péni s[42] conclusion that equilibria between paramolybdates and other isopoly species are relatively slowly established under such conditions.

The conductometric data support the structure suggested above for these 6-heteropoly molybdates: (1) by indicating that the initial rapid formation of the complexes in the cold occurs by direct reaction between the tervalent ion and the paramolybdate ion itself and (2) by supporting the idea of the formation of mixtures of isopoly molybdates from expelled fragments.[44]

General.—The general results of this investigation make it clear that 6-heteropoly anions as a class cannot be represented by a single formula or by a single structural model, as is usually attempted. At least three fundamentally different structural types are now known for 6-heteropoly tungstates and molybdates: (1) the 6-molybdotellurate(VI) ion has the Anderson-Evans structure. (2) The anions herein described have a different empirical formula and a polymeric, probably dimeric, structure. (3) The 6-heteropoly tungstates of cobalt have an entirely different type of dimeric structure, which we have elucidated by chemical evidence and X-ray investigation.[45]

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(44) Figure 4 of the paper of Hall and Eyring is more difficult to interpret because the titration involved the addition of an unspecified amount of ammonium hydroxide. Enough ammonium hydroxide was apparently added so that the acid produced by the reaction was all consumed.

(45) L. C. W. Baker and T. P. McCutcheon, abstracts of papers presented at the Fourth Meeting-in-Miniature of the Philadelphia Section, American Chemical Society, pp. 81–83 (January 1951).

PHILADELPHIA 4, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

The Equilibrium $2LiOH(s) = Li_2O(s) + H_2O(g)$

BY N. W. GREGORY AND R. H. MOHR

RECEIVED NOVEMBER 22, 1954

Equilibrium pressures of water vapor above LiOH and Li_2O have been measured between 250 and 400° using both transpiration and effusion methods. Data correlate well with third law entropies of Johnston and Bauer[1] leading to the equation $\Delta F^0 = 32359 - 4.177T \ln T + 0.0116T^2 - 12.661T$. An estimate of the accommodation coefficient (*ca.* 0.01) for the condensation of water on lithium oxide has been made from steady-state effusion pressures.

The lithium hydroxide–lithium oxide–water system has been studied recently by Johnston and coworkers.[1-3] Johnston and Bauer have calculated thermodynamic properties at 25° from low temperature heat capacity measurements and from heat of solution data of de Forcrand.[4] Ditmars and Johnston[3] have attempted to confirm these values in a study of the equilibrium

$$2LiOH(s) = Li_2O(s) + H_2O(g)$$

using the effusion method. We have observed that, although a rough check of the heat of reaction was obtained, the pressures reported are approximately one hundredth as large as those predicted from third law entropies.

Considerable deviation of effusion steady-state pressures from equilibrium values has been observed in this Laboratory in the study of decomposition reactions in halide systems. We believe this to indicate a small accommodation coefficient for the condensation process. The present study was undertaken to see if the low pressures reported by Ditmars and Johnston were associated with a similar difficulty. A transpiration method has been developed which permits the equilibrium to be studied in the same pressure range used in effusion. Two additional series of experiments have been carried out in effusion cells with larger and smaller orifices, respectively, than used by the previous investigators.

Experimental

Lithium hydroxide was prepared by adding an excess of lithium carbonate to calcium hydroxide (Baker's C.P. reagents). After boiling the solution several hours, the supernatant liquid was separated by filtration and concentrated in a nitrogen atmosphere, resulting in crystallization of the monohydrate of LiOH. A five-gram sample (prepared in several batches) was transferred to a nickel boat (under nitrogen) and the anhydrous form, partially decomposed, obtained by heating for two hours at 150° and five hours at 400° under high vacuum in the transpiration apparatus. Analysis of a portion of the material after completion of the transpiration experiments (by titration against standard HCl and gravimetric determination of lithium as the sulfate) indicated that 46.4 mole per cent. of the hydroxide had decomposed and that the original purity was 99.7%.

An independent sample of oxide was prepared by passing oxygen over lithium iodide at 300–400°. The product was found to contain 3.25% $LiIO_3$. After hydration and removal of excess water as described above, equilibrium pressures were found identical with those for the material prepared from the carbonate.

The transpiration apparatus is shown in Fig. 1. The flow of nitrogen, introduced through a P_2O_5 drying trap P, was measured with a calibrated sulfuric acid flowmeter N. Cold traps on each side of the meter were kept at −80°. The temperature of the sample (in furnace M) was measured with five calibrated chromel–alumel thermocouples spaced around the Pyrex tube, and controlled with a Micromax regulator within ±1° of the desired value. Furnaces K and L were used to preheat the carrier gas. The pressure of nitrogen was measured with a manometer attached between E and F; the gas was exhausted through a cold trap (liquid oxygen) and capillary tube at G. The water vapor carried out of the decomposition chamber was collected in H (cooled in liquid oxygen). After completion of an experiment, the system was evacuated to J, and the water collected transferred to the capillary U tube at C. The amount present was determined by observing the pressure produced on vaporization in the calibrated volume between D and B, using a cathetometer and the differential mercury manometer AB. Pressures were measured at 15 mm. or less (v.p. H_2O = 23.8 at 25°). The total volume of the calibrated section

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(1) H. L. Johnston and T. W. Bauer, THIS JOURNAL, **73**, 1119 (1951).

(2) T. W. Bauer, H. L. Johnston and E. C. Kerr, *ibid.*, **72**, 5174 (1950).

(3) W. E. Ditmars and H. L. Johnston, *ibid.*, **75**, 1830 (1953).

(4) H. R. de Forcrand, *Ann. chim. phys.*, [8] **15**, 433 (1908).

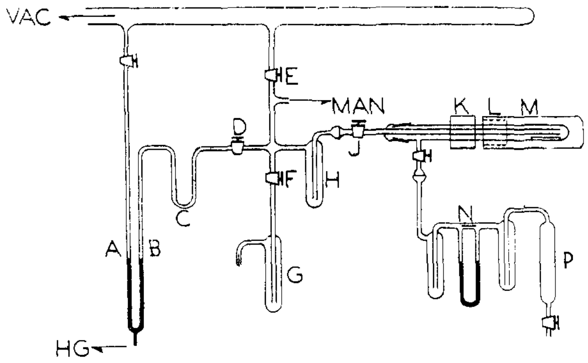

Fig. 1.—Transpiration apparatus.

was 5.6 ml. The time of each experiment was chosen so that *ca.* 10^{-6} mole of water was collected. Several PV measurements were made with each sample and an average taken (maximum variation did not exceed 10%) to determine the number of moles.

Flow rates were varied from 1.2 to 6 liters/hour. Apparent equilibrium pressures for a given temperature were constant within experimental error at flows between 2 and 5 liters/hour and were taken to represent equilibrium values. Thirty-three measurements were made with random variation in the order in which temperatures were selected.

After transfer of the sample from the nickel boat to the effusion cell, effusion experiments were conducted in the same apparatus. The last third of the measurements were made after replacing the line leading from the sample to trap H with a larger diameter stopcock (10 mm. bore) and connecting tubing (25 mm. i.d.) than used in the original transpiration design. Results were not materially affected by the increased pumping speed, however. Two effusion cells were used.

Cell	Length, cm.	Inside diameter, cm.	Orifice diameter, cm.	Orince wall thickness, cm.	K
1 (monel)	3.5	1.7	0.037	0.0175	0.67
2 (nickel)	3.5	1.7	.137	.005	.96

Cells were bored out of metal stock and equipped with tight fitting screw caps with orifices formed by drilling and tapering in a lathe. Orifice dimensions were determined with a calibrated measuring microscope and the Clausing factor K computed as described by Whitman.[5]

The same sample was used in both effusion cells as in transpiration studies. The amount of water leaving the orifices (external pressure maintained below 10^{-5} mm.) was determined in the same way. This procedure permitted the temperature of the sample to be maintained constant for long periods with measurements initiated by placing liquid oxygen around H and stopped by closing stopcock J. Care was taken to assure that trap H and the capillary U tube had come to thermal equilibrium with the room during transfer of the water to the measuring volume and in the final determination of number of moles present, respectively.

Seventeen measurements were made in cell 1 and thirty-three in cell 2; temperatures were selected at random. The sample was rehydrated twice during the effusion experiments. Results from cell 1, Table I, agree with those of the transpiration studies and were assumed to represent equilibrium values.

TABLE I

VAPOR PRESSURES OF H_2O IN THE SYSTEM $LiOH(s)$–$Li_2O(s)$–H_2O (EFFUSION CELL 1)

°K.	P(atm.) $\times 10^7$	Time, min.	°K.	P(atm.) $\times 10^7$	Time, min.
537	6.25	117	589	127	12
533	8.25	65	589	135	6
533	7.03	80	589	136	5
557	37.4	24	598	231	2
557	35.4	24	598	234	3
557	29.6	24	598	220	2
585	117	7	619	505	2
585	135	7	620	531	2
			621	648	2

Pressures were calculated from the equation $P(\text{atm.}) = 0.09568nT^{1/2}/KAt$ with n the number of moles of water collected in t seconds, A the orifice area, K the correction factor for the geometry of cell,[5] and T the absolute temperature. Steady-state pressures from the cell with larger orifice were materially lower than equilibrium values (shown on Fig. 2, results at the same temperature have been averaged).

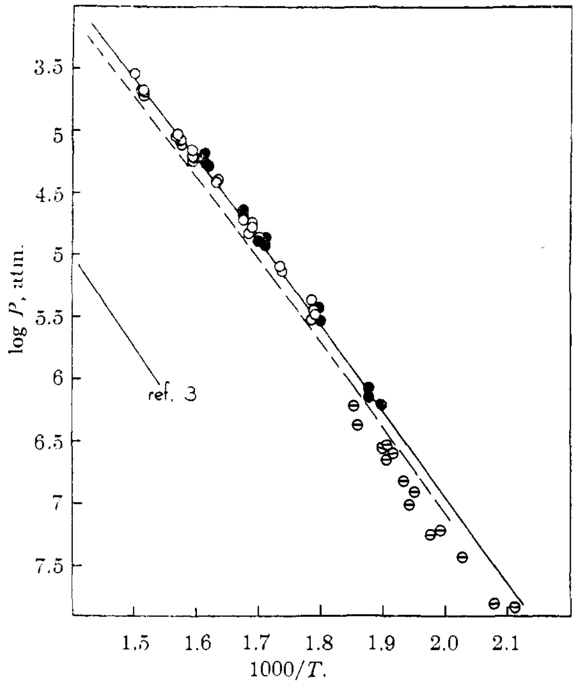

Fig. 2.—Equilibrium pressures of water vapor above LiOH and Li_2O: ○, transpiration; ●, effusion (cell 1); ⊖, effusion (cell 2).

Discussion

Data from the transpiration method and from effusion cell 1 (Fig. 2) can be correlated well by the equation

$$\log P(\text{atm.}) = \frac{-7073}{T} + 2.102 \log T - 2.54 \times 10^{-3}\, T + 2.767 \quad (1)$$

which is shown as the solid curve. The average deviation of log P experimental from calculated values is 0.8%. Equation 1 was derived by adjusting the constants in the general expression

$$\Delta F^0 = \Delta H_0^0 - \Delta\alpha T \ln T - {}^1/_2\Delta\beta T^2 + IT$$

to give $\Delta C_p = -2.76$ cal./° and $\Delta S^0 = 33.70$ e.u. (from Johnston and Bauer) at 25°, and $\Delta S^0 = 29.8$ e.u. and $\Delta H^0 = 30.8$ kcal. at 314° (experimental values from the slope of log P *vs.* $1/T$ plot at the mean temperature of our measurements). Equation 1 leads to the following values at 25° which may be compared with those of Johnston and Bauer (given in parentheses).

$\Delta H^0 = 32.6$ kcal. (32.8)
$\Delta F^0 = 22.5$ kcal. (22.7)
$\Delta S^0 = 33.7$ e.u. (33.85; 33.70 3rd law)

The discrepancy in the heat of reaction, also re-

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[5] C. I. Whitman, *J. Chem. Phys.*, **20**, 161 (1952).

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

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

$$\frac{\Delta F^0}{T} = \frac{35186}{T} + 1.1536 \log T + 0.0108835T - \frac{0.18678(10^6)}{T^2} - 45.758 \quad (2)$$

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.

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SEATTLE, WASHINGTON

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(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), ΔS^0 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]

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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).