ammonium hydroxide, *p*H 8.1, copper and cadmium were found to suppress the reduction wave of tellurium(VI) in a manner analogous to that observed by Lingane, while nickel ion was found to have no effect, possibly because the nickel–ammonia complex is strong enough to prevent the precipitation of nickel telluride in this medium. Of the anions investigated, bromide was without effect in concentrations up to 0.1 *M;* fluoride at this same concentration depressed the apparent wave height by 20%; while tellurite at a concentration of 0.1 millimolar depressed the apparent wave height by 10%. No explanation is offered for the depressive effect of fluoride and tellurite ions on the reduction wave of tellurium(VI).

Polarography of Selenium(VI).—A solution of selenic acid was prepared by the method of Gilbertson and King.[15] Polarograms of this solution were obtained in the following media: 1 *M* NH_4Cl–NH_4OH, *p*H 7.7; 0.1 *M* NH_4Cl–NH_4OH, *p*H 9.0; 1 *M* NH_4 tartrate–NH_4OH, *p*H 8.2; 1 *M* KCl; 0.1 *M* NaOH; 0.5 *M* NH_4 citrate–NH_4OH, *p*H 6.2; saturated NH_4 oxalate–NH_4OH, *p*H 4.9. In no case was a selenium(VI) wave observed prior to the hydrogen wave, thus bearing out the statement of Lingane and Niedrach[2b] that the +6 state of selenium is not reduced at the dropping mercury electrode.

Acknowledgment.—We are grateful to Professor Lingane and Dr. Niedrach for consultation during the course of the present work.

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(15) L. I. Gilbertson and G. B. King, THIS JOURNAL, **58**, 180 (1936).

UPTON, LONG ISLAND, N. Y.

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Vapor Pressures of Inorganic Substances. X. Dissociation Pressures of Lithium Hydroxide between 650° and 800°K.[1]

BY WALTER E. DITMARS AND HERRICK L. JOHNSTON

RECEIVED SEPTEMBER 29, 1952

By means of the dynamic effusion method the dissociation pressure of LiOH has been measured in the temperature range 648–795°K. The empirical equation, log $P = (-7635.1/T) + 5.6786$, was derived. The procedure is described, and an evaluation of results given.

Introduction

The dissociation pressure of LiOH has been measured by the dynamic effusion method in the temperature range 648–795°K. The study was made with the use of nickel Knudsen cells in a simple high vacuum apparatus. The only earlier work found in the literature was the research by J. Johnston[2] whose data were obtained in a completely different temperature range (823–1176°K.) than that of this research. Due to the experimental difficulties of handling the material at higher temperatures, these earlier values are believed to be somewhat uncertain.

Apparatus and Procedure

The procedure employed, to measure the dissociation pressure of LiOH, resembles that of the Knudsen method of vapor pressure measurements.[3] Details of the special apparatus are shown in Fig. 1, the heater and control circuits are shown in Fig. 2. The cell was pressed, in two sections, from sheet nickel 0.025 cm. in thickness. The main section is in the form of a cup 2.54 cm. in diameter by 2.54 cm. in height. This was closed by a cap pressed into position, and electrically welded in an atmosphere of hydrogen. The orifice was formed by drilling a hole through the center of the bottom of the cup, and producing a sharp edge by means of a lathe. The orifice diameter was measured by means of a travelling microscope and, since the hole was not quite round, the area was computed from the average of eight readings.

The LiOH, in the form of a fine powder, was introduced into the cell through the orifice, in a dry nitrogen atmosphere, and the filled cell was kept in a vacuum desiccator preliminary to measurements.

The cell was mounted, in an inverted position, on the end of a monel tube, as shown in the figure. Previous to heating, the system was evacuated from 3 to 18 hours to a pressure of 3×10^{-6} mm. Additional evacuation after this pressure was reached had no effect on the experimental results. A preliminary degassing run was then made to ensure decomposition of any $LiOH \cdot H_2O$. The pressure maintained in the cell during LiOH decomposition runs, was approximately 1×10^{-4} mm. Precautions were taken to avoid contact with air during cell weighings, and during introduction in or removal from the apparatus.

The iron–constantan thermocouple was calibrated by directly comparing a couple made from this same wire with a standardized Pt–10% Pt, Rh thermocouple.

Preliminary runs were made on relatively pure LiOH obtained from the Metalloy Corporation of Minneapolis. The experimental runs were made on material (approximately 99.9% pure) prepared by Dr. Thomas W. Bauer.[4]

The Knudsen cell on which the preliminary runs were made was subsequently cut open. No apparent reaction had occurred between the nickel and lithium compounds, nor between the nickel and the water vapor.

Experimental Results

Dissociation pressures were calculated from the formula

$$P = \frac{\Delta W C}{A_{\text{orifice}} l_{\text{eff}}} \sqrt{\frac{2\pi RT}{\text{M. W. }(\text{H}_2\text{O})}} \qquad (1)$$

where ΔW, the weight loss was measured on an analytical balance; T, the absolute temperature was read directly from the calibrated pyrometer-controller dial; R is the universal gas constant $= 8.3156 \times 10^{-7}$ dyne/cm.^{2}; $C = 9.8692 \times 10^{-7}$ is the conversion factor to atm., A_{orifice} was directly measured at 25°, and coefficient of thermal expansion data from "The Metals Handbook, 1949" were

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(1) This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

(2) John Johnston, *Z. physik. Chem.*, **62**, 339 (1908).

(3) R. Speiser and H. L. Johnston, *Am. Soc. Metals*, **11**, 3 (1949).

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

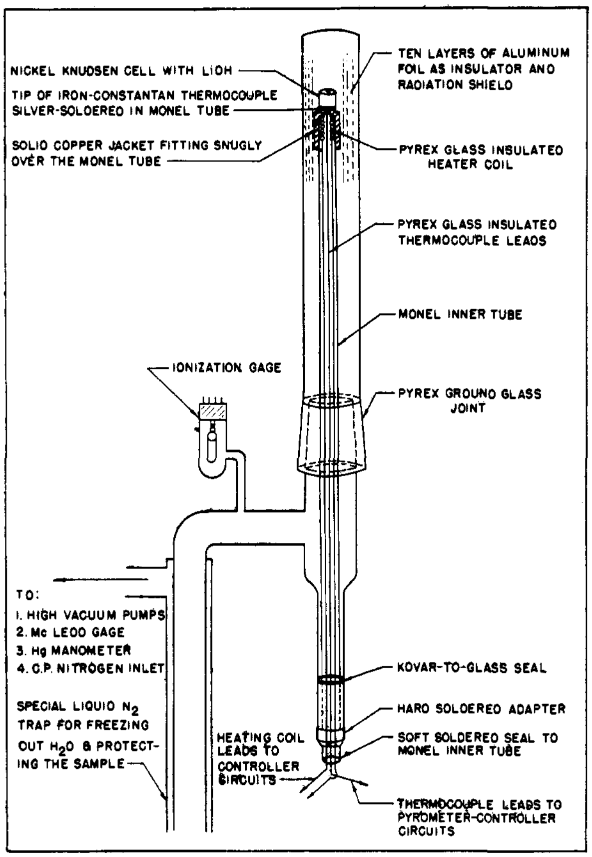

Fig. 1.—LiOH dissociation pressure apparatus.

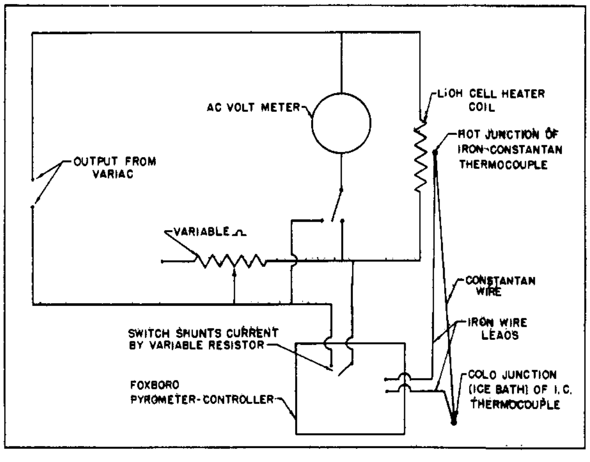

Fig. 2.—LiOH heater-controller circuits.

used to obtain correct values at higher temperatures. Correction for small variations of the temperature, while the samples were coming up to temperature and cooling at the end of the runs, were made by a method similar to that used by Johnston and Marshall.[5]

The data are given in Table I and illustrated in Fig. 3. The straight line curve of Fig. 3 fits the equation

$$\log P \text{ (atm.)} = -(7635.1/T) + 5.6786. \quad (2)$$

This corresponds to a ΔH of 34.94 kcal., and agrees, within experimental error, with the value $\Delta H_{298} =$ 32.82 ± 0.11 kcal. computed by Johnston and Bauer[4] for the reaction

$$2\text{LiOH(s)} \rightleftarrows \text{Li}_2\text{O(s)} + \text{H}_2\text{O(g)} \quad (3)$$

TABLE I

VAPOR PRESSURE DATA FOR LiOH

Run No.	Temp., °K.	Effective time, sec.	Total wt. loss, g.	Evap. rate g. cm.$^{-2}$ sec.$^{-1}$ × 10^6	Pressure, atm. × 10^{-6}
10	648	50045	0.00193	4.064	0.550
13	663	48813	.00706	15.233	2.084
3	677	37907	.00557	15.474	2.140
17	692	39155	.01768	47.535	6.645
7	707	26523	.01095	43.458	6.141
19	707	17544	.00960	39.695	5.609
11	722	24698	.02446	104.215	14.890
15	722	24705	.02686	114.409	16.340
2	736	18803	.01969	110.147	15.88
6	736	19262	.01650	90.103	12.99
18	736	18692	.04358	245.238	35.36
1	752	18574	.05051	285.83	41.65
8	752	18130	.04329	250.972	36.58
12	766	8720	.04731	570.50	83.91
14	766	8692	.02045	247.395	36.39
4	781	5872	.02477	443.053	65.80
9	781	6581	.02319	370.104	54.97
16	795	5632	.04795	894.028	134.00

The ratio of the mean free path of the gaseous molecules inside the Knudsen cell to the orifice diameter, at several temperatures and pressures is shown in Table II. Measurements were undertaken with a second Knudsen cell for testing the

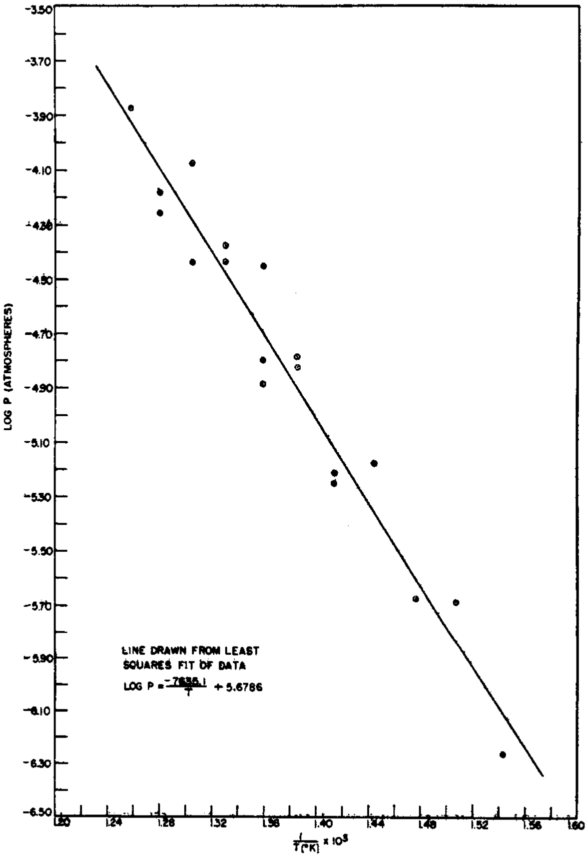

Fig. 3.—Dissociation pressure of lithium hydroxide.

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(5) H. L. Johnston and A. L. Marshall, *ibid.*, **62**, 1382 (1940).

condition for the equilibrium determination of the vapor pressure.[4] Unfortunately, the system broke down at the beginning of these measurements and only one datum of value was obtained.

TABLE II

Temp., °K.	Press., atm.[a]	Mean free path, cm.	Diameter of orifice of Knudsen cell, cm.	Ratio of mean free path to orifice diameter
795	1.34×10^{-4}	0.78	0.11012	7.06
781	6.5×10^{-5}	1.64	.11010	14.9
766	8.39×10^{-5}	1.24	.11094	13.7
736	3.54×10^{-5}	2.85	.11002	25.9
692	6.7×10^{-6}	14.4	.10996	131.0
			.13248	108.5

[a] The pressures given are taken from the run measurements.

Experimental Errors

For reaction (3) we may write

$$\Delta F = -RT \ln K = -RT \ln P_{\mathrm{H_2O}} \qquad (4)$$

From the kinetic gas theory

$$\log P = K + \log \Delta W + {}^1/_2 \log T = \log A_{\mathrm{orif}} - \log t_{\mathrm{eff}} \qquad (5)$$

where P = pressure, K = a constant, ΔW = loss in weight for a run, T = absolute temperature, A_{orif} = area of the orifice, t_{eff} = effective time of run. From the known sources of error in temperature measurements, the measured area of the black body hole, the measurement of the time, and the measurement of the weight loss, it was calculated that the standard deviation of the experimental log P's should be 0.02. The actually observed standard deviation from the least squares curve is 0.14.

It is felt that the discrepancy between the calculated error and the actual average error is due primarily to an uncertainty in ΔW. By experiment it was found that a long period of storage in the desiccator resulted in a weight gain of the sample of only 0.006 g. which cannot account for an error of 0.14. The procedure in handling the sample during each run was standardized as much as possible; however, the atmospheric humidity and the length of time of exposure of the vapor pressure system itself to the atmosphere varied widely from run to run. It is felt that this variation accounts for the uncertainty in ΔW, since the sample itself may have received some moisture from the system after being placed in the apparatus.

It was mentioned previously that the length of the degassing period (when there was no heating in the system) had no apparent effect on the experimental results; however, during the heating periods it was observed that the pressure in the system rose, initially, to maximum values that varied among the runs, but later returned to the usual equilibrium value of $\sim 1 \times 10^{-4}$ mm. This is probably associated with varying amounts of adsorbed water held by the sample.

Acknowledgment.—We wish to acknowledge the suggestions of Dr. James W. Edwards in the design of the cell.

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[CONTRIBUTION FROM THE BATTELLE MEMORIAL INSTITUTE]

The Solubility of Carbon and Oxygen in Liquid Bismuth

BY C. B. GRIFFITH[1a] AND M. W. MALLETT[1b]

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Analytical methods for determining carbon and oxygen in bismuth are described. Using these methods, the solubility limits of oxygen (400 to 750°) and carbon (300 to 750°) in liquid bismuth were determined. The solubility of oxygen in liquid bismuth varies with temperature according to the equation, $\log_{10}$ weight per cent. oxygen = $-(3400/T) + 1.48$. An equation for the variation of liquid solubility of carbon in bismuth with temperature is, $\log_{10}$ weight per cent. carbon = $-(360/T) - 3.17$.

Introduction

In melting bismuth in a Vycor crucible, in a vacuum, an evolution of gas occurred. Analysis of the gas showed it to be CO_2 with traces of CO, N_2 and H_2O.

A search of the literature showed new data on gases in bismuth. Sieverts and Krumbhaar observed no occlusion of hydrogen[2a] or nitrogen[2b] by bismuth at temperatures up to 600°. Smith[3] states that occlusion of hydrogen by bismuth is improbable on general consideration.

No data on the solubility of oxygen in bismuth were found.

Incidental to vapor pressure studies, Ruff and Bergdahl[4] obtained the following estimates of the solubility of carbon in bismuth.

Temp., °C.	1385	1408	1490
Carbon, wt. %	0.012	0.017	0.023

Because the principal gas extracted from liquid bismuth is CO_2, a study was made of the solubilities of the constituents, carbon and oxygen, from which it is derived. The investigation was limited to the temperature range 300 to 750° in order to avoid interference from the vaporization of bismuth which occurs at higher temperatures.

The method of analysis for carbon used by Ruff and Bergdahl was rather insensitive and the experimental technique is questionable. Because of this and the wide intervening temperature range between the temperatures used by them and those

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(1) (a) Based on work performed under AEC Contract No. W-7405-eng-92. (b) Battelle Memorial Institute, Columbus, Ohio.

(2) (a) A. Sieverts and W. Krumbhaar, *Ber.*, **43**, 896 (1910); (b) **43**, 894 (1910).

(3) D. P. Smith, "Hydrogen in Metals," The University of Chicago Press, 1948, p. 286.

(4) O. Ruff and B. Bergdahl, *Z. anorg. allgem. Chem.*, **106**, 91 (1918).