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Measured Enthalpy and Derived Thermodynamic Properties of Solid and Liquid Lithium Tetrafluoroberyllate, Li_2BeF_4, from 273 to 900 K[1]

Thomas B. Douglas and William H. Payne[2]

Institute for Basic Standards, National Bureau of Standards, Washington, D.C. 20234

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The enthalpy of a sample of lithium tetrafluoroberyllate, Li_2BeF_4, of 98.6 percent purity was measured relative to 273 K at eleven temperatures from 323 to 873 K. Corrections were applied for the impurities and for extensive premelting below the melting point (745 K). The enthalpy and heat capacity, and the entropy and Gibbs free-energy function relative to the undetermined value of $S^\circ_{298.15}$, were computed from empirical functions of temperature derived from the data, and are tabulated from 273 to 900 K.

Key words: Drop calorimetry; enthalpy data; lithium beryllium fluoride; lithium tetrafluoroberyllate; premelting; thermodynamic properties.

1. Introduction

As part of a long-term research program at the National Bureau of Standards on the thermodynamic properties of the simpler light-element compounds, the measurements of high-temperature enthalpy have included several well-defined substances which may be regarded as double oxides or double fluorides of two metals. Such results have been published in two papers for $BeO \cdot Al_2O_3$ ($BeAl_2O_4$) and $BeO \cdot 3Al_2O_3$ ($BeAl_6O_{10}$) [1],[3] are being obtained for $3LiF \cdot AlF_3$ (Li_3AlF_6), and are presented in this paper for $2LiF \cdot BeF_2$ (Li_2BeF_4). The standard heats of formation and heat capacities of some "double" compounds of this type are very nearly the same as the values calculated additively from the parent binary compounds (in the same state), but in other cases there are considerable differences.

The United States molten salt reactor program has in recent years provided several notable demonstrations of feasible examples. In nearly any foreseeable thermal reactor of this type, the solvent for the fissile and/or fertile material is an LiF-BeF_2 mixture of composition near that of Li_2BeF_4 [2]. Accordingly, the thermodynamic properties of this compound are of great practical importance in this developing technology.

The temperature-composition phase diagram of the condensed phases of the LiF–BeF_2 system has been investigated in a number of laboratories. The version in a fairly recent compilation of phase diagrams [3] is based on the results of two groups of workers [4, 5]. Another composite diagram [6] is based on the results of the above workers, as well as on those from two other publications [7, 8] and additional work unpublished at that time. A more recent version of the phase diagram, which is in essential agreement with the two already mentioned, is reproduced here as figure 1; it is based largely on a comprehensive study at the Oak Ridge National Laboratory [9]. One group of workers [5] reported a compound $LiF \cdot 2BeF_2$ not found in other laboratories. There is general agreement, however, on the existence of the two solid compounds in the LiF–BeF_2 system indicated in figure 1. It will be noted that Li_2BeF_4, the compound of interest in this paper, is not quite congruent-melting, showing a peritectic point. The liquid field is continuous, but when it has the stoichiometric composition of Li_2BeF_4 it may be regarded as the liquid phase of this compound.

Crystalline Li_2BeF_4 exhibits an unusually small volume change when it melts (no more than 2 or 3 percent [10]). This is attributed to the existence of two continuous void channels penetrating the unit cell of the crystal, an unusual feature revealed by a recent quantitative structure determination [11]. A consequence of this feature is that the crystal density of Li_2BeF_4 is about 15 percent less than that computed additively from the two component binary fluorides. An investigation of the thermodynamic activities of

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[2] Present address: Science Information Exchange, 1730 M St., N.W., Washington, D.C. 20036.

[3] Figures in brackets indicate the literature references at the end of this paper.

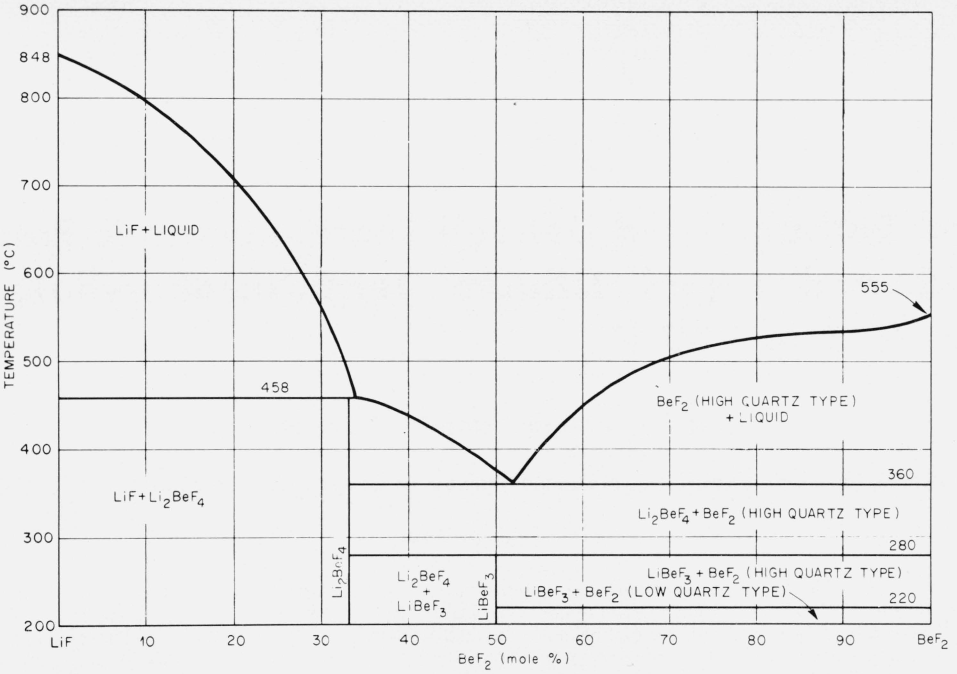

FIGURE 1. *The temperature-composition phase diagram of the LiF-BeF$_2$ system (from ref. [9]).*

the components of the liquid LiF$-$BeF$_2$ system has recently been published [12].

Besides the above solid compounds in the LiF$-$BeF$_2$ system, two gaseous compounds are known: from mass-spectrometric work the heats of formation at 900 K of LiBeF$_3$(g) [13] and Li$_2$BeF$_4$(g) [14] have been reported. The heat of formation of crystalline Li$_2$BeF$_4$ at 298 K also has been reported [15].

The measurements of enthalpy of Li$_2$BeF$_4$ reported in this paper cover the temperature range 0 to 600 °C. Because the sample was only 98.6 percent pure, there was extensive "premelting" in the region 400$-$470 °C, and the large corrections which this necessitated are sufficiently uncertain as to leave the derived heat of fusion much more uncertain than if the sample had been highly pure. In addition, no low-temperature heat-capacity measurements on Li$_2$BeF$_4$ are available to enable the calculation of values of absolute entropy from the data.

2. Sample

The sample of lithium tetrafluoroberyllate was prepared by the Oak Ridge National Laboratory, of Oak Ridge, Tenn., by heating together in calculated proportions LiF and BeF$_2$ to form a single liquid phase, followed by distillation of NH$_4$HF$_2$ from the material in order to replace any oxygen present by fluorine. According to subsequent petrographic and x-ray examinations at ORNL, the colorless crystalline sample consisted of a single phase within the detection limits of these methods.

After the sample was received, a portion of it (about 3.3 g) was encased in a container of pure silver and heated electrically in an efficient dry box for an hour at about 400 °C, in order to remove any volatile impurities that might have been produced by the accidental entrance of moisture during handling. The silver container was then sealed gas-tight by flame-welding, and further enclosed within a container of 80 Ni$-$20 Cr as a further precaution against escape of the toxic sample by volatilization or leakage during the subsequent enthalpy measurements.

After the completion of the enthalpy measurements, described in section 3, the sample was analyzed chemically and spectrochemically in the Analytical Chemistry Division of the Bureau. The results of the chemical analyses are given in table 1. The qualitative spectrochemical analysis indicated the presence of the following additional elements in the ranges of abundance stated as weight percentages: 0.001$-$0.01 percent each of Ag, Al, Cu, Fe, K, Mn, Na, Si, Ti, and Zr; 0.0001$-$0.001 percent each of Ba, Ni, and Pb. (Thirty-five other elements were sought but not detected.)

The deduction of the chemical composition of the sample was based entirely on table 1. It was assumed that the metals were present in their highest oxidation states, and the deficiency of fluorine in relation to the total equivalents of metal was assumed to be accounted for by oxygen, which was not analyzed for. Using the mean analyses given in the last column of table 1, this procedure accounted for 99.8 percent by weight of the sample. However, the percentage of fluorine is obviously the least precisely determined, so the percentage of this element was then taken to be 76.34 so that the percentages would add to exactly 100 percent. The corresponding elemental composition of the sample then becomes the same as that of table 2, which was used for correcting the thermal data to the basis of pure Li$_2$BeF$_4$ in the manner described in section 4.

TABLE 1. *Chemical analysis of the sample*

Element	Individual analyses	Mean
	Weight %	*Weight %*
Li	[a]13.87, [a]13.85	[b]13.85
Be	9.36, 9.33	9.34
F	76.42, 75.90, 75.56, 75.91	75.95
Ca	< 0.01	0.005
Mg	0.01	.01
Cr	< 0.01	.005
Sr	0.02	.02

[a] Uncorrected for Ca, Mg, Cr, and Sr.

[b] This value includes a correction of −0.01 percent to account for the Ca, Mg, Cr, and Sr.

TABLE 2. *Assumed chemical composition of the sample*

Substance	Relative No. of moles	Substance	Relative No. of moles
Li_2BeF_4	1	SrF_2	0.0002
BeO	0.0269	CaF_2	.0001
BeF_2	.0121	CrF_3	.0001
MgF_2	.0004		

3. Enthalpy Measurements

The enthalpy measurements were made using the "drop" method, which, as used in this laboratory, is described in detail in a recent publication [16]. Briefly, the method is as follows. The sample in its container is suspended inside a vertical thick-wall silver pipe in a furnace until it has had time to reach the temperature of the silver. It is then dropped into a Bunsen ice calorimeter, which precisely measures the heat evolved by the sample and container in cooling to 0 °C (273.15 K). In order to account for the enthalpy change of the container itself and the small amount of heat lost from its surface during the drop, a separate measurement is made on the empty container at the same furnace temperature. In the present case the measurements with and without the sample present employed the same outer (80 Ni–20 Cr) container, but utilized different though entirely comparable inner containers of pure silver having identical masses.

For the present measurements the furnace temperature was measured by two Pt/Pt–10 percent Rh thermocouples (as a precaution against any sudden shifts in the differences between their readings, which did not occur). One of these thermocouples was calibrated before the enthalpy measurements by the NBS Pyrometry Laboratory, and it agreed with another similarly calibrated thermocouple when the two were compared in the furnace.

The heats observed in individual measurements are listed (in joules) in table 3 (columns 3 and 4). These values are for the actual sample and container used, except that corrections have been applied for very small unavoidable departures from the "standard" masses of parts of the container system, but not for impurities or premelting. For each furnace temperature the values are given in chronological order, although the different furnace temperatures were run in somewhat random order. As always with this method, the times in the furnace adequate for reaching thermal equilibrium were predetermined from preliminary measurements at one temperature with deliberately inadequate times. The times actually used are shown in column 2 of table 3. As a further precaution, considerably different times for duplicate measurements at most of the temperatures were deliberately chosen. A second precaution was to hold the sample for a few minutes at temperatures higher than the final ones, in the case of one measurement at 470.05 °C and one at 500.10 °C (see table 3), to hasten the slow process of fusion at these temperatures near the melting point. However, there is no correlation between columns 2 and 3 of the table that might suggest the appreciable lack of thermal equilibrium for any of the measurements.

The derivation of columns 5–9 of table 3 is discussed in the next section.

4. Treatment of the Data

The purpose of the present investigation was to determine thermodynamic properties (those derivable from enthalpy data) of pure Li_2BeF_4, not the actual sample measured nor even an odd composition of the LiF-BeF_2 system. It is convenient to correct the enthalpy data for the deviation of the sample composition from pure Li_2BeF_4 in two steps, firstly for the impurities indicated by table 2 and secondly for the "premelting" of the Li_2BeF_4 which they caused.

Figure 1 shows qualitatively the expected equilibrium behavior as the temperature is raised above 200 °C. No polymorphic transition of pure Li_2BeF_4 is indicated, but at the peritectic temperature it decomposes completely into a liquid richer in BeF_2 and a small amount of LiF(*c*), and several degrees higher (when the highest liquidus curve is crossed) all solid has disappeared and the liquid has regained the composition Li_2BeF_4. If the actual sample represented by table 2 behaved as Li_2BeF_4 with a small proportion of additional BeF_2, it was completely solid at and below 300 °C, but had successively increasing proportions of liquid at 400, 425, and 450 °C, and may have been all liquid at 470 °C.

After averaging the entries in column 3 of table 3 for each furnace temperature (column 1), subtracting the corresponding average for the empty container (column 4), and converting this net enthalpy to a molar basis (defining 1 mole as 1 gram-formula-weight of Li_2BeF_4), the total correction listed in column 5 for the impurities given in table 2 was applied on the basis of replacing the impurities by the same mass of Li_2BeF_4. The correction for BeO(*c*) was computed from accurate results obtained in this laboratory [17], that for BeF_2(*c*) was computed from results of drop calorimetry elsewhere [18], and that for the small amounts of the four additional fluorides was assumed to be equivalent to the same number of atoms of BeF_2. A further impurity correction of −293 J (per mole of Li_2BeF_4) was applied above 300 °C: without knowing what fraction of the impurities was dissolved in the liquid solutions or what their heats of solution are, this minor correction was estimated as half the heat of fusion (derived below) of the amount of Li_2BeF_4 having the same number of atoms as the impurities.

The corrections for premelting can be predicted to be large, and in the absence of further experimental data (such as enthalpy measurements on another sample of somewhat different composition) no rigor-

TABLE 3. *Relative enthalpy of lithium tetrafluoroberyllate,* Li_2BeF_4

1. Furnace temperature,[a] t	2. Time sample in furnace	Individual enthalpy measurements		Corrections		Net enthalpy of Li_2BeF_4 [g]		9. Mean obs. — calc.
		3. Container plus sample [b, c]	4. Empty container [d]	5. Impurities[e]	6. Premelting[f]	7. Mean observed [h]	8. Calc. from equations	
°C	*min*	*J*	*J*	*J mol⁻¹*	*J mol⁻¹*	*J mol⁻¹*	*J mol⁻¹*	*J mol⁻¹*
50.00	56	609.36	378.48	+21	0	6,837	6,763	+74
	60	610.57	380.12					
100.00	…	…	780.65	+34	0	13,849	13,898	−49
	…	…	782.95					
	…	…	777.97					
	54	1,248.55	778.77					
	59	1,247.71	778.77					
	…	…	781.65					
	…	…	782.12					
	…	…	782.78					
200.05	…	…	1,601.1	+67	0	29,296	29,296	0
	44	2,592.9	1,603.7					
	33	2,594.7	1,610.8					
	…	…	1,604.0					
	…	…	1,603.6					
300.05	46	4,015.4	2,455.0	+100	0	46,183	46,178	+5
	30	4,015.1	2,455.8					
	62	4,014.1	…					
400.10	44	5,562.8	3,341.6	−134	−1,218	64,559	64,561	−2
	46	5,567.6	3,340.4					
425.10	35	5,987.0	3,554.8	−109	−2,276	69,408	69,387	+21
	48	5,988.5	3,553.7					
450.05	58	6,496.7	3,791.7	−50	−5,820	74,279	74,295	−16
	38	6,496.7	3,788.7					
470.05	42	8,097.6	3,961.3	+464	0	122,528	122,637	−109
	[i] 86	8,096.6	3,963.2					
500.10	41	8,612.7	4,243.5	+494	0	129,721	129,612	+109
	[j] 78	8,617.6	4,240.5					
	…	…	4,241.3					
550.10	…	…	4,707.5	+531	0	141,059	141,218	−159
	47	9,458.4	4,697.4					
	76	9,457.6	4,708.2					
	48	9,462.2	4,701.2					
	…	…	4,704.9					
600.15	62	10,333.0	5,173.7	+577	0	152,984	152,833	+151
	39	10,332.5	5,176.4					

[a] International Practical Temperature Scale of 1968 [20].

[b] Sample mass = 3.3463 g.

[c] Uncorrected for sample impurity.

[d] Before computing the mean net enthalpy of the sample, the mean of the values in this column for each of four temperatures was incremented by a small amount to agree with a smooth plot of $(H-H_{0\,°C})/t$ versus t for the empty container: −6.4 J at 400.10 °C, +3.9 J at 425.10 °C, −5.7 J at 450.05 °C, and +4.1 J at 470.05 °C.

[e] For all temperatures above 300.05 °C this column includes a correction of −293 J (per mole of Li_2BeF_4) for the assumed heat of fusion of the impurities (see text).

[f] See text.

[g] Molecular weight = 98.884. Enthalpy relative to that of the solid at 0 °C.

[h] Corrected for sample impurity and for premelting.

[i] Temperature of container plus sample first raised momentarily to 500 °C to hasten completion of fusion.

[j] Temperature of container plus sample held at 525–550 °C for first 10 min of heating period to insure completion of fusion.

ously accurate means of determining them is available. This fact made it desirable first to derive tentative enthalpy-temperature equations for the pure solid and liquid, later testing them for consistency with the best empirical estimation of the premelting corrections that could be devised.

The heats of the small amounts of solid-phase reproportionation below 400 °C (see fig. 1) were considered negligible, and the four mean observed enthalpies up to and including that at 300.05 °C (table 3, column 7) were used to derive (by the least-square method) the coefficients of an equation which was tentatively assumed to apply to pure solid Li_2BeF_4 up to its melting point [identical with eq (2), sec. 5, except referred to the enthalpy of the crystal at 0 °C]. (In an attempt to decrease the deviations, which are the first four entries in column 9 of the table, fits were tried using an additional term proportional to T^{-n}, with n varying from 0.5 to 4, but the standard deviations of fit were considerably greater.) The four mean observed enthalpies at and above 470.05 °C (table 3, column 7) vary almost linearly with temperature, and were similarly used to derive the coefficients of an equation assumed to apply to pure liquid Li_2BeF_4 relative to the solid at 0 °C [identical with eq (6), sec. 5, except that its constant term differs by the amount indicated by eq (2)]. Since these two enthalpy equations for the solid and the liquid are both based on the solid at the same temperature (0 °C), their difference represents the heat of fusion as a function of temperature. For simplicity, the incongruent melting of Li_2BeF_4 over the short temperature range from the peritectic temperature to the "freezing point" was ignored as though this incongruency were suppressed (fig. 1), and the liquidus curve below the peritectic temperature was extrapolated to a "congruent" melting point of 472 °C ($T_m = 745.2$ K).[4] At this temperature the heat of fusion of Li_2BeF_4, arrived at as described above, is 44,400 J mol^{-1} (equivalent to the reasonable value of 2.03 cal g-atom^{-1} K^{-1} for the entropy of fusion).

Since premelting over a range of some 70 kelvins is to be considered, its thermodynamic consideration should not involve unnecessary approximations applicable only to temperatures much nearer the melting point. It can be shown that if the impurities are insoluble in the main substance when it is solid but form ideal solutions with it when it is liquid, the enthalpy correction for premelting, per mole of main substance at absolute temperature T, is

$$\Delta H = -nL_f \Big/ \left\{\exp \int_T^{T_m} [L_f(T)/RT^2]dT\right\} - 1, \qquad (1)$$

where T_m and L_f are respectively the absolute melting point and molar heat of fusion of the main substance, n being the number of moles of impurity in solution in the liquid part of one mole of the main substance, and R being the molar gas constant. Equation (1) is applicable also to non-ideal solutions if actual molecular weights are replaced by effective ones (which may change somewhat with temperature), but for electrolytic solutions such as the present one, it is difficult to say what these effective molecular weights are. However, taking the formula weight of Li_2BeF_4 as its molecular weight and, as above, $T_m = 745.2$ K, the constant value of n with which eq (1) gives the best fit of the mean observed corrected enthalpy values at 400.10, 425.10, and 450.05 °C to the above enthalpy equation for the solid (which is based wholly on observed values at lower temperatures) proved to be 0.03216. (This is about 80 percent of the sum of the moles of impurity in table 2.) The corresponding corrections for premelting are given in column 6 of table 3. [Corrections of roughly the same respective magnitudes can be calculated by ignoring eq (1) and using instead the "$Li_2BeF_4(c)$" liquidus curve of the phase diagram (fig. 1).]

It is striking that the three non-zero premelting corrections in table 3 are in magnitude many times the corresponding final deviations between the observed and equation values given in column 9. This good agreement for the calculated premelting corrections, while probably somewhat fortuitous, seems to justify regarding the tentative enthalpy equation for the solid [eq (2)] as a good representation of the enthalpy below the melting point. Nevertheless, it corresponds to a heat capacity increasing strictly linearly with temperature [eq (3)], whereas many pure ionic solids are now known to possess heat capacity-temperature curves with appreciable upward curvature near the melting point owing to lattice vacancies. Such an effect in Li_2BeF_4 would lead to a lower heat of fusion than that calculated in this paper.

5. Thermodynamic Functions

The following numerical equations, which resulted from the enthalpy equations derived from the data as outlined in section 4, gives the final values of the enthalpy (H), heat capacity (C_p), and entropy (S) of solid and liquid lithium tetrafluoroberyllate, Li_2BeF_4, adopted in this paper. Since enthalpy and heat-capacity data on this substance are not available below 273.15 K, the enthalpy and entropy are given relative to the respective values for the solid at the standard thermodynamic temperature 298.15 K, though the equations for the solid are valid (with increasing uncertainty, as mentioned later) down to 273.15 K. The units are joules per mole for energy (with 1 mole = 98.884 g), and kelvins (International Practical Temperature Scale of 1968 [20]) for the absolute temperature T.

Solid $Li_2BeF_4(c)$, 273.15–745.2 K:

$$H^\circ - H^\circ_{298.15} = -33698.8 + 90.7970T + 0.0745589T^2 \qquad (2)$$

$$C^\circ_p = 90.797 + 0.149118T \qquad (3)$$

$$S^\circ - S^\circ_{298.15} = -561.786 + 90.7970 \ln T + 0.149118T \qquad (4)^5$$

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[4] This temperature was estimated by consideration of the phase diagram of reference [6] as well as that of figure 1, and is uncertain by a few degrees.

[5] "ln" indicates the natural logarithm (base e).

Fusion, 745.2 K:

$$\Delta H^\circ_m = 44400; \qquad \Delta S^\circ_m = 59.58 \tag{5}$$

Liquid $Li_2BeF_4(l)$, 745.2–900 K:

$$H^\circ(l) - H^\circ_{298.15}(c) = -53187.0 + 232.0907T \tag{6}$$

$$C^\circ_p = 232.09 \tag{7}$$

$$S^\circ(l) - S^\circ_{298.15}(c) = -1325.550 + 232.0907 \ln T \tag{8}$$[5]

Values calculated from eqs (2)–(4) and (6)–(8) are listed in table 4, the Gibbs free-energy function relative to the entropy of the solid at 298.15 K being computed from the thermodynamic relation

$$[-(G^\circ - H^\circ_{298.15})/T - S^\circ_{298.15}] = [S^\circ - S^\circ_{298.15}] - [(H^\circ - H^\circ_{298.15})/T]. \tag{9}$$

For convenience, table 4 is repeated as table 5 except in terms of the defined calorie (= 4.1840 joules) instead of the joule, since the defined calorie is commonly used in the calculations of chemical thermodynamics.

While experimental data are presently lacking from which a reliable value for $S^\circ_{298.15}$ of the solid can be evaluated, an estimated value may be used with table 4 or 5 to provide estimated values of the absolute

TABLE 4. *Thermodynamic functions for lithium tetrafluoroberyllate (Li_2BeF_4) solid and liquid phases (in terms of* **JOULES** *per mole)*

(1 mole=98.884 g; International Practical Temperature Scale of 1968)

T	$H^\circ - H^\circ_{298}$	C°_p	$S^\circ - S^\circ_{298}$	$-(G^\circ - H^\circ_{298})/T - S^\circ_{298}$
K	*J mol⁻¹*	*J mol⁻¹ K⁻¹*	*J mol⁻¹ K⁻¹*	*J mol⁻¹ K⁻¹*
		Solid Phase		
273.15	−3335	131.53	−11.68	0.53
275	−3091	131.80	−10.79	.45
298.15	0	135.26	0	0
300	251	135.53	.84	.00
325	3686	139.26	11.83	.49
350	7214	142.99	22.29	1.68
375	10835	146.72	32.28	3.39
400	14549	150.44	41.87	5.49
425	18357	154.17	51.10	7.91
450	22258	157.90	60.02	10.56
475	26252	161.63	68.66	13.39
500	30339	165.36	77.04	16.36
525	34520	169.08	85.20	19.45
550	38794	172.81	93.15	22.62
575	43161	176.54	100.91	25.85
600	47621	180.27	108.51	29.14
625	52174	184.00	115.94	32.46
650	56820	187.72	123.23	35.81
675	61560	191.45	130.39	39.18
700	66393	195.18	137.42	42.57
725	71319	198.91	144.33	45.96
745.2	75367	201.92	149.84	48.70
		Liquid Phase		
745.2	119767	232.09	209.42	48.70
750	120881	232.09	210.91	49.73
775	126683	232.09	218.52	55.06
800	132486	232.09	225.89	60.28
825	138288	232.09	233.03	65.41
850	144090	232.09	239.96	70.44
875	149892	232.09	246.68	75.38
900	155695	232.09	253.22	80.23

H°_{298} and S°_{298} are, respectively, the enthalpy and entropy of the solid at 298.15 K and 1 atm pressure.

TABLE 5. *Thermodynamic functions for lithium tetrafluoroberyllate (Li_2BeF_4) solid and liquid phases (in terms of* **CALORIES** *per mole)*

(1 cal=4.1840 J; 1 mole= 98.884 g; International Practical Temperature Scale of 1968)

T	$H^\circ - H^\circ_{298}$	C°_p	$S^\circ - S^\circ_{298}$	$-(G^\circ - H^\circ_{298})/T - S^\circ_{298}$
K	*cal mol⁻¹*	*cal mol⁻¹ K⁻¹*	*cal mol⁻¹ K⁻¹*	*cal mol⁻¹ K⁻¹*
		Solid Phase		
273.15	−797	31.44	−2.79	0.13
275	−739	31.50	−2.58	.11
298.15	0	32.33	0	0
300	60	32.39	.20	.00
325	881	33.28	2.83	.12
350	1724	34.17	5.33	.40
375	2590	35.07	7.72	.81
400	3477	35.96	10.01	1.31
425	4387	36.85	12.21	1.89
450	5320	37.74	14.34	2.52
475	6274	38.63	16.41	3.20
500	7251	39.52	18.41	3.91
525	8250	40.41	20.36	4.65
550	9272	41.30	22.26	5.41
575	10316	42.19	24.12	6.18
600	11382	43.08	25.93	6.96
625	12470	43.98	27.71	7.76
650	13580	44.87	29.45	8.56
675	14713	45.76	31.16	9.37
700	15868	46.65	32.84	10.17
725	17046	47.54	34.50	10.98
745.2	18013	48.26	35.81	11.64
		Liquid Phase		
745.2	28625	55.47	50.05	11.64
750	28891	55.47	50.41	11.89
775	30278	55.47	52.23	13.16
800	31665	55.47	53.99	14.41
825	33052	55.47	55.70	15.63
850	34438	55.47	57.35	16.84
875	35825	55.47	58.96	18.02
900	37212	55.47	60.52	19.18

H°_{298} and S°_{298} are, respectively, the enthalpy and entropy of the solid at 298.15 K and 1 atm pressure.

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[5] "ln" indicates the natural logarithm (base *e*).

entropy and the Gibbs free-energy function. One compilation [19] has estimated for this constant 29.8 ± 2 cal mol^{-1} K^{-1} (124.7 ± 8 J mol^{-1} K^{-1}), taken as the sum of the entropies at this temperature of two moles of LiF(c) and one mole of $BeF_2(c)$.

From a consideration of the sources of systematic error and the precision of the enthalpy values, the corrected heat capacities as given by eqs (3) and (7) and in tables 4 and 5 are estimated to have general uncertainties of ± 2 percent for the solid from 298 to 600 K and ± 3 percent for the liquid from 750 to 850 K. However, the error in the derived heat capacity may reach several percent near the lower end of the experimental range (below 298 K). Between 600 and 750 K the large, rather uncertain corrections for premelting introduce additional uncertainties for the solid and the heat of fusion which are difficult to estimate, but no additional uncertainty for the enthalpy of the liquid as given by eq (6), and very little for the entropy of the liquid as given by eq. (8).

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