	LiCl, reaction 4	HCl·12.731H ₂ O, reaction 5	Li ₂ Al ₂ Si ₈ O ₂₀ , reaction 6
0.714	-19.135	-6.722	10.354	-377.268
.720	-18.996	-6.717	10.387	-377.236
.714	-19.126	-6.717	10.272	-377.278
.722	-19.028	-6.706	10.302	-377.434
.719	-19.116	-6.722	10.351	-377.466
.723	-19.289		10.299	-377.366
.715	-19.296		10.309	-377.290
	-19.052		10.324	-378.056
¹ .718	¹ -19.130	¹ -6.717	¹ 10.325	¹ -377.424
±.003	±.079	±.006	±.026	±.190

¹Mean.

Reaction 4, the heat of solution of LiCl, was determined following reaction 3. Granular lithium chloride stored at 120° C was used to make pellets, which were restored to the 120° C oven. Preweighed samples of pellets were heated overnight at 420° C prior to use. No sample weight change was detected during handling.

Reaction 5, the heat of mixing of HCl·12.731H₂O, was made as the first reaction in a change of acid. The experimentally determined values and their uncertainties are listed in table 3.

Reaction 6, the heat of solution of the mineral petalite, was conducted in the soluting following reaction 5. The experimentally determined heats of solution for this reaction, together with their uncertainties, appear in table 3. This heat of solution value was determined for the formula weight and composition of the original mineral as represented by the extended formula, column 2, table 1. Correcting this value (-377.424 ± 0.200 kcal per formula weight of 615.473 grams) for 0.37 percent adsorbed water (H₂O⁻), which was 0.304 kcal, and for the weight correction for this amount of water provides -379.131 ± 0.200 kcal. This value was then corrected for the new impurity substitutions and deviations from stoichiometry, shown in columns 4 and 5, table 1, and calculated for the formula weight for the ideal composition shown in column 6. This final heat of solution value was found to be -372.567 ± 0.400 kcal. The uncertainty was doubled to compensate for the correction procedure.

The final solution, after conducting reactions 1 through 4 consecutively, is identified with the solution resulting from the combination of reactions 5 and 6. These reactions and their heats were therefore combined as indicated in table 2, according to the scheme

$$\Delta H_7 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_5 - \Delta H_6,$$

to obtain the resulting reaction 7, the overall calorimetric reaction with a heat change of 31.224 ± 0.65 kcal.

To derive the standard enthalpy of formation of petalite, the heats of formation of alpha-quartz (SiO_2), water, lithium-chloride (LiCl), $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, and hydrochloric acid solution of the composition $\text{HCl} \cdot 12.731 \text{ H}_2\text{O}$ were required as represented in table 4 by reactions 9-12 with their enthalpy values and uncertainties. The sources for the values for these reactions are as follows: SiO_2 from Wise (39), H_2O and $\text{HCl} \cdot 12.731 \text{ H}_2\text{O}$ from Wagman (36), LiCl from the JANAF tables (9), and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ from Coughlin (5).

TABLE 4. - Enthalpy of formation of petalite

Reaction	$\Delta H_{298.15}$, kcal/mole	Uncertainty, \pm kcal	Reference
(8) $\text{Si}_{(c)} + \text{O}_{2(g)} = \text{SiO}_{2(c)} \dots\dots\dots$	-217.720	0.34	28
(9) $\text{H}_{2(g)} + 1/2 \text{O}_{2(g)} = \text{H}_2\text{O}_{(l)} \dots\dots\dots$	-68.315	.010	27
(10) $\text{Li}_{(c)} + 1/2 \text{Cl}_{2(g)} = \text{LiCl}_{(c)} \dots\dots\dots$	-97.578	.27	24
(11) $1/2 \text{H}_{2(g)} + 1/2 \text{Cl}_{2(g)} + 12.731 \text{H}_2\text{O}_{(l)}$ $= \text{HCl} \cdot 12.731 \text{H}_2\text{O}_{(l)} \dots\dots\dots$	-38.82	.05	27
(12) $\text{Al}_{(c)} + 3/2 \text{Cl}_{2(g)} + 6\text{H}_{2(g)} + 3 \text{O}_{2(g)}$ $= \text{AlCl}_3 \cdot 6\text{H}_2\text{O}_{(c)} \dots\dots\dots$	-643.600	.21	3
(13) $2\text{Al}_{(c)} + 3/2 \text{O}_{2(g)} = \text{Al}_2\text{O}_{3(c)} \dots\dots\dots$	-400.55	.3	16
(14) $2\text{Li}_{(c)} + 1/2 \text{O}_{2(g)} = \text{Li}_2\text{O}_{(c)} \dots\dots\dots$	-142.9	.5	10
$\Delta H_{15} = \Delta H_7 + 8\Delta H_8 - 8\Delta H_9 + 2\Delta H_{10} - 8\Delta H_{11} + 2\Delta H_{12}$			
(15) $2\text{Li}_{(c)} + 2\text{Al}_{(c)} + 8\text{Si}_{(c)} + 10\text{O}_{2(g)} = \text{Li}_2\text{Al}_2\text{Si}_8\text{O}_{20(c)}$ $\Delta H_{15} = -2,335.812 \pm 2.84 \text{ kcal} = -2,335.8 \pm 3.0 \text{ kcal}.$			
$\Delta H_{16} = \Delta H_7 + 2\Delta H_{10} - 8\Delta H_{11} + 2\Delta H_{12} - \Delta H_{13} - \Delta H_{14} - 8\Delta H_9$			
(16) $8\text{SiO}_{2(c)} + \text{Li}_2\text{O}_{(c)} + \text{Al}_2\text{O}_{3(c)} = \text{Li}_2\text{Al}_2\text{Si}_8\text{O}_{20(c)}$ $\Delta H_{16} = -50.602 \pm 1.18 \text{ kcal} = -50.6 \pm 1.20 \text{ kcal}.$			

The enthalpy of formation of petalite for reaction 15 from the constituent elements was derived from these reactions and heats according to the scheme

$$\Delta H_{15} = \Delta H_7 + 8\Delta H_8 - 8\Delta H_9 + 2\Delta H_{10} - 8\Delta H_{11} + 2\Delta H_{12}.$$

This combination of reactions and heats provided

$$\Delta H_{298.15}^\circ = 2,335.812 \pm 2.84 \text{ kcal}.$$

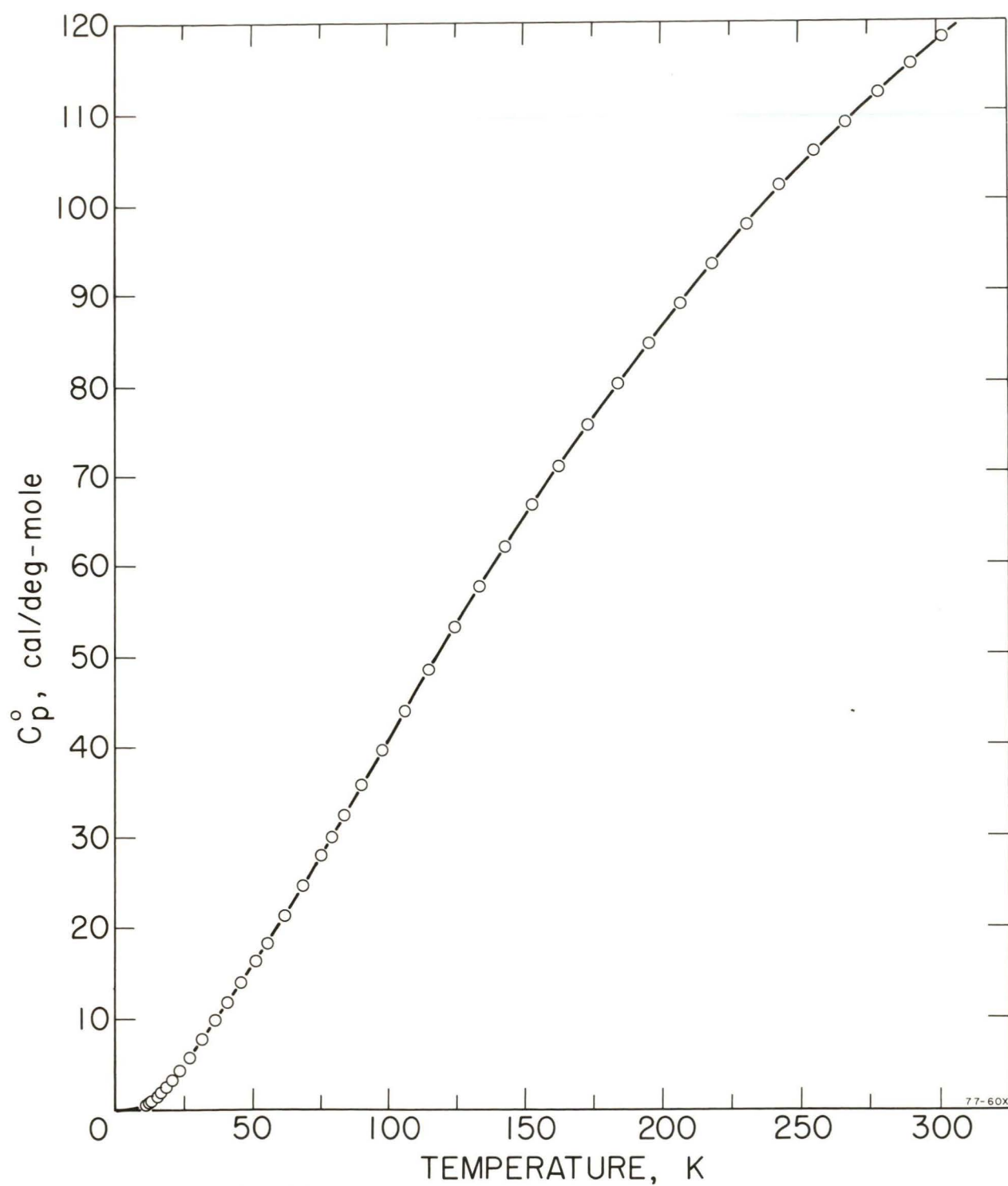


FIGURE 1. - Low-temperature heat capacity of petalite.

To derive the enthalpy of petalite from its constituent oxides, the enthalpies of formation of Al_2O_3 and Li_2O are needed in addition to data already quoted, and are represented by reactions 13 and 14 with their enthalpy values and uncertainties. The source for the data for reaction 15 was Mah (22), and the data source for reaction 14 was Johnson (15). Combination of reactions and enthalpies according to the scheme

$$\Delta H_{16} = \Delta H_7 + 2\Delta H_{10} + 2\Delta H_{12} - 8\Delta H_{11} - \Delta H_{13} - \Delta H_{14} - \Delta H_9$$

provides ΔH_{298}° (from oxides) = -50.602 ± 1.18 kcal.

Low-Temperature Heat Capacity

The heat capacity of petalite was measured by adiabatic calorimetry over the nominal temperature range 10 to 300 K. Design data and operational details of this calorimeter have been described elsewhere (34).

The low-temperature petalite sample was dried at 383 K before loading into a 90-ml copper calorimeter vessel. Prior to sealing, the loaded calorimeter vessel was evacuated and backfilled with about 10^{-4} moles of helium gas to enhance thermal conductivity. Approximately 0.174 g-mole of petalite was used for heat capacity measurements. The empty calorimeter assembly had a heat capacity of about 9 cal/K at 300 K.

Above 15 K, temperatures of the sample were measured with a calibrated platinum resistance thermometer in accordance with IPTS-68 (3). Below 15 K, temperature was determined with a calibrated germanium resistance thermometer for greater resolution. All measurements of time, voltage, and resistance were based on standards traceable to NBS certification.

Adiabatic heat capacity measurements were accomplished using the incremental heating method. The resulting experimental values are listed in table 5 and displayed graphically in figure 1. These data have been corrected to an ideal petalite formula $\text{Li}_2\text{Al}_2\text{Si}_8\text{O}_{20}$ with a molecular weight of 612.521. The values for heat capacity and related functions at even temperatures were obtained by computer smoothing the experimental data, and the resulting values are given in table 6. The entropy below 10 K was determined by extrapolation using a modified Debye function. The overall uncertainty of the tabulated smooth heat capacities varied with temperature and was estimated as 2 pct for 10 to 20 K, 0.5 pct for 20 to 50 K, and 0.2 pct for 50 to 300 K. Some of the tabulated data are reported to greater resolution only for convenience of rounding.

TABLE 5. - Experimental low-temperature heat capacities of petalite

T, K	C_p° , cal/deg-mole	T, K	C_p° , cal/deg-mole	T, K	C_p° , cal/deg-mole
10.69	.485	55.18	18.24	162.32	70.85
11.65	.647	61.39	21.28	172.98	75.38
12.82	.879	68.32	24.69	184.14	79.98
14.95	1.395	74.98	27.98	195.42	84.44
16.54	1.860	79.04	30.01	206.84	38.81
18.27	2.423	83.36	32.35	218.61	93.14
20.55	3.258	89.76	35.70	231.08	97.42
23.26	4.318	97.55	39.50	242.91	101.74
26.79	5.746	105.97	43.80	255.43	105.58
31.34	7.740	115.14	48.49	266.91	108.73
36.04	9.802	124.51	53.15	278.83	112.09
40.71	11.792	133.57	57.59	290.56	115.23
45.52	13.953	142.88	61.99	302.11	118.18
51.02	16.33	152.50	66.63		

TABLE 6. - Low-temperature thermodynamic properties of petalite

T, K	C_p° , cal/deg-mole	S° , cal/deg-mole	$-(G^\circ-H_0^\circ)/T$, cal/deg-mole	$H^\circ-H_0^\circ$, cal/mole
10	0.408	0.111	0.021	0.904
15	1.399	.435	.097	5.067
20	3.044	1.053	.253	16.008
25	5.020	1.941	.498	36.074
30	7.149	3.043	.828	66.46
35	9.326	4.308	1.233	107.64
40	11.515	5.696	1.703	159.74
45	13.704	7.179	2.228	222.79
50	15.89	8.736	2.801	296.77
60	20.71	12.056	4.063	479.61
70	25.67	15.62	5.457	711.4
80	30.72	19.38	6.964	993.3
90	35.81	23.29	8.558	1325.9
100	40.90	27.32	10.225	1709.5
110	45.96	31.46	11.971	2143.8
120	50.96	35.67	13.766	2628.5
130	55.86	39.95	15.62	3162.7
140	60.64	44.26	17.51	3745.3
150	65.29	48.61	19.44	4375.0
160	69.79	52.96	21.39	5051
170	74.14	57.33	23.39	5770
180	78.33	61.68	25.39	6533
190	85.37	66.03	27.41	7337
200	86.27	70.35	29.45	8180

TABLE 6. - Low-temperature thermodynamic properties of petalite--Continued

T, K	C_p° , cal/deg-mole	S° , cal/deg-mole	$-(G^\circ-H_0^\circ)/T$, cal/deg-mole	$H^\circ-H_0^\circ$, cal/mole
210	90.02	74.65	31.50	9061
220	93.63	78.92	33.56	9980
230	97.10	83.16	35.63	10933
240	100.43	87.37	37.70	11921
250	103.63	91.53	39.76	12942
260	106.69	95.66	41.84	13993
270	109.62	99.74	43.91	15075
273.15	110.51	101.02	44.53	15422
280	112.41	103.78	45.98	16185
290	115.08	107.77	48.04	17323
298.15	117.18	110.99	49.72	18269
300	117.65	111.71	50.09	18487

High-Temperature Enthalpy Determinations

The enthalpies above 298 K were determined with the copper-block drop calorimeter described by Douglas (8). This apparatus was modified to incorporate a more sensitive potentiometric system. The copper block has a heat capacity of approximately 1.51 kcal/deg. Before and after measurements were made of substances, the calorimeter was calibrated electrically and the entire apparatus was checked by measuring the enthalpy of magnesium oxide.

The sample of petalite that weighed 6.0511 grams was corrected for vacuum and was loaded into the platinum-10 pct rhodium alloy sample container. It was then dried to constant weight at 873 K to remove the 0.37 pct excess water shown in table 1. X-ray analysis indicated that no change occurred due to drying. The capsule was evacuated in a drybox and backfilled with 1 atmosphere of nitrogen. The capsule neck was squeezed gastight and was fusion-sealed in air, while the sample portion was immersed in ice water. The enthalpy of the empty capsule was determined separately and was about 20 pct of the total.

The experimental enthalpy values, which were corrected according to the adjusted formula, are given in table 7. These enthalpies were computer-fitted with a smooth curve by a polynomial function (17). During this fitting procedure, care was taken to merge the high-temperature enthalpies with the low-temperature data given previously. The smooth curve and the experimental enthalpies are shown in figure 2. The smooth enthalpy values are listed in table 8 along with related thermodynamic properties that were also derived from the polynomial function.

TABLE 7. - Experimental high-temperature enthalpies of petalite

T, K	H°-H ₂₉₈ °, kcal/mole	T, K	H°-H ₂₉₈ °, kcal/mole	T, K	H°-H ₂₉₈ °, kcal/mole
402.6	13.55	702.0	61.26	1001.1	115.00
452.5	20.74	752.5	70.04	1052.8	124.70
502.5	28.32	802.0	78.84	1101.8	133.90
554.9	36.56	851.6	87.75	1147.4	142.40
601.1	44.18	901.6	96.87	1193.6	151.20
651.8	52.63	952.2	106.10		

TABLE 8. - High-temperature thermodynamic properties of petalite

T, K	C _p °, cal/deg-mole	S°, cal/deg-mole	-(G°-H ₂₉₈ °)/T, cal/deg-mole	H°-H ₂₉₈ °, kcal/mole
298.15	117.2	111.0	111.0	0.
300	117.6	111.7	111.0	.22
350	130.0	130.9	112.5	6.43
400	139.7	148.9	116.0	13.18
450	147.8	165.8	120.5	20.37
500	154.6	181.7	125.8	27.94
550	160.4	196.8	131.7	35.82
600	165.3	210.9	137.6	43.96
650	169.4	224.3	143.8	52.33
700	173.0	237.0	150.0	60.90
750	175.9	249.0	156.2	69.62
800	178.4	260.5	162.4	78.48
850	180.5	271.4	168.5	87.45
900	182.3	281.7	174.4	96.53
950	183.8	291.6	180.3	105.7
1000	185.1	301.1	186.2	114.9
1050	186.3	310.2	191.9	124.2
1100	187.4	318.8	197.4	133.5
1150	188.5	327.2	202.9	142.9
1200	189.7	335.2	208.2	152.4
1250	191.0	343.0	213.5	161.9

The following standard form equation, derived by the method described by Kelley (18), represents the smooth enthalpy increments. The equation is expressed in kilocalories per mole and shows the temperature range of validity and the percent average deviation from the experimental data in parentheses.

$$\begin{aligned} \text{Petalite: } H^\circ - H_{298}^\circ &= 147.175 \times 10^{-3}T + 22.191 \times 10^{-6}T^2 \\ &+ 38.409 \times 10^2T^{-1} - 58.735 \quad (298-1,250 \text{ K}; 0.4 \text{ pct}) \end{aligned}$$

Enthalpy determinations were discontinued at 1,194 K because X-ray analysis on several separate samples showed that petalite decomposed to substantial

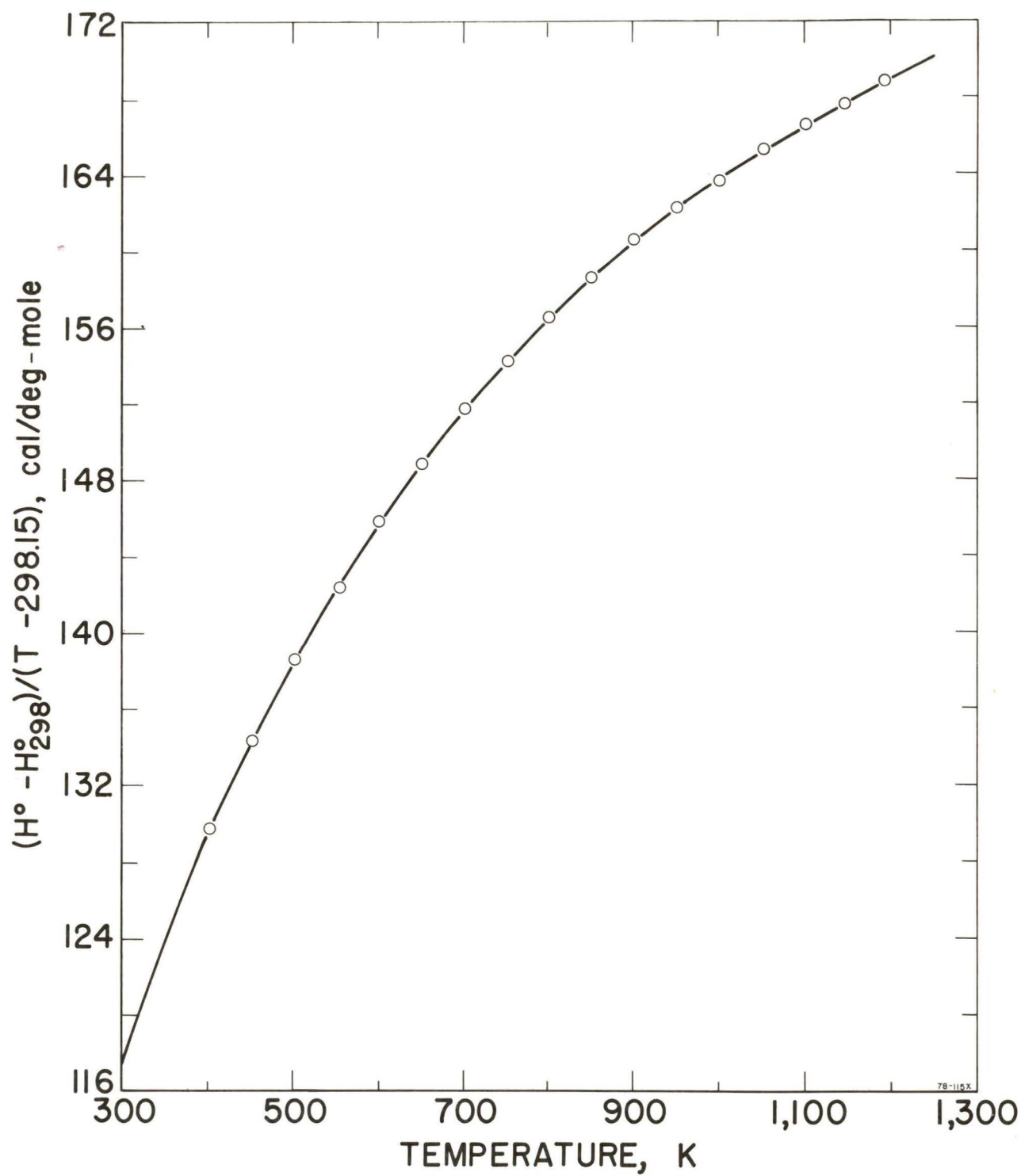


FIGURE 2. - High-temperature mean heat capacity of petalite.

amounts of β -spodumene above this temperature. Roy (29) found the upper limit of stability of naturally occurring petalite to be $953 \pm 10\text{K}$ before decomposition to β -spodumene.

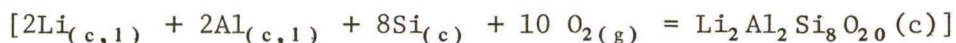
Enthalpies and Gibbs Energies of Formation

The experimental data for petalite presented in the foregoing sections of this report were combined with the necessary data for the constituent elements and oxides to calculate the enthalpies and Gibbs energies of formation. The information on the thermodynamic data not previously quoted is presented in table 9, which shows the type of data for each element or compound and the literature source.

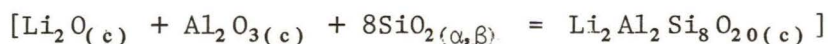
TABLE 9. - Auxiliary thermodynamic data

Element or compound	Function	Source	Reference
Al(c,l).....	S_{298}°	CODATA No. 28.....	12
	All other data.....	Hultgren.....	11
Al ₂ O ₃ (α ,l).....	S_{298}°	CODATA No. 28.....	12
	$\Delta H_f^{\circ}{}_{298}$	Mah.....	22
	$H_T^{\circ}(\text{c})$	Ditmars.....	7
Li (c,l).....	S_{298}°	CODATA No. 28.....	11
	All other data.....	Hultgren.....	11
Li ₂ O (c).....	$\Delta H_f^{\circ}{}_{298}$	Johnson.....	15
	S_{298}°	Johnston.....	16
	H_T°	Shomate.....	30
O ₂ (g).....	All data.....	JANAF.....	9
Si (c,l).....	All data.....	Hultgren.....	11
SiO(α , β).....	$\Delta H_f^{\circ}{}_{298}$	Wise.....	39
	S_{298}°	Kelley.....	19
	H_T°	Moser.....	24
	H_T°	Roth.....	27
	H_T°	White.....	37
	H_T°	Wietzel.....	38

The enthalpy and Gibbs energy values for the formation of petalite from the elements and oxides are given in tables 10 and 11. Petalite is shown to be stable relative to the elements throughout the range of the data with a decreasing stability. It is shown to be stable, with increasing stability, relative to the oxides. This may appear anomalous; however, it is owing to the relative changes of stability of lithia compared with the more refractory corundum and silica, (4).

TABLE 10. - Formation data for petalite from the elements

T, K	ΔH_f° , kcal	ΔG_f° , kcal	Log K	T, K	ΔH_f° , kcal	ΔG_f° , kcal	Log K
298.15	-2,335.8	-2,203.8	1,615.43	800	-2,332.6	-1,931.1	541.21
300	-2,335.8	-2,203.0	1,604.88	900	-2,330.6	-1,937.2	470.42
400	-2,336.4	-2,158.6	1,179.40	² 933.61	-2,329.9	-1,922.5	450.04
¹ 453.7	-2,336.3	-2,134.7	1,028.30	933.61	-2,335.1	-1,922.5	450.04
453.7	-2,337.7	-2,134.7	1,028.30	1,000	-2,333.6	-1,893.2	413.76
500	-2,337.4	-2,114.0	924.03	1,100	-2,331.4	-1,849.3	367.42
600	-2,336.3	-2,069.5	753.81	1,200	-2,329.0	-1,805.5	328.83
700	-2,334.6	-2,025.1	632.26	1,250	-2,327.8	-1,783.8	311.88

¹Melting point of Li.²Melting point of Al.TABLE 11. - Formation data for petalite from the oxides

T, K	ΔH_r° , kcal	ΔG_r° , kcal	Log K	T, K	ΔH_r° , kcal	ΔG_r° , kcal	Log K
298.15	-50.6	-53.5	39.22	¹ 847	-53.0	-58.5	15.09
300	-50.5	-53.5	38.97	847	-54.4	-58.5	15.09
400	-50.5	-54.5	29.78	900	-54.4	-58.7	14.25
500	-50.6	-55.4	24.22	1,000	-54.4	-59.2	12.94
600	-50.8	-56.4	20.54	1,100	-54.3	-59.7	11.86
700	-51.1	-57.3	17.89	1,200	-54.0	-60.1	10.95
800	-52.0	-58.1	15.87	1,250	-53.9	-60.4	10.56

¹Transition point of SiO₂.

DISCUSSION

There are no known thermodynamic data on the mineral petalite, a lithium aluminosilicate appearing in the system Li₂O-Al₂O₃-SiO₂. Other closely related minerals in this system with lithia-alumina-silica ratios of 1:1:2 (eucryptite) and 1:1:4 (spodumene) were studied by this laboratory, and the thermodynamic data were published (1, 26).

This oxide system has been investigated in detail by Roy (29), whose group was able to synthesize petalite over a wide range of composition with oxide ratios from 1:1:4 to 1:1:12. Their X-ray structural determinations use 1:1:8 as the most probable formula, and that formula was used for this study. The chemical analysis for this specimen of petalite adapted most closely to this composition.

An analysis reported by Nel (25) for a petalite from Karibib, South West Africa, is very close to the composition of the material used for this study. He expressed the unit cell formula as $\text{Li}_4\text{Al}_4\text{Si}_{16}\text{O}_{40}$. Calculations used in this work follow the example of Deer (6) using 20 oxygen atoms.

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