flected in the free energy, is well within experimental error.[6]

Johnston and Bauer's values[1] were derived from equation[7] 2

$$\frac{\Delta F^0}{T} = \frac{35186}{T} + 1.1536 \log T + 0.010835T - \frac{0.18678(10^6)}{T^2} - 45.758 \quad (2)$$

which they developed using the data of J. Johnston[8] obtained from equilibrium studies at higher temperatures. Pressures calculated from this equation are shown as the dotted line in Fig. 2. The close approach of the two curves (and the 25° values) shows general agreement of our results with those of J. Johnston, considering that the latter's measurements were made above the melting point of LiOH.

Pressures obtained using effusion cell 2 are observed to fall materially below those calculated from equation 1, indicating that true equilibrium was not established. If one attributes the deviation to the accommodation coefficient, alpha may be approximated using the equation $P_e/P_s = 1 + (f/\alpha)$, derived from the steady-state condition, where P_e is the equilibrium pressure, P_s the observed steady state pressure, and f the ratio of the area of the orifice to the area of the sample. The latter has been taken as the cross-sectional area of the effusion cell, assumed to be the effective area involved in exchange of molecules between vapor and solid. For cell 2, $f = 0.0074$ and $P_e/P_s = 2$ (average value); hence $\alpha = 0.007$. In view of the assumption concerning the sample area and the rather large scatter of our results from cell 2, we regard this as only a rough estimate of the accommodation coefficient. However, this value does predict that essentially equilibrium pressures should be observed with cell 1, where $f = 5.73 \times 10^{-4}$ giving $P_e/P_s = 1.08$, a deviation within the limit of our experimental error. In this comparison, allowance has not been made for a possible variation of alpha with temperature.

We are unable to explain the very low values observed by Ditmars and Johnston. The line representing their least squares equation is shown on Fig. 2 (marked ref. 3). Even though the accommodation coefficient appears rather small, our estimate is much larger than would be required to give values of P_e/P_s of the order of 100. The orifice diameter of their cell was intermediate between the two used in this work.

This research was supported in part by the Office of Ordnance Research, U. S. Army.

SEATTLE, WASHINGTON

[6] NOTE ADDED IN PROOF.—Recently a paper has appeared by C. H. Shomate and A. J. Cohen (THIS JOURNAL, **77**, 285 (1955)) reporting high temperature heat capacities for Li_2O and LiOH. Using their results with similar data for water vapor (D. D. Wagman, *et al.*, *J. Research, Natl. Bur. Stds.*, **34**, 143 (1945)) and the third law data of Johnston and Bauer (ref. 1), $\Delta S°$ is calculated to be 30.50 e.u. at 600°K. for the reaction $2LiOH(s) = Li_2O(s) + H_2O(g)$. With our equilibrium constant at 600°K., this entropy change leads to a calculated heat of reaction of 31.22 kcal., 0.42 kcal. larger than the value taken above (at 587°K.). The deviation is easily within probable experimental error.

[7] This expression has been corrected for an error in the sign of the fourth term on the right in the reference cited.

[8] J. Johnston, *Z. physik. Chem.*, **62**, 339 (1908).

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS AND THE KNOLLS ATOMIC POWER LABORATORY]

Lithium: Heat Content from 0 to 900°, Triple Point and Heat of Fusion, and Thermodynamic Properties of the Solid and Liquid[1]

BY THOMAS B. DOUGLAS,[2] LEO F. EPSTEIN,[3] JAMES L. DEVER[2] AND WILLIAM H. HOWLAND[3]

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Lithium was distilled at 650–700° *in vacuo* and sealed in stainless steel type 347. From chemical analysis the purity of the first sample was 99.98 atomic % and that of the second sample, obtained with the still *in vacuo*, was approximately 99.99 atomic %. The melting curves, which are consistent with these analyses, gave a triple point of 180.54°. Using a Bunsen ice calorimeter and a drop method, the relative heat content was measured from 0 to 900°. The observations were combined with available adjusted low temperature heat capacities and vapor pressures at high temperatures, with use of the Sackur–Tetrode equation, to determine the thermodynamic properties of the solid and liquid from 298.16 to 1200°K. A value of 38800 cal. per g.-atom was derived for the cohesive energy of the metal.

The increased importance in recent years of the common alkali metals and some of their alloys as heat-transfer media has stimulated the accurate determination of their pertinent properties. Following purification of sodium, potassium and three of their alloys at the Knolls Atomic Power Laboratory, their heat contents from room temperature to approximately 800° were measured previously at the National Bureau of Standards.[4,5] The present paper reports similar work on lithium. The purification of this metal to a high degree presented some unusual difficulties. Accurate measurements on it have additional value because of the unusually wide discrepancies in the heretofore available heat capacity data on the liquid. Furthermore, the simplicity of lithium as a chemical element has led to numerous theoretical attempts to derive its properties and to understand them in considerable detail. In such work accurate experimental values are invaluable for comparison.

Experimental

Purification and Sealing of Samples.—Lithium metal reacts voraciously with oxygen, nitrogen and all the other constituents of air except the rare gases. Consequently, the oxide and nitride are the principal impurities normally encountered in the material. Other than these compounds, small amounts of sodium and other alkali metals, calcium

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[1] This work was supported by the Atomic Energy Commission.

[2] National Bureau of Standards, Washington, D. C.

[3] Knolls Atomic Power Laboratory, Schenectady, New York. The Knolls Atomic Power Laboratory is operated by the General Electric Company for the United States Atomic Energy Commission, and the work reported here was carried out under Contract No. W-31-109 Eng-52.

[4] D. C. Ginnings, T. B. Douglas and A. F. Ball, *J. Research Natl. Bur. Standards*, **45**, 23 (1950).

[5] T. B. Douglas, A. F. Ball, D. C. Ginnings and W. D. Davis, THIS JOURNAL, **74**, 2472 (1952).

and heavy metals such as iron and nickel might be expected to be present. To obtain lithium metal of the degree of purity desired for these experiments, a number of possible methods were considered for eliminating these contaminants. Vacuum distillation[6] in a still made of type 347 stainless steel was finally used, and at a temperature in the range 650 to 700°, where the vapor pressure of lithium lies between 0.1 and 0.8 mm. The stills described below were loaded in a dry-box containing argon gas which was continuously purified over hot calcium chips; all other operations involving the handling of solid lithium were carried out in this way. Liquid lithium was exposed only to vacuum, since at elevated temperatures there was some possibility of reaction with the residual oxygen and nitrogen present as impurities in the dry-box atmosphere, the total estimated to be of the order of 1 to 10 p.p.m. Several transfer vessels and other devices were designed and used to carry out the required manipulations so that the lithium was at no time exposed to air after the initial loading into the dry-box. In all the distillations, only the center cut was retained, the first low-boiling third of the still charge and the high-boiling pot residue being discarded.

The starting material was lithium metal obtained from the Maywood Chemical Co. and reported by the manufacturer to contain 0.2% by weight of metallic impurities, mostly sodium. No analysis for the initial oxygen and nitrogen content was available.

The first still used was in the form of a cylinder 5 cm. in diameter and 25 cm. high, and was made of stainless steel 0.3 cm. thick. A flat bottom was welded to one end, and the other end was equipped with a flange gasketted with neoprene rubber to assure vacuum tightness. A stainless steel cold finger, about 2.5 cm. in diameter, extended from the top flange down to within about 5 cm. of the bottom of the still, and this, as well as the gasketted flanges, was cooled by running water. The bottom half of the still was inserted in a vertical cylindrical furnace, and after evacuation through a side tube the still was heated and distillation commenced. With this system, a crop of lithium crystals was obtained on the cold finger at a rate of about 20 g. per hr. Several distillations had to be made before enough satisfactory material could be obtained for sample 1.

On analysis it was found that lithium prepared in this way contained by weight approximately 0.028% of oxygen and 0.003% of nitrogen. While this was not considered to be excessive, the reason for this relatively high gaseous impurity content was sought. Examination of data on the diffusion of oxygen and nitrogen through steel at 700° suggested that while the rates of diffusion of these gases through the 0.3 cm. steel wall were low, the accumulative effect after the approximately 2 hr. required for the distillation might be enough to account for a significant fraction of the observed impurity in the lithium.[7] Consequently, for the preparation of sample 2 a method was used which would eliminate the possibility of air diffusion through the steel wall. The modified design is shown in Fig. 1, drawn to scale.

The new still consisted of a cylinder 4 cm. in diameter, 11.5 cm. high, and 0.3 cm. thick; this was provided with a baffle arrangement to minimize entrainment of liquid droplets by the lithium vapor. After loading with lithium in the dry-box, the cap was inserted and welded in place as shown, using the same inert-atmosphere induction-welding technique that was used for the heat content containers themselves (see below). The whole assembly, in the dry-box, was placed under a glass bell jar sealed to a metal base plate. The system was evacuated and thoroughly degassed through the stopcock shown, while being heated by means of a water-cooled induction coil connected to a 2 Kva, high-frequency generator. The resulting distillate collected in the receiving cup below the still. Some care was required to make sure that the condensation did not occur in the still-pot discharge tube. Approximately 60 g. of lithium was charged into the still initially, and as in the case of sample 1, the first third of the distillate was discarded by opening the apparatus in the dry-box and replacing the receiving cup with an empty one. The apparatus was then resealed, and the next third was then distilled, collected and used, leaving approximately 20 g. of material as still-pot residue.

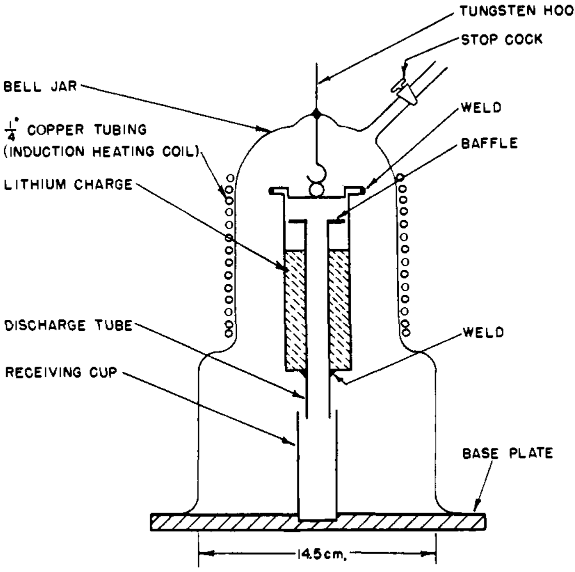

Fig. 1.—Distillation apparatus.

The containers used for the heat content work were identical with those previously described.[4] They were 1.6 cm. in diameter and 7.0 cm. long, and were made of type 347 stainless steel 0.050 cm. thick. The weight of each capsule, including the empty containers, was adjusted to 16.848 ± 0.001 g. The lithium obtained in the distillations described above was stored in sealed evacuated glass envelopes until required, and was transferred into the containers using the dry-box and vacuum-melting techniques. Before sealing, the capsules were evacuated and filled with dry purified helium gas at 25 mm. pressure. Closure was effected by induction welding the caps in place, using the technique described by Bondley.[8]

Each of the stainless steel containers, whether containing lithium or not, had to be carefully leak-tested after sealing. This was accomplished by heating the containers in a closed evacuated system by induction to 850°, and checking for the appearance of helium using a mass-spectrometer leak detector. The maximum observed leak rate, determined in this fashion, was $3\,(10^{-13})$ cc. per sec. of helium (at standard temperature and pressure).

Chemical Analysis.—Samples of the lithium used, taken with extreme care from the same batches from which samples were loaded into the containers, were analyzed for the following contaminants, using the techniques indicated: (1) nitrogen, the Kjeldahl method; (2) sodium, standard flame photometer technique; (3) aluminum, the aurintricarboxylate method (interfering metals are removed by electrolysis with a mercury cathode); (4) iron, the colorimetric α,α'-dipyridyl method (the ferric ion is reduced with hydroxylamine hydrochloride); (5) oxygen: the oxide and nitride are separated by amalgamation of the sample and then titrated (the technique of Pepkowitz and Judd[9] for sodium was used with a modification (to be described elsewhere) to avoid an otherwise almost explosive reaction between lithium and mercury; oxide is determined by combination of these results with the Kjeldahl nitrogen analysis); (6) calcium, the 8-hydroxyquinoline method of Rynasiewicz[10]; (7) nickel, colorimetric dimethylglyoxime procedure.

These analyses indicated the following impurities (in weight %): in sample 1, 0.028% O, 0.003% N, 0.0036% Fe, 0.0006% Ni, 0.029% Ca, and 0.016% Na; in sample 2,

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[6] L. F. Epstein and W. H. Howland, *Science*, **114**, 443 (Oct. 26, 1951). A similar technique of distillation was used by P. S. Baker, F. R. Duncan and H. B. Greene, *ibid.*, **118**, 778 (Dec. 25, 1953).

[7] An attempt was made to use finely powdered active zirconium metal, prepared by the dissociation of the hydride, as a getter for oxygen and nitrogen in lithium by distilling the alkali metal over the zirconium; but this was not successful.

[8] R. J. Bondley, "Welding Handbook," 3rd edition, American Welding Soc., New York, N. Y., 1950, Chap. 20, p. 465.

[9] L. P. Pepkowitz and W. C. Judd, *Anal. Chem.*, **22**, 1283 (1950).

[10] J. Rynasiewicz, *ibid.*, **21**, 1398 (1949).

0.0006% Fe, 0.0003% Ni, 0.001% Ca, and 0.003% Na. No trustworthy values for the oxygen and nitrogen in sample 2 were obtained, but these are believed to have been less than half the respective amounts found in sample 1.

Cryoscopic Measurements; Triple Point.—After completion of the heat content measurements, the temperatures of the two lithium samples at various stages of fusion were determined in the same manner as previously used for potassium.[5] According to the laws of ideal solutions the temperature of such a sample should be a linear function of the reciprocal of the fraction that has been melted. Seven equilibrium temperatures determined between 59 and 96% completion of fusion of lithium sample 2 agreed with the best linear relation to within an average of ±0.001°; these data indicated that the freezing point of this sample (when all melted) was 180.47° and that the triple point of pure lithium is 180.54°. The freezing point lowering of 0.07° corresponds to a total liquid-soluble, solid-insoluble impurity of 0.011 atomic %. However, the temperatures observed on this sample before fusion was half complete were considerably higher than those corresponding to an extrapolation of the above linear relation. This fact suggests the presence of some solute sufficient in amount to maintain saturation of the smaller amounts of liquid lithium then present.

A similar interpretation can be applied to the results on sample 1. Eight equilibrium temperatures, determined between 21 and 91% completion of fusion, agreed with the best linear relation to ±0.002° on the average, though the total temperature change involved was 0.13°. These data indicated a freezing point of sample 1 of 180.42° and an apparent triple point temperature of pure lithium of 180.45°. If the triple point of 180.54° as found from sample 2 be assumed correct, the lower apparent value indicated by sample 1 may be attributed to the presence of an impurity saturating this sample throughout its fusion. The 0.09° difference corresponds to a minimum of 0.014 atomic % of such impurity in the whole sample, and the apparent freezing point lowering of 0.03° corresponds to 0.005 atomic % of other impurity wholly in solution during the observed part of the fusion. Thus the total impurity found cryoscopically in sample 1 has a minimum value of 0.019 atomic %, which is close to the total of 0.024 atomic % found by chemical analysis.

Calorimetric Procedure.—The apparatus and method of heat content measurement have been described in detail elsewhere.[4,5,11] Briefly, the sample in its container is heated in a silver-core furnace to a known temperature which is measured by a platinum resistance thermometer up to 600° and by a platinum—platinum-rhodium thermocouple above. It is then dropped into a Bunsen ice calorimeter that measures the heat evolved in cooling to 0°. By repeating at a number of furnace temperatures and subtracting the corresponding heats found for the empty container, the heat capacity of the sample can be derived by the usual methods.

The measurements of the relative heat content of the empty containers were actually carried out on two sealed vessels constructed from the same piece of stainless steel as the containers for the lithium. As other measurements[4,5] on containers of the same alloy have established the highly regular variation of the heat content with temperature between 0 and 200°, the empty container values were found by interpolation at four temperatures in this range where no direct measurements were made. Small corrections were applied to the measured heats in order to place the results in a given set on the basis of the same temperature, mass of container, and mass of oxide on the container surface. The last correction did not exceed 17 joules and was usually very much smaller. All weights were corrected to a vacuum basis. The error caused by evaporation of lithium inside the container was shown to be negligible in all cases.

Heat Content Data.—The mean measured heat at each furnace temperature (International Temperature Scale of 1948[12]) is given for the empty containers in Table I and for the containers with samples in Table II, together with the average deviation from the mean.[13] These values have been fully corrected except for the small, inaccurately known heat lost during the drop into the calorimeter, which very nearly canceled in subtracting the values of Table I from those of the second column of Table II to obtain the net heat due to the sample. The smoothed values of Table I were obtained from an empirical deviation plot. The calculated values referred to in the last column of Table II were obtained from the empirical equations given later.

TABLE I

EMPTY CONTAINERS

Furnace temp., t, °C.	Measured heat (mean),[13] abs. joules: First container	No. of runs	Second container	No. of runs	Smoothed heat, abs. joules
50.00					401.1
100.00	815.7 ± 0.7	3			815.4
140.00					1154.5
170.00					1413.0
185.00					1543.6
200.00			1674.4 ± 0.8	3	1675.0
300.00	2569.7 ± 0.7	3			2569.7
400.00			3492.2 ± 2.4	3	3492.2
500.00	4443.6 ± 1.4	3			4442.0
600.00	5413.5 ± 0.7	3			5417.8
698.7	6411.2 ± 0.6	2	6398.5 ± 1.5	6	6404.7
795.7	7401.4 ± 3.4	5	7387.0 ± 1.1	3	7396.9
895.3	8441.0 ± 3.5	2	8429.9 ± 5.2	5	8435.6

TABLE II

LITHIUM

Furnace temp., t, °C.	Measured heat (mean),[13] container + lithium, abs. joules	No. of runs	Relative heat content of Li ($H_t - H_{0°C.}$): Mean obsd. abs. joules g.$^{-1}$	Calcd. − obsd. abs. joules g.$^{-1}$
50.00	1194.5 ± 1.1	3	177.88	0
100.00	2440.7 ± 2.2	3	364.41	0
140.00	3483.4 ± 3.0	4	522.18	0
170.00	4292.8 ± 0.2	3	645.70	0
185.00	6637.5 ± 1.8	3	1142.13	−0.24
200.00	7058.8 ± 1.4	3	1207.14	+ .29
300.00	9882.1 ± 3.3	3	1639.54	.00
400.00	12695.2 ± 0.3	3	2063.44	− .18
500.00	15507.3 ± 0.2	3	2481.01	− .06
	(14485.2 ± 2.2)[a]	3	(2480.35)[a]	(+ .60)
600.00	18340.8 ± 4.8	4	2897.54	+ .19
698.7	21161.4 ± 0.7	3	3308.69	− .31
795.7	23948.2 ± 1.2	2	3711.04	+ .23
895.3	26830.0 ± 1.2	2	4124.32	− .06

[a] On sample 1 (4.0491 g. of lithium). All other runs on lithium were on sample 2 (4.4600 g. of lithium).

Derived Properties

Relative Heat Content, Heat of Fusion and Heat Capacity.—The first four mean observed heat content values in Table II are for temperatures below the triple point. These values determined the coefficients of the following empirical equation, which represents the heat content of solid lithium in absolute joules per g. at t, °C., from 25° to the triple point

$$H_t\text{ (solid)} - H_0°\text{ (solid)} = 3.5096t + 4.625(10^{-4})t^2 + 1.1041(10^{-5})t^3 - 2.221(10^{-8})t^4 \quad (25 \text{ to } 180.54°) \quad (1)$$

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[11] D. C. Ginnings, T. B. Douglas and A. F. Ball, THIS JOURNAL, **73**, 1236 (1951).

[12] H. F. Stimson, *J. Research Natl. Bur. Standards*, **42**, 209 (1949).

[13] After adjusting to the basis of an infinite number of observations by multiplying the observed average deviation by the factor $\sqrt{n/(n-1)}$, where n is the number of observations actually made.

This equation has been limited to temperatures of 25° and above because of the enhanced uncertainty in its curvature near 0°, the lower limit of the range of measurement.

The best single equation found for the relative heat content of liquid lithium, in absolute joules per g. at T, °K., is

$$H_T \text{ (liquid)} - H_{273.16} \text{ (solid)} = -275.73 + 3.52675T + 3.9444(10^{-4})T^2 - 9.567(10^{-8})T^3 - 124649/T \quad (453.70 \text{ to } 1173°\text{K.}) \quad (2)$$

This equation, found by the method of least squares, represents the observed values within their precision, but in calculations was replaced for convenience by the two equations (in abs. joules per g. at t, °C.)

$$H_t\text{(liquid)} - H_0{}^0\text{(solid)} = 318.07 + 4.53062t - 4.191\ (10^{-4})t^2 \ (180.54 \text{ to } 420°) \quad (3)$$

$$H_t\text{(liquid)} - H_0{}^0\text{(solid)} = 386.21 + 4.20755t - 3.615\ (10^{-5})t^2 \ (420 \text{ to } 900°) \quad (4)$$

These two equations fit the observations even more closely than equation 2. However, the fact that their second temperature derivatives are discontinuous at 420° should not be construed as evidence for a real discontinuity in the properties of liquid lithium.

Equations 1 and 3 give a value of 432.3 absolute joules per g. for the heat of fusion of lithium at its triple point, 180.54°.

The vapor pressure of lithium does not exceed approximately 10 mm. up to 900°. Consequently, simple differentiation of the above heat content equations gives the heat capacity, which within the observational error may be considered to be that either along the path of the vapor pressures or at the standard thermodynamic pressure of 1 atm. The derivatives of equations 1 and 2 are represented by the curves above 298°K. in Figs. 2 and 3, respectively. The points shown as observed by the authors were computed without smoothing from the observed values of Table II. (In Fig. 3 the point at 192° (465°K.) is much less reliable than the others of the present investigation, as it resulted from two heat content values at temperatures only 15° apart.)

Estimated Accuracy.—The heat content of both samples of lithium was measured at one temperature (500°) primarily as a check on the accuracy of the sample masses. As seen from Table II, the two mean values agree within 0.03%. The other principal sources of systematic error in the method and apparatus have been discussed in detail in an earlier paper.[4] As a result of combining the precision with estimates of systematic errors, it is believed that the accuracy of values derived from equations 1–4 may be represented by the following probable errors: the heat capacity of the solid from 25 to 160° and the heat of fusion, ±0.5%; the heat capacity of the liquid from 250 to 800°, ±0.3%; and the triple point temperature, ±0.03°. In making the last estimate it was assumed that no "saturated" solute such as is believed to have existed in sample 1 invalidated the triple point indicated by the purer sample 2.

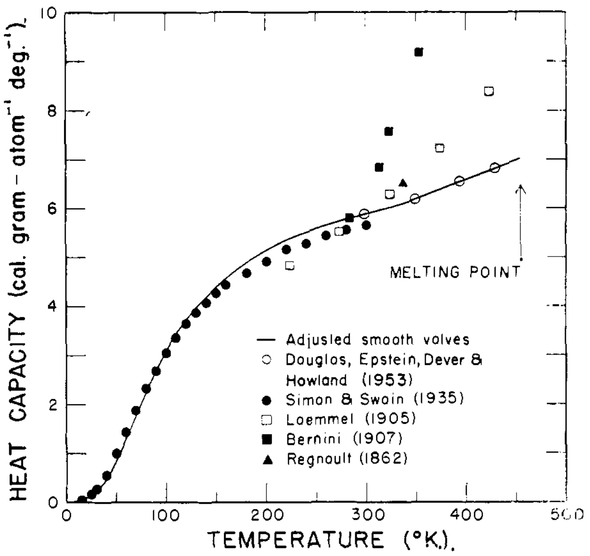

Fig. 2.—Heat capacity of solid lithium.

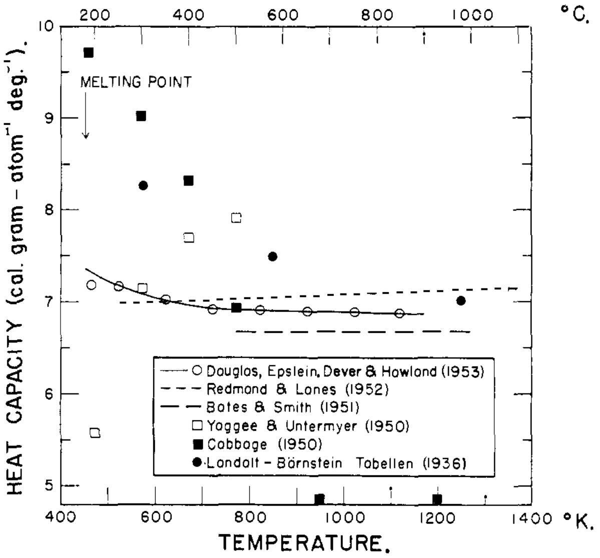

Fig. 3.—Heat capacity of liquid lithium.

Thermodynamic Functions.—The best data available for computing the absolute entropy of lithium at 298°K. are the heat capacity values determined by Simon and Swain[14] from 15 to 300°K. Unfortunately, their value is about 4% lower than that of the authors at the only temperature common to both series of measurements, 300°K. They also measured synthetic sapphire (aluminum oxide) in the same calorimeter from 30 to 280°K.,[14] their heat capacities being also approximately 4% lower than another series of precise values on this material, recently measured at the National Bureau of Standards.[15] The values of Kerr, Johnston and Hallett[16] agree with the latter in general within 0.2%.

Simon and Swain gave no discussion of their experimental procedure from which an inference of systematic error might be drawn, but several com-

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[14] F. Simon and R. C. Swain, *Z. physik. Chem.*, **B28**, 189 (1935).

[15] D. C. Ginnings and G. T. Furukawa, THIS JOURNAL, **75**, 522 (1953).

[16] E. C. Kerr, H. L. Johnston and N. C. Hallett, *ibid.*, **72**, 4740 (1950).

mon sources of error in adiabatic calorimetry tend to produce constant percentage error in the heat capacity, regardless of the substance being measured. In fact, a suggestion that some suspicion may be attached to their temperature scale is afforded by the fact that the discrepancies on synthetic sapphire change sign at the oxygen point. The authors have adjusted each of Simon and Swain's values for lithium in the ratio of the NBS value[15] to theirs on synthetic sapphire[14] at the same temperature. Their original values are shown as points in Fig. 2, but the part of the smooth curve below 298°K. passes through the adjusted values and joins smoothly to the curve above 298°K., the latter curve being based on the authors' values.

From the adjusted values the entropy at 298.16°K. was found to be 6.78 cal. g.-atom^{-1} deg.-K.,$^{-1}$ [17] and the heat content at this temperature (less that at 0°K.) is 1090 cal. g.-atom^{-1}. From these values and equations 1, 3 and 4, the common thermodynamic functions relative to the solid at 0°K. were calculated and are given in Table III.[18]

TABLE III

THERMODYNAMIC FUNCTIONS OF LITHIUM (CAL. DEG.$^{-1}$ G.-ATOM^{-1})

T, °K.	$C_p{}^0$	S^0	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$
298.16	5.892	6.777	3.656	3.121
300	5.899	6.814	3.670	3.144
320	5.999	7.197	3.812	3.385
340	6.126	7.565	3.945	3.620
360	6.273	7.919	4.070	3.849
380	6.433	8.262	4.190	4.072
400	6.599	8.596	4.306	4.290
420	6.765	8.922	4.419	4.503
440	6.922	9.241	4.530	4.711
453.70(s)	7.022	9.455	4.604	4.851
453.70(l)	7.264	11.035	6.184	4.851
460	7.255	11.135	6.198	4.937
480	7.227	11.444	6.242	5.202
500	7.200	11.738	6.281	5.457
520	7.172	12.020	6.316	5.704
540	7.144	12.290	6.347	5.943
560	7.116	12.549	6.375	6.174
580	7.088	12.798	6.400	6.398
600	7.060	13.038	6.422	6.616
620	7.033	13.269	6.443	6.826
640	7.005	13.492	6.460	7.032
660	6.977	13.707	6.477	7.230
680	6.949	13.915	6.491	7.424
700	6.928	14.116	6.504	7.612
750	6.922	14.594	6.532	8.062
800	6.916	15.041	6.556	8.485
850	6.910	15.460	6.577	8.883
900	6.904	15.854	6.595	9.259
950	6.898	16.228	6.611	9.617
1000	6.892	16.581	6.626	9.955
1050	6.886	16.917	6.638	10.279
1100	6.880	17.238	6.649	10.589
1150	6.874	17.543	6.659	10.884
1200	6.868	17.836	6.668	11.168

Vapor Pressure.—At any temperature at which the vapor pressure is not greater than a fraction of an atmosphere, lithium vapor in equilibrium with the liquid can probably be considered ideal except for an equilibrium between the monomer and a small proportion of the dimer. The total vapor pressure may be computed from a spectroscopic value of the equilibrium constant and the partial pressure P_1 of the monomer in the saturated vapor. This partial pressure P_1 may be obtained by combining the thermodynamic equation relating the entropy of the monomer S_1 to the thermal data

$$S_1 = L_0/T + S_{1\text{iq}} + 5/2 - (H_{1\text{iq}} - H_{0(\text{s})})/T \quad (5)$$

and the Sackur–Tetrode equation, if L_0, the heat of vaporization at 0°K., is known. For lithium the Sackur–Tetrode equation, including R ln 2 for the doublet ground atomic state, is

$$S_1 = 11.4392 \log_{10}T - 4.5757 \log_{10}P_1 + 4.8384 \quad (6)$$

where S_1 is in cal. g.-atom^{-1} deg.K.$^{-1}$ and P_1 is in atmospheres.

Gordon[19] has utilized the accurate spectroscopic data summarized by Loomis[20] to calculate the equilibrium between the two gaseous species over a wide temperature range, taking into account anharmonicity and molecular stretching. His values of $T \log_{10} K$, where K is the equilibrium constant $P_1{}^2/P_2$, were increased by 100 to change to the basis of a dissociation energy of 1.12 electron-volts. Following Loomis, Gordon had used 1.14, but Gaydon[21] later re-examined carefully the extrapolation of vibrational levels and recommended the lower value.

The most precise measurements of the vapor pressure of lithium found in the literature were reported by Hartmann and Schneider,[22] who measured in an argon atmosphere eight boiling temperatures from 1208 to 1353°K., in which range the vapor pressure varies from approximately 17 to 94 mm. The partial pressures of the monomer computed from the seven highest of these vapor pressure values gave by equations 5 and 6 a mean value for L_0 of 37960 ± 15 cal. g.-atom^{-1}.

Values of the partial pressure of the monomer in the saturated vapor over a wide temperature range were computed from this value of L_0, the thermal data of Table III, and equations 5 and 6. The corresponding pressures of the dimer and the total vapor pressures were obtained using the gaseous equilibrium constants, and are given in Table IV. All the tabulated total vapor pressures (P, atm.) are represented within approximately 0.1% by the equations

$$\log_{10}P(\text{solid}) = 14.2121 - 8551.18/T - 3.79295 \log_{10}T + 6.7167(10^{-3})T - 6.400(10^{-6})T^2 + 2.684(10^{-9})T^3 \quad (298 \text{ to } 453.70°\text{K.}) \quad (7)$$

$$\log_{10}P(\text{liq.}) = 10.1184 - 8442.53/T - 1.64098 \log_{10}T + 2.5968(10^{-4}\,T) \quad (453.70 \text{ to } 1350°\text{K.}) \quad (8)$$

Equation 8 gives 1600°K. as the extrapolated value of the normal boiling point. Kelley[23] gave 1645°K.

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(18) With 1 cal. = 4.1840 abs. joules, 0°C. = 273.16°K. and the atomic weight of lithium = 6.940. The pressure may be considered constant at 1 atm.

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TABLE IV

VAPOR PRESSURE OF LITHIUM (IN MM.)

T, °K.	Pressure of Li_2	Total vapor pressure	T, °K.	Pressure of Li_2	Total vapor pressure
298.16	2.4×10^{-27}	3.41×10^{-20}	825	1.7×10^{-4}	0.0156
300	4.1×10^{-27}	5.07×10^{-20}	850	3.8×10^{-4}	.0302
325	2.6×10^{-24}	7.13×10^{-18}	875	8.3×10^{-4}	.0562
350	6.7×10^{-22}	4.94×10^{-16}	900	1.7×10^{-3}	.101
375	8.2×10^{-20}	1.94×10^{-14}	925	3.5×10^{-3}	.176
400	5.4×10^{-18}	4.78×10^{-13}	950	6.7×10^{-3}	.297
425	2.1×10^{-16}	8.09×10^{-12}	975	0.012	.488
450	5.6×10^{-15}	9.95×10^{-11}	1000	.022	.782
453.70[a]	8.8×10^{-15}	1.41×10^{-10}	1025	.039	1.22
475	9.7×10^{-14}	9.04×10^{-10}	1050	.067	1.88
500	1.2×10^{-12}	6.54×10^{-9}	1075	.11	2.82
525	1.2×10^{-11}	3.90×10^{-8}	1100	.18	4.16
550	9.7×10^{-11}	1.98×10^{-7}	1125	.28	6.03
575	6.5×10^{-10}	8.66×10^{-7}	1150	.44	8.59
600	3.6×10^{-9}	3.36×10^{-6}	1175	.66	12.1
625	1.8×10^{-8}	1.16×10^{-5}	1200	.98	16.7
650	7.7×10^{-8}	3.66×10^{-5}	1225	1.4	22.8
675	3.0×10^{-7}	1.06×10^{-4}	1250	2.1	30.8
700	1.0×10^{-6}	2.83×10^{-4}	1275	3.0	41.0
725	3.3×10^{-6}	7.06×10^{-4}	1300	4.1	54.0
750	9.7×10^{-6}	1.66×10^{-3}	1325	5.7	70.5
775	2.7×10^{-5}	3.68×10^{-3}	1350	7.8	91.0
800	6.9×10^{-5}	7.76×10^{-3}			

[a] Triple point.

Though the uncertainty in the dissociation energy of Li_2 introduces a substantial uncertainty into the proportions of monomer and dimer, the values of *total* vapor pressure given are consistent with the observed values around 1300°K., and at lower temperatures are relatively insensitive to errors in the dissociation energy. The effect of the uncertainty in extrapolating the heat capacity of the liquid to 180° above the range of measurement also is small.

Discussion

A number of observers have reported measurements of the heat capacity of lithium. Most of these values are shown for comparison with the authors' values in Fig. 2 for the solid and in Fig. 3 for the liquid.

The mean heat capacity of solid lithium between 27 and 100° was measured by Regnault.[24] Laemmel,[25] using a crude drop method, made measurements from −80 to 170°, and Kleiner and Thum[26] reported values from 25 to 182°. Bernini[27] using a Bunsen ice calorimeter, covered several temperature ranges from 0 to 157°. The values of Simon and Swain[14] were discussed above.

Most of the heat capacity measurements on liquid lithium were made very recently, and these show some very large discrepancies. Cabbage,[28] using a drop method, determined values from the melting point (180°) to 1000°, with a precision of approximately ±20%. Yaggee and Untermyer[29] computed the heat capacity from 200 to 500° from their measurements of the relative cooling rates of lithium and aluminum, and claimed an accuracy of ±10% for the values on lithium. The measurements of Bates and Smith[30] from 500 to 1000° and those of Redmond and Lones[31] from 200 to 1100° were made with ice calorimeters, and agree with the authors' values within their estimated uncertainties of ±5%.

Several direct measurements of the melting point of lithium, which is almost identical with the triple point, have been reported previously. Guntz[32] found 190°, and Kahlbaum[33] gave the widely quoted value of 186°. The value 180°, reported by Bunsen and Matthiessen[34] and by Ruff and Johannsen,[35] agrees with that of the authors, which is 180.54°. Losana[36] actually observed 180.2°. The value found by Zukowsky[37] and by Kilner,[37a] 179°, is close.

The authors' value for the heat of fusion of lithium, 432.3 abs. joules per g., may be compared with those of other observers in the same units. Kilner[37a] found 416 ± 40, and the recent compilation of Kubaschewski[38] lists 416 ± 20; these agree with the authors' value within their stated tolerances. Kelley[39] gave 660, which is based on the analysis of several solid–liquid phase diagrams involving lithium as one component. For many years the value of Thum,[40] 137.3, seems to have been the only directly measured one, and though it has been widely quoted, some authors were unwilling to believe that the atomic entropy of fusion of lithium differs from those of the other alkali metals by the large amount indicated by this value. The heat of fusion more recently given by Binayendra[41] agrees exactly with the authors' value.

In Fig. 4 are shown the deviations of three investigations from the vapor pressures of Table IV. Three observers have found values at lower temperatures than those of Hartmann and Schneider[22] by determining the rate of evaporation into a vacuum. Bogros[42] worked in the range from 732 to 845°K., and Maucherat's[43] measurements, on lithium very carefully freed of traces of sodium, were from 735 to 915°K. Lewis's[44] values are over the range 852 to 926°K. and though fairly interconsistent, are more than 200% higher than those of Table IV and are not shown in Fig. 4. He used commercial lithium which is thought[43] to have been contaminated with sodium, which is much more volatile.

The cohesive energy of lithium metal is greater

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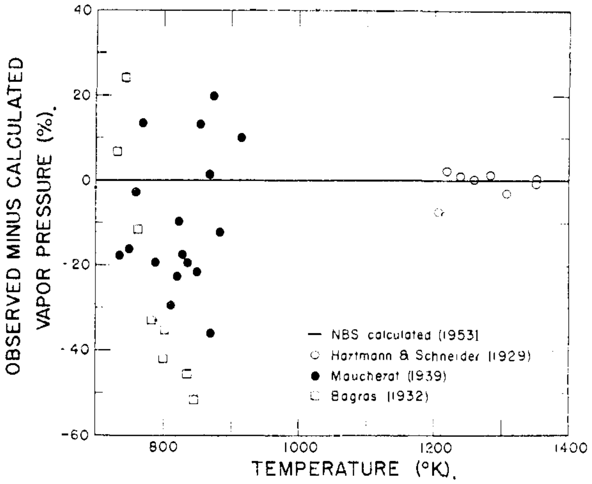

Fig. 4.—Observed and calculated vapor pressure of lithium.

than the heat of vaporization at 0°K., found above to be 37960 cal. g.-atom^{-1}, by the zero point energy of the crystal. An estimate of the latter may be made from the Debye theory, which gives $(9/8)R\theta_D$ per gram atom, where θ_D is the Debye characteristic temperature. The values of C_V of Simon and Swain,[14] corrected as described above, give values of θ_D showing no trend between 40 and 180°K. and averaging 393°K., which corresponds to a zero point energy of 880 cal. g.-atom^{-1}. The resulting "observed" cohesive energy of approximately 38800 cal. g.-atom^{-1} may be compared with that calculated independently of thermodynamic data by quantum-mechanical methods, which is 36200.[45] Seitz believed that the discrepancy is probably due largely to the use in the theoretical calculations of an approximate free-electron expression for the electronic correlation energy.

As shown in Figs. 2 and 3, the heat capacity of lithium increases rapidly with temperature just below the melting point and then decreases more gradually above. This fact may be associated with the unusually low entropy of fusion (0.8 R), and is analogous to the behavior of the alkali metals sodium[4] and potassium.[5]

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[Contribution from the Minerals Thermodynamics Branch, Region III, Bureau of Mines, United States Department of the Interior]

Low-Temperature Heat Capacities and Entropies at 298.16°K. of Some Titanates of Aluminum, Calcium, Lithium and Zinc

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Heat capacity measurements in the temperature range 51 to 298°K. were conducted for aluminum titanate, tricalcium dititanate, lithium metatitanate and zinc-titanium spinel. Regular behavior was observed for all four substances. The following entropy values (cal./deg. mole) at 298.16°K. were obtained: 26.2 ± 0.2 for aluminum titanate; 56.1 ± 0.4 for tricalcium dititanate; and 21.9 ± 0.1 for lithium metatitanate. The measurements and ordinary extrapolation for zinc-titanium spinel yield $S^\circ_{298.16} = 32.8 \pm 0.2$ cal./deg. mole. This value should be increased by an at present unknown amount to take account of randomness in the crystal structure.

Thermodynamic values for titanates are of importance in evaluating methods of treating titaniferous ores and of utilizing high titania slags. Titanates also are becoming increasingly important as ceramic constituents. Several[1-6] previous papers from this Laboratory have dealt with low-temperature heat capacities and entropies at 298.16°K. of titanates. The present paper is a continuation of this work, and presents data for aluminum titanate (Al_2TiO_5), tricalcium dititanate ($Ca_3Ti_2O_7$), lithium metatitanate (Li_2TiO_3), and zinc–titanium spinel (Zn_2TiO_4). No previous similar data are to be found in the literature for any of these substances.

Materials.—Aluminum titanate was prepared[7] from pure hydrated alumina and pure titania. A stoichiometric mixture was pressed into pellets and heated five times for a total of 96 hours between 1400 and 1500° and 43 hours between 1500 and 1570°. After each heat the material was quenched to room temperature, to minimize residence time in the reported region of instability between 750 and 1300°.[8] Grinding, mixing, chemical analysis and adjustment of composition were conducted between heats. The final product analyzed 43.95% titania, as compared with the theoretical 43.93%. The principal impurity is 0.06% silica. The X-ray diffraction pattern agrees with those reported in the literature.[8,9]

Tricalcium dititanate was prepared[10] from reagent grade

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