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EQUILIBRIUM DISSOCIATION PRESSURES OF LITHIUM HYDRIDE AND LITHIUM DEUTERIDE

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EQUILIBRIUM DISSOCIATION PRESSURES OF LITHIUM HYDRIDE AND LITHIUM DEUTERIDE

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ABSTRACT

The equilibrium dissociation pressures and thermodynamic properties of lithium hydride and lithium deuteride have been determined from 450 to 750° C.

CONTENTS

SUMMARY

The equilibrium dissociation pressures of plateau composition lithium hydride and lithium deuteride have been measured from 450 to 750° C. These data were used to derive the relationship of dissociation pressure with temperature over this range, and to calculate several thermodynamic properties of these materials. Thermodynamic properties determined included: the enthalpy, entropy, and free energy of formation; the enthalpy and entropy of fusion; and the melting points.

INTRODUCTION

Several investigations on the dissociation pressure of lithium hydride have been conducted over the past 30 years. A summary of the results of these studies has been compiled by Messer.[1] Most of this work was done at temperatures above the melting point of lithium hydride (~688° C), with only that of Hill[2] and Hurd and Moore[3] giving any data below 688° C.

The present study, conducted at the Oak Ridge Y-12 Plant,(b) was initiated to determine equilibrium hydrogen and deuterium plateau dissociation pressures over lithium hydride and deuteride from 750° C down to the lowest temperature possible with the available equipment (~450° C). A benefit of this objective is that the dissociation pressure study allows a calculation of the plateau thermodynamic properties of lithium hydride and deuteride over the temperature range from 450 to 750° C.

(b) Operated by the Union Carbide Corporation's Nuclear Division for the Department of Energy.

EQUILIBRIUM DISSOCIATION PRESSURES OF LITHIUM HYDRIDE AND LITHIUM DEUTERIDE

PLATEAU EQUILIBRIUM DISSOCIATION PRESSURES AND THERMODYNAMIC PROPERTIES AT 450 - 750° C

Experimental Study

Experiments were performed using an all-metal (Type 304 SS) vacuum system. Equilibrium pressures were measured with a calibrated MKS Baratron differential capacitance manometer, using pressure heads with ranges from 0 to 1 333.2 and from 0 to 13 332.2 Pa.(c) The reference side of the differential manometer was maintained at all times at a pressure of less than 26.7 μPa. The zero position of the instrument was checked daily by evacuation of the system. No significant zero drift was observed, and any drift that did occur ($<$ 0.1%) was corrected each day.

Samples of hydride or deuteride were contained in sealed (electron-beam-welded) tubes made of niobium-1 weight percent zirconium alloy (Nb-1 Zr). A view of such a sample tube is presented in Figure 1. This alloy is an almost ideal container for hydrogen dissociation pressure experiments because it is impermeable and chemically compatible with liquid lithium metal and lithium hydride, while also being much more permeable to hydrogen than is pure iron, the material commonly used in earlier experiments.[1 - 3] In this study, equilibrium hydrogen pressures across the tube wall were established in less than 12 hours at 450° C, less than four hours at 650° C, and in approximately one hour at 750° C. These times can be contrasted with Hill's[2] experiments using iron capsules in the temperature range from 750 to 578° C, where 48 to 72 hours were required to attain equilibrium. Thus, use of the Nb-1 Zr alloy not only makes measurements at lower temperatures possible, but also greatly diminishes the time required for each measurement.

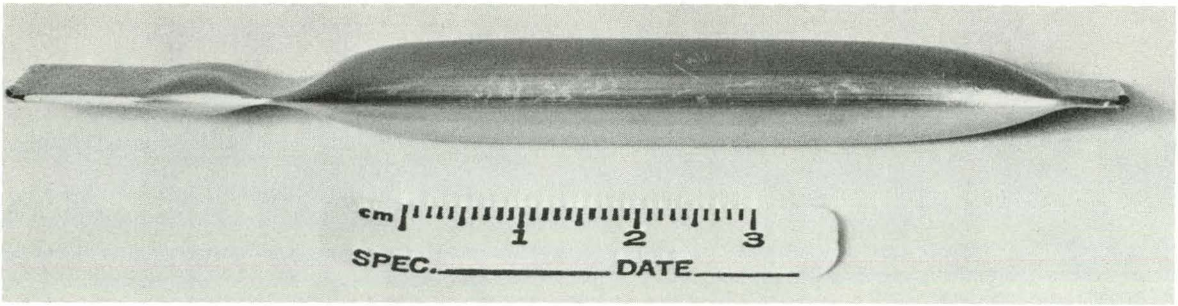

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Figure 1. Niobium-1 Weight Percent Zirconium Alloy Sample Tube.

(c) One torr is equivalent to 133.32 Pa.

The niobium alloy sample container was placed in the Type 304 SS reactor vessel in physical contact with a thermocouple well. The amplitude of the sinusoidal variation of the reactor temperature about the desired value was minimized by the use of two concentric furnace elements surrounding the reactor vessel. Power to the larger outer element (1 650 watts, max) was supplied by a 10-ampere Variac which was manually adjusted to produce a temperature that was 10 to 30° C below that desired. Power to the small (~100-watt) inner furnace element was supplied by a Leeds & Northrup Controlall. Actual sample temperatures were measured using a Chromel-Alumel thermocouple and a Leeds & Northrup millivolt potentiometer. The concentric furnace arrangement reduced the temperature variation about the desired value to less than ± 0.5° C.

Analyses for sample impurities indicated the following: for LiH—95 ppm sodium, 48 ppm potassium, <10 ppm calcium, and 0.28 weight percent oxygen; for lithium deuteride—49 ppm sodium, 25 ppm potassium, 467 ppm calcium, and 0.58 weight percent oxygen. A sufficient number of pieces (about 2 mm in diameter and totaling 0.5 gram) were loaded into the Nb-1 Zr sample tubes (3" L, 1/4" OD, 0.015" wall), one end of which had already been closed by electron-beam welding. After loading the lithium hydride or deuteride sample, the tube was evacuated and pinched closed. It was then removed from the argon box (<1 ppm H_2O) and taken to the electron-beam welder for final closure. The final electron-beam weld was made under a vacuum of approximately 6.67 mPa. After welding was completed, the sealed tube was etched briefly in a 46% nitric acid-8% hydrofluoric acid-46% water solution to remove any oxide film which might have formed during handling. Preliminary experience had shown that oxide films on this alloy greatly impeded hydrogen permeation through the walls of the tube.

The Nb-1 Zr tube was placed in the reactor vessel and the whole system evacuated to 0.667 mPa while the sample temperature was raised to 400° C. This hot vacuum treatment was maintained for 24 hours before measurements commenced, and served to accomplish the following purposes: (1) the reactor vessel was outgassed, (2) any lithium hydroxide which might be present on the lithium hydride sample was also outgassed, and (3) the hydrogen content of the lithium hydride sample was decreased to make certain that the stoichiometry was in the "plateau" region. Upon completion of the hot outgassing treatment, the high vacuum valve between the reactor vessel and vacuum system was closed and measurements were begun.

Most of the measurements were taken during the decomposition of lithium hydride by evacuating the sample tube to <0.13 mPa, closing the valve to the pump, and observing the pressure rise until a constant pressure was attained at a given temperature. About 25% of the measurements were taken during the formation reaction in which a small overpressure of hydrogen was applied and the decrease in pressure observed until no further change occurred. When both techniques were applied at a constant temperature, the final pressures agreed to within 1 to 2%, thus demonstrating that chemical reversibility was present and that equilibrium pressures were being observed.

Results and Discussion

The plateau-equilibrium-dissociation pressure data obtained for lithium hydride are reported in Table 1; that for lithium deuteride in Table 2. The data were found to fit the usual relation[1] between the dissociation pressure and the Kelvin (K) temperature; ie, a relation of the form:

$$\mathrm{Log}_{10}P(\mathrm{Pa}) = \frac{-A}{T(K)} + B, \tag{1}$$

where A and B are constants related to the enthalpy and entropy changes, respectively, of the dissociation (or formation) reaction.

Table 1

PLATEAU EQUILIBRIUM DISSOCIATION PRESSURE OF LITHIUM HYDRIDE

Pressure (Pa)	Temperature(1) (° C)	Pressure (Pa)	Temperature(1) (° C)	Pressure (Pa)	Temperature(1) (° C)	Pressure (Pa)	Temperature(1) (° C)
1 015.04	650	26.90	534	3.32	483.5	4 942	716.5
1 050.77	651	45.17	549	3.57	486	5 870.7	725
1 056.74	651	89.17	569	2.19	472	5 930.8	726
1 060.49	651.5	143.13	583.5	2 197	676	5 946.6	726
1 131.85	652	213.00	596	1 649.1	666	5 880.9	725.5
1 280.93	657	313.17	609	1 347.9	658.5	7 102	736
1 282.05	657	420.87	618.5	1 721.6	668.5	7 182	736
1 362.31	659	423.70	619	2 549	681.5	7 186	736
1 325.28	658	635.73	633	2 541	681.5	8 450	746
1 355.92	659	888.63	644	2 357	679	8 413	746
867.18	643.5	1 178.18	654	1 977	673	9 937	755
868.12	643.5	1 148.79	653	2 033	674	9 899	755
867.80	643.5	1 145.96	653	3 179	691	11 754	765.5
623.12	632	298.06	606.5	2 836.3	686.5	11 828	766
385.60	616	296.99	607	2 668	683.5	12 318	768.5
252.38	602	143.91	582	2 662	683.5	9 683	755
168.92	589	143.12	584	3 831.7	701.5	9 343	752.3
94.71	571	72.07	562	3 683.2	700	7 939	743.5
52.70	553.5	78.34	565	3 599.7	698.5	7 361.8	738
32.13	539.5	78.07	565	3 562.6	698	5 969.4	727
20.81	529	48.42	551	3 511.4	697.5	5 847.8	727
13.04	515.5	27.86	532	3 439.7	696.2	5 898.4	727
9.25	506	28.45	536	3 364.5	695	5 939.8	727
4.04	485	16.99	522	3 342.1	694.5	5 380.9	721
2.20	472.5	16.72	521.5	3 335.7	694	5 405	721
1.45	463	16.93	522	3 323.5	694	4 480	710
4.00	488	11.84	513	3 335.5	694	3 754.1	701
3.93	487	12.17	514	3 986.3	704	3 702.4	700
6.17	497	8.57	504	4 010.3	704.5	3 345.1	694
9.60	507.5	8.83	505.5	3 966.6	704	3 269.1	692
17.16	523	6.68	499	4 926	716.2	3 231.7	692
		6.67	500				

(1) Degrees Celsius (C) can be converted to degrees Kelvin (K) by adding 273.15 to the Celsius reading.

Table 2

PLATEAU EQUILIBRIUM DISSOCIATION PRESSURES OF LITHIUM DEUTERIDE

Pressure (Pa)	Temperature(1) (° C)	Pressure (Pa)	Temperature(1) (° C)	Pressure (Pa)	Temperature(1) (° C)	Pressure (Pa)	Temperature(1) (° C)
9.89	499	1 172.44	641.5	164.52	578.5	6 352	712.5
5.63	485.5	1 196.30	642	237.63	590	7 333	719.5
5.84	486.5	108.68	563	232.22	589	7 330	719.5
1.73	460.5	108.16	563.5	338.75	601	7 822	723.5
1.85	461	174.05	578.5	1 976	661	7 815	723.5
3.00	472	175.48	579	1 703	655.2	8 377	727.8
3.16	472	277.36	593.5	1 701	655	8 287	726.5
5.83	487	288.80	594	1 408	647.5	9 702	735.5
5.84	486.5	286.14	594	1 356	646.5	9 733	735.5
10.21	499.5	403.81	605.5	1 857	658.8	9 722	735.5
10.35	499.5	408.89	606	2 312	667	10 984	743
17.44	512.5	671.68	623	2 335	667	10 972	743
17.56	512.5	660.62	622	2 806	675	12 290	749.2
25.92	522.5	1 021.81	637	2 798	674	12 314	749.2
26.02	523	18.76	507	3 034	676	14 311	759.2
42.34	537	2.77	470	3 384	680	14 207	759
42.80	537	2.81	470	4 088	688	13 387	755.5
71.09	551.5	1.87	461	3 594	683	13 322	755
71.66	552	1.97	460	4 077	687.5	12 995	754
99.46	562	1.92	461.5	4 382	690	12 966	754
100.30	562.5	1.79	460.5	4 453	691	12 372	751
171.59	577	6.72	491	4 348	690.5	12 324	751
185.05	580.5	6.92	491.5	4 302	690	11 292	746
184.11	579.5	10.97	502	4 022	688	11 247	746
167.45	577	11.20	502	3 970	687	11 270	746
251.05	589.5	17.27	513.5	3 962	687	10 679	742.5
239.98	589.0	17.51	513.5	3 861	686.5	10 687	742.5
246.67	589.0	28.74	527	3 814	686	9 958	739
9.31	497.5	28.50	526.8	4 677	694	9 953	739
357.30	602	42.85	538	4 724	695	9 327	735.5
367.25	602	41.66	537	4 724	695	8 097	727.2
355.25	602	63.46	548.5	6 061	709	7 714	724.5
523.49	614	64.34	548.8	5 944	708	5 272	702
512.36	614	87.75	558.5	5 178	700	5 618	705.5
684.49	623	89.33	559.5	5 180	700	5 549	704.5
685.14	623.5	132.19	570.5	5 620	705	5 736	706.5
1 121.91	640	133.50	571.0	5 620	705	5 902	708
1 137.24	640	134.34	571.5	7 138	718.5	5 909	708.2
1 164.70	641	176.60	579.5	7 138	718.5	5 020	699
		159.69	577	6 846	715.8		

(1) Degrees Celsius (C) can be converted to degrees Kelvin (K) by adding 273.15 to the Celsius reading.

A graphical representation of the data is presented in Figure 2, in which $\log_{10}P$ is plotted as a function of the reciprocal of the absolute temperature. The data for each compound fall on two intersecting straight lines. The intersection or abrupt change in slope occurs for both compounds very near their reported melting point of approximately 688° C.[1] This change in the relationship of equilibrium pressure with temperature upon passing from the gas/solid equilibrium to the gas/liquid equilibrium was expected, but it has apparently not been observed by previous investigators of lithium hydride.

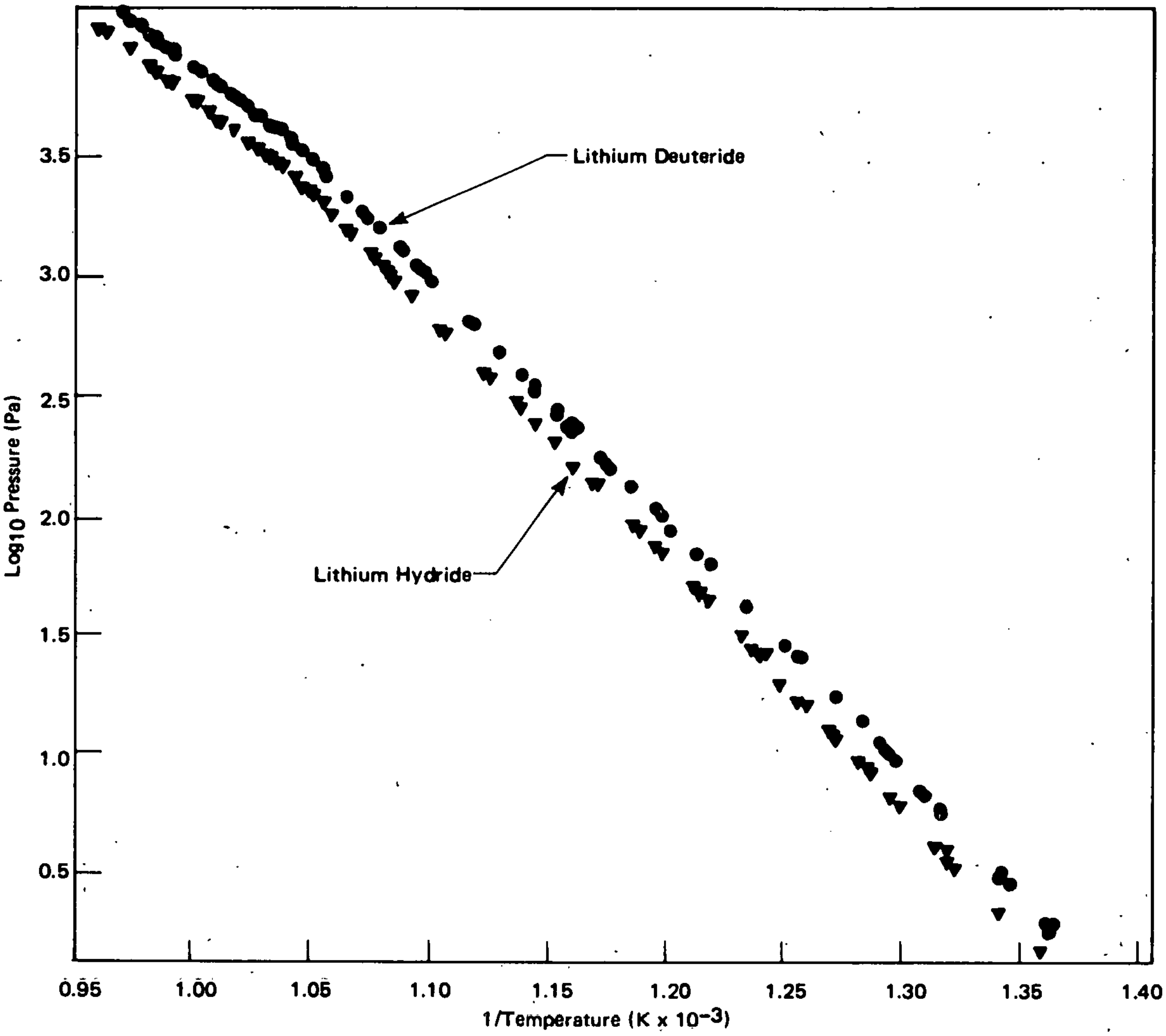

Figure 2. Equilibrium Plateau Dissociation Pressure Measurements.

Data above 691 to 750° C and all that below the melting points of both materials (681 to 450° C) were subjected to separate least-squares analyses, using a general linear hypothesis program (BMD31GR).[4] In each temperature region for each compound, the data were fitted to an equation of the type previously mentioned (Equation 1).

Data taken near the melting point (between 681 and 691° C) for lithium hydride and lithium deuteride were not included in the least-squares analyses so that the results would not be biased. Although the melting points of lithium hydride and lithium deuteride are reported as near 688° C,[1] the exact value can be somewhat dependent on stoichiometry and impurity content. It will be shown later that the melting points can be calculated from the least-squares analyses.

Results of the least-squares analyses for lithium hydride and lithium deuteride above and below their melting points are listed in Table 3. The indicated plus or minus (±) quantities for Constants A and B in each temperature region are the standard deviations for these constants as derived from the analyses. An indication of the accuracy of the results reported here can be obtained by comparing the dissociation pressure of lithium hydride at 700° C (found to be 3 692.96 Pa) with that reported by Heumann and Salmon[5] and by Messer, et al[6] (3 732.96 ± 133.32 Pa). A similar comparison with lithium deuteride at 700° C does not yield such good agreement, however. Heumann and Salmon[5] report a pressure of 5 999.4 Pa at 700° C for lithium deuteride, whereas this study indicates a pressure of 5 132.82 Pa. As a check, two more samples of lithium deuteride were tested at 700° C. Both gave pressures between 5 119.49 and 5 172.82 Pa. No immediate explanation for this lack of agreement is available.

Table 3

CONSTANTS FOR LITHIUM HYDRIDE AND LITHIUM DEUTERIDE FITTED TO THE EQUATION

$\mathrm{Log}_{10}P(\mathrm{Pa}) = -A/T(\mathrm{K}) + B$

Lithium Hydride	Lithium Deuteride
Solid	
A = 10,355 ± 18	A = 10,328 ± 16
B = 14.243 ± 0.022	B = 14.362 ± 0.019
Liquid	
A = 7,675 ± 30	A = 7,491 ± 39
B = 11.456 ± 0.031	B = 11.409 ± 0.039

It was mentioned earlier that the melting points of these samples of lithium hydride and lithium deuteride could be found from the results of the least-squares analyses. This information was obtained by equating the expressions for $\log_{10}P$ for the two temperature regions of each material and solving for the temperature, since the solid and liquid are in equilibrium at the temperature where their dissociation pressures are equal. The melting points found were 688.6° C for lithium hydride and 687.7° C for lithium deuteride. These values are in good agreement with the melting points reported by Messer,[1] namely: 688 ± 1° C for lithium hydride and 686 ± 5° C for lithium deuteride.

Constants A and B for each material can be used to calculate the thermodynamic quantities in each temperature region. A and B are related, respectively, to the enthalpy and entropy of formation of one mole of lithium hydride or lithium deuteride by the following relations:[7]

$$A = \frac{-2\Delta H_p}{2.303\ R}, \text{ and} \qquad (2)$$

$$B = \mathrm{Log}_{10}760 - \frac{2\Delta S_p}{2.303\ R}, \qquad (3)$$

where R represents the ideal gas constant (8.314 J K^{-1} mol^{-1}). The quantities ΔH_p and ΔS_p are the enthalpy and entropy of formation of one mole of lithium hydride or lithium deuteride saturated with metal from one mole of metal saturated with hydride (deuteride) and 1/2 mole of hydrogen or deuterium gas at one atmosphere pressure. These quantities would approach the standard enthalpy and entropy of formation (ΔH^o and ΔS^o) as the solubilities of metal in hydride and of hydride in metal approach zero. Results of the calculations for each temperature region of each compound are summarized in Table 4. An expression for the free energy of formation, ΔF_p, as a function of temperature is also included in Table 4. Free energy of formation is calculated from the relation:

Table 4

CALCULATED THERMODYNAMIC QUANTITIES FOR LITHIUM HYDRIDE AND LITHIUM DEUTERIDE

Lithium Hydride	Lithium Deuteride
(a) For the reaction $Li(l)_{sat} + 1/2\ H_2 \rightarrow LiH(s)_{sat}$ (733 - 961 K): ΔH_p = −99.13 ± 0.17 kJ mol^{-1} ΔS_p = −88.41 ± 0.21 J K^{-1} mol^{-1} ΔF_p = −99.13 + 0.08841 T(K) kJ mol^{-1}	(a) For the reaction $Li(l)_{sat} + 1/2\ D_2 \rightarrow LiD(s)_{sat}$ (733 - 961 K): ΔH_p = −98.87 ± 0.17 kJ mol^{-1} ΔS_p = −89.58 ± 0.21 J K^{-1} mol^{-1} ΔF_p = −98.87 − 0.08958 T(K) kJ mol^{-1}
(b) For the reaction $Li(l)_{sat} + 1/2\ H_2 \rightarrow LiH(l)_{sat}$ (961 - 1023 K): ΔH_p = −73.48 ± 0.31 kJ mol^{-1} ΔS_p = −61.76 ± 0.25 J K^{-1} mol^{-1} ΔF_p = −73.48 + 0.06176 T(K) kJ mol^{-1}	(b) For the reaction $Li(l)_{sat} + 1/2\ D_2 \rightarrow LiD(l)_{sat}$ (961 - 1023 K): ΔH_p = −71.71 ± 0.42 kJ mol^{-1} ΔS_p = −61.30 ± 0.33 J K^{-1} mol^{-1} ΔF_p = −71.71 − 0.0613 T(K) kJ mol^{-1}
(c) Latent heat of fusion: ΔH (fusion, 961 K) = 25.65 ± 0.50 kJ mol^{-1} Latent entropy of fusion: ΔS (fusion, 961 K) = 26.65 ± 0.46 J mol^{-1}	(c) Latent heat of fusion: ΔH (fusion, 961 K) = 27.16 ± 0.59 kJ mol^{-1} Latent entropy of fusion: ΔS (fusion, 961 K) = 28.28 ± 0.54 J K^{-1} mol^{-1}
(d) Calculated melting point: 961.8 K	(d) Calculated melting point: 960.9 K

$$\Delta F_p = \Delta H_p - T(K)\Delta S_p. \tag{4}$$

As with the enthalpy and entropy, the free energy thus calculated is that for the plateau region, and would approach the standard free energy of formation, ΔF^o, only as the solubilities of metal and hydride in each other approach zero.

Finally, the latent enthalpy and entropy of fusion of lithium hydride and lithium deuteride may be calculated from the differences between the enthalpies and entropies of formation, respectively, of the liquid and solid phases. These results are also given in Table 4.

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