Solid and Liquid Lithium Enthalpy: Experimental Investigation Near the Melting Point

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Lithium enthalpy experimental data in the range from 320 to 700 K are obtained by the drop method with use of an ice calorimeter. The lithium enthalpy of fusion calculated from the experimental data is equal to 435.4 ± 3.9 $J \cdot g^{-1}$. The vacancy formation energy calculated from the solid lithium heat capacity data is equal to 0.6 ± 0.2 eV.

1. INTRODUCTION

The available experimental enthalpy and heat capacity data on lithium are not recent, and they "either scatter greatly or have the uncertainty of the results" [1]. The most accurate heat capacity data concerning lithium were obtained by Douglas in 1955 [2], and the latest data found in literature were published in 1969 [3].

2. MEASUREMENTS AND RESULTS

In the present work enthalpy measurements were performed in the range 320 to 700 K by the drop method with use of an ice calorimeter; its construction and measurement method were described in ref. [4]. The container with lithium was heated in an electrical furnace having three separate heaters. The container temperature was measured by four Pt/Pt10%Rh thermocouples, three of which were placed in a molybdenum cylinder and one directly inside the cylinder on the surface of the sample

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container. The lithium enthalpy was calculated as

$$(H_T - H_{273.15}) = K \frac{Q - H_c m_c}{m} \tag{1}$$

where K is the calibration factor obtained electrically and is equal to 64.516 ± 0.066 cal $\cdot$ g^{-1} of Hg, Q is the total heat evolved by the container with lithium taking into account heat leaks within the calorimeter, H_c is the enthalpy of stainless steel, m_c is the mass of the empty container, and m is the mass of lithium equal to 0.8023 g.

The lithium studied had the following composition (wt.%): Li, $\geqslant 99.5$; Na, < 0.06; K, < 0.005; Mg, < 0.02; Ca, < 0.03; Mn, < 0.001; Fe, < 0.005; Al, < 0.003; SiO$_2$, < 0.01; N (nitrides), < 0.05. During the experiments the amount of iron in the lithium increased from 0.005 to 0.01 wt.%, which can be explained by iron of the container dissolving in lithium. In filling the container with lithium metal, precautions against contamination and oxidation were taken.

The experimental results of the mean heat capacity of the container material (stainless steel of the 1X18H10T type) are presented in Table I. The data obtained were fit by the following equation with the standard mean deviation $\pm 0.6\%$:

$$(H_T - H_{273.15})/(T - 273.15) = 0.4269 + 0.18923 \times 10^{-3} T$$

$$- 0.73070 \times 10^{-7} T^2 \tag{2}$$

Table I. Experimental Results of Stainless Steel Mean Heat Capacity and Its Deviation from Smoothed Values of Eq. (2)

T (K)	$\dfrac{H_T - H_{273.15}}{T - 273.15}$ (J $\cdot$ g^{-1} $\cdot$ K^{-1})	Deviation from smoothed values (%)
302.15	0.4805	0.64
327.15	0.4836	0.53
342.25	0.4794	-0.77
343.15	0.4792	-0.84
404.45	0.4920	0.10
441.05	0.4952	-0.19
452.65	0.4987	0.22
493.85	0.5036	0.20
506.65	0.5056	0.30
515.55	0.5018	-0.64
552.75	0.5141	0.97
649.15	0.5186	-0.05
660.35	0.5159	0.77
751.15	0.5291	0.25

Table II. Experimental Enthalpy Results of Solid and Liquid Lithium

T (K)	$H_T - H_{273.15}$ (J·g^{-1})	Deviation from Eqs. (3) and (4) (%)
328.00	192.14	− 1.30
333.15	213.74	0.26
343.15	250.98	0.53
345.05	253.87	− 1.06
349.45	273.07	0.27
382.45	398.04	0.68
395.75	445.73	− 0.08
407.75	488.25	− 0.99
416.85	529.89	0.04
427.35	571.38	− 0.31
427.95	577.46	0.30
433.95	604.93	0.59
434.35	600.27	− 0.47
436.15	612.45	0.25
441.15	632.84	0.00
442.45	639.79	0.16
442.75	640.74	0.10
444.05	642.27	− 0.56
444.15	646.28	− 0.01
447.25	662.03	0.24
448.95	665.06	− 0.47
449.35	670.79	0.10
450.55	677.48	0.26
451.75	678.28	− 0.43
452.45	684.54	0.00
457.35	1142.75	− 0.01
462.25	1166.27	0.06
476.45	1225.88	− 0.19
487.75	1278.24	0.17
532.45	1459.63	0.04
535.35	1462.95	− 0.53
540.15	1497.57	0.48
596.25	1726.70	0.14
598.25	1728.58	− 0.23
631.95	1876.93	0.06
660.05	1993.18	− 0.01
695.25	2134.90	− 0.09

where $(H_T - H_{273.15})/(T - 273.15)$ is in J·g^{-1}·K^{-1} and T is in K. The enthalpy data for solid and liquid lithium are presented in Table II.

To calculate the lithium enthalpy of fusion, the following empirical equations were obtained by the least squares method using the present

experimental enthalpy data on solid and liquid lithium:

$$H_T - H_{273.15} = 725.92 - 16.836T + 87.972 \times 10^{-3}T^2$$

$$- 0.17345 \times 10^{-3}T^3 + 0.12955 \times 10^{-6}T^4 \qquad (3)$$

for solid lithium and

$$H_T - H_{273.15} = 9982.82 - 38.6729T + 61.707 \times 10^{-3}T^2$$

$$- 30.634 \times 10^{-6}T^3 - 208,065/(T - 273.15) \qquad (4)$$

for liquid lithium, where enthalpy is in $J \cdot g^{-1}$ and temperature is in K. The standard deviations of experimental points from the smoothed values are equal to $\mp 0.52\%$ and $\mp 0.25\%$ for Eqs. (3) and (4), respectively.

The lithium enthalpy of fusion calculated from Eqs. (3) and (4) at the assumed melting temperature 453.7 K is equal to 435.4 ± 3.9 $J \cdot g^{-1}$ and coincides with 432.3 $J \cdot g^{-1}$ recommended in [1] within the accuracies declared. The accuracy of the enthalpy measurements of solid and liquid lithium and the enthalpy of fusion were estimated as $\pm 0.9\%$, $\pm 0.5\%$, and $\pm 0.9\%$, respectively.

3. DISCUSSION

In Fig. 1 the solid lithium enthalpy experimental data are compared with those of ref. [2], the latter being obtained by the same method using an ice calorimeter with an accuracy of $\pm 0.5\%$. As seen in Fig. 1, the data of ref. [2] lie 1% higher than those of the present work almost through the entire temperature range. In approaching the melting temperature, the results coincide. According to Shpilrain et al. [1], the data of other authors scatter greatly.

In the range from the melting temperature to 700 K, the most accurate work was carried out by Redmond (from ref. [1]), Douglas [2], and Novikov [3]. All the data were obtained by the drop method with use of an ice calorimeter. In Fig. 2, the lithium enthalpy experimental data deviations of all authors from those of the Douglas equation are presented [2]. The equation is

$$H_t - H_{0°C} = 318.07 + 4.53062t - 0.0004191t^2$$

where $H_t - H_{0°C}$ is in $J \cdot g^{-1}$ and t is in °C. The liquid enthalpy data of the present work coincide with those of refs. [2] and [3] within 1%.
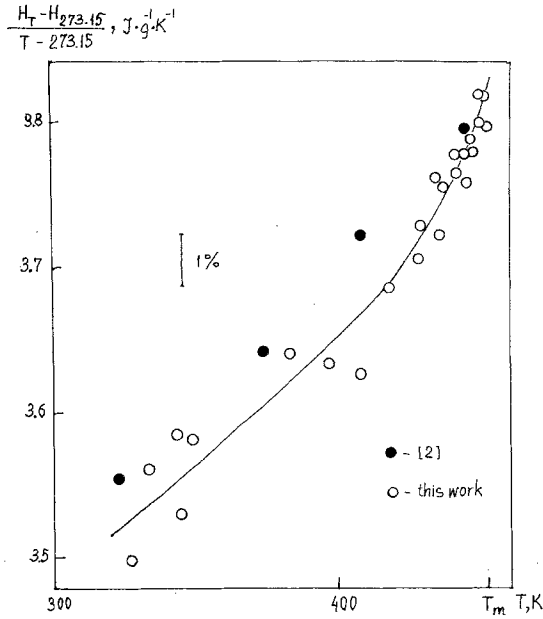
Fig. 1. Experimental data on lithium enthalpy obtained in this work (the solid curve corresponds to the smoothed values) and in ref. [2].
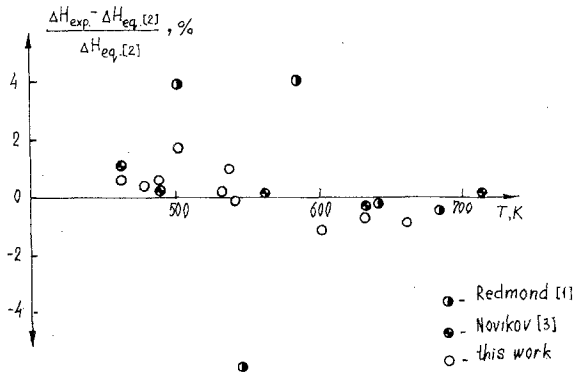

Fig. 2. Liquid lithium enthalpy experimental deviations of various authors from the Douglas equation [2].

The formation energy of vacancies in lithium was calculated assuming that the deviation of the present heat capacity curve from a straight line in approaching the melting temperature is caused by vacancy formation. Then the vacancy contribution to the heat capacity is equal to

$$c_p = \frac{AE^2}{kT^2} \exp\left(-\frac{E}{kT}\right) \tag{5}$$

where E is the formation energy of vacancies, if the vacancy assumption is correct. The quantity $\ln(\Delta c_p T^2)$ versus reciprocal temperature must be represented by a straight line, the slope of which depends on the vacancy formation energy, E.

In this work $c_{p,\text{exp}}$ was determined from the relation

$$c_{p,\text{exp}} = \bar{c}_{p,\text{exp}} + t\,\frac{d\bar{c}_p}{dt} \tag{6}$$

where $\bar{c}_{p,\text{exp}}$ is the mean heat capacity experimental points determined as $(H_t - H_{0°C})/t$, and $d\bar{c}_p/dt$ was determined by differentiating the equation for the mean heat capacity temperature dependence,

$$\bar{c}_p = 3.205 + 0.9148 \times 10^{-2}t - 0.7445 \times 10^{-4}t^2 + 0.2368 \times 10^{-6}t^3 \tag{7}$$
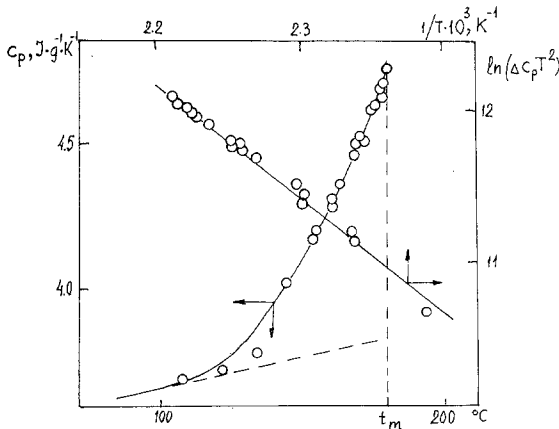

Fig. 3. Lithium heat capacity near the melting point (for the calculation of the vacancy formation energy). The solid straight line is $\ln(\Delta c_p T^2)$ vs $1/T$ obtained by the least squares method; the solid curve corresponds to the smoothed values of c_p; the sloped dotted line corresponds to the equation $c_p = 3.484 + 0.0020774t$.

Table III. Vacancy Formation Energy Values of Various Investigators for Lithium Metal

E (eV)	Method	Ref.
0.6 ± 0.2	Calorimetric measurements	This work
0.34 ± 0.04	Length and lattice parameter measurements	[5]
0.40 ± 0.03	Excess resistivity measurements	MacDonald (from [5])
0.41	Calculated	[6]

where $\bar{c}_p$ is in $J \cdot g^{-1}$ and t is in °C. Then the heat capacity deviations, $\Delta c_{p,\mathrm{exp}}$, from the linear heat capacity temperature dependence, $c_p = 3.484 + 0.0020774t$ were obtained, and a straight line $\ln(\Delta c_{p,\mathrm{exp}} T^2)$ versus $1/T$ was calculated by the least squares method, the slope of which gives us the vacancy formation energy equal to 0.6 ± 0.2 eV (Fig. 3). The standard deviation of $\ln(\Delta c_p T^2)$ from the straight line is equal to $\pm 6\%$, and the estimated accuracy of the vacancy formation energy given by the slope is equal to $\pm 30\%$. The vacancy formation energy values for lithium metal of various investigators are presented in Table III.

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