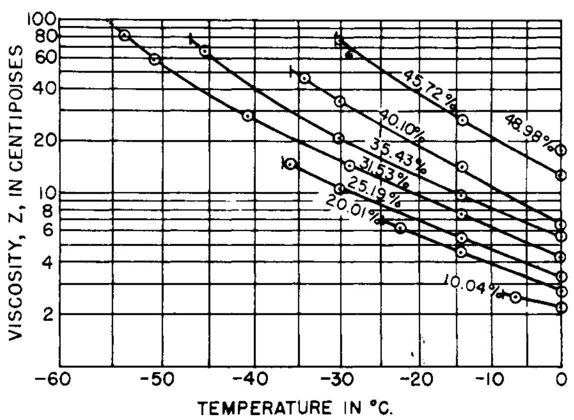

Figure 1. Viscosities of various concentrations of aqueous potassium hydroxide solutions plotted vs. low temperatures, ° C.

using the melting point of pure water and the freezing points of high purity spectrograde carbon tetrachloride (−22.9° C.), monochlorobenzene (−45.2° C.), and chloroform (−63.5° C.).

Densities, or viscosities, were measured while the pycnometer, or viscometer, was all but submerged in the cold methanol test bath. The bath methanol was kept cold by circulating chilled methanol through a submerged helical section of copper tubing in a controlled manner. The recirculated methanol was cooled by a mixture of dry-ice and acetone. The temperature of the test bath could be maintained constant within 0.1° C. or better.

Time. Time of efflux was measured with a stopwatch having a full sweep of pointer in seconds, and marked in 0.1-sec. divisions, readable to 0.05 sec.

The stopwatch, checked at room temperature against a chronometer, was consistently slow by 0.1%, including the human response.

At least four measurements were taken in determining time of efflux.

Density. These measurements were carried out at the various low temperatures using a boiled-water-calibrated glass pycnometer shaped like a volumetric flask of about 37 ml. capacity. The neck of the flask was of 1-mm. bore, 13 cm. long, and ending in a ground tapered male joint. To its tapered female joint, serving as a liquid expansion reservoir, was attached a short 1-mm. bore tube having a miniature stopcock.

Weighings were made on an analytical balance, using weights newly calibrated against those of the Bureau of Standards.

RESULTS

The viscosities and densities of the KOH solutions are given in Table I along with concentrations expressed in terms of molality as well as % KOH by weight. Viscosities were calculated from the data after the manner of Hitchcock and McIlhenny (*3*).

Figure 1 shows the viscosities (*Z*) in centipoises plotted against temperature in degrees centigrade.

Except for the 31.53% KOH curve, the "limits" of these curves correspond to temperatures of incipient crystallization as supplied by Pickering (*5*) and Cohen-Adad and Michaud (*1*).

The precision of the foregoing measurements is estimated as 0.1% for analysis, 0.01% for density, 0.05% for time of efflux, and 0.1% for the constant, *K*.

Relation of Viscosity Data to Data of Others. To get a measure of the over-all accuracy of this present work, a set of graphs was made from viscosity (and density) data at the low temperatures and the best data of others at higher temperatures.

That results at the low temperatures are consistent with those at higher temperatures has been established by the smooth curvilinear transitions in viscosities from the lower to the higher temperatures. For these graphs which plot viscosity against concentration of KOH, the particular values of concentration selected were smoothed values (up to 60° C.) at 10, 20, 25, and 40% KOH, obtained from Solvay's Technical and Engineering Bulletin (*6*), crediting reference (*3*). These smoothed concentrations most closely approximated the values 10.04, 20.01, 25.19, and 40.11% KOH taken from Table I for the check on accuracy.

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Vapor Pressure of Liquid Metal Solutions: Mercury-Lead

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THE PRESENT study is a continuation of experimental work on a binary system containing mercury and tin (*7*). The apparatus and operation have been discussed previously (*7, 8*). Vapor pressure data of mercury-lead are available at 324° C. (*3*), and this work extends these data to other temperature regions.

EXPERIMENTAL

The vapor pressure still was constructed of a 1½-inch diameter, 304 stainless steel pipe. The liquid metal in the still had a depth of 0.5 to 1.0 cm. Helium was used to transmit the vapor-phase pressure to a mercury manometer the interface of which was about 8 inches above the liquid level in the still. This difference of levels decreases with an increase of the pressure in the still so that its effect on

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Vapor pressures of liquid metal solutions were determined experimentally for compositions ranging from 0.1 to 0.9 atomic fraction of mercury in lead. Data are correlated and isobars are plotted for the liquid region of phase diagram. Thermodynamic functions such as activity coefficients and heat of vaporization were also calculated and presented.

manometer reading is less than 0.01 mm. of Hg. The vapor-phase pressure is maintained at a constant level by a manostat connected to a vacuum system. A very small amount of helium is fed from a gas cylinder to the top of the still to assure satisfactory operation of the manostat. Detailed descriptions have been reported (*7, 8*).

Homogeneous liquid metal solutions were prepared by mixing the heated metals under an inert helium atmosphere at about 1 p.s.i.g. Compositions of solutions were computed from those weighted charges of pure metals, and homogeneity of solutions was checked by comparing melting points of respective solutions with those in the literature (*5*). The following metals were used in this investigation. Mercury (F. W. Berk and Co.) was triple distilled and had the following maximum impurities: nonvolatile, 0.001; insoluble in HNO_3, 0.000; and base metal, 0.000%. Lead (Fisher Scientific Co.) had the following maximum impurities: silver, 0.002; copper, 0.005; iron, 0.001; and arsenic, 0.000%.

Table I. Experimental Data

t, ° C.	P, Mm. of Hg	t, ° C.	P, Mm. of Hg	t, ° C.	P, Mm. of Hg
0.100 Pb[a]		0.400 Pb		0.700 Pb	
225.7	35.29	222.0	26.72	260.2	52.68
263.9	103.16	257.5	73.85	269.7	66.50
291.0	195.41	284.3	142.63	277.6	76.40
304.6	266.96	300.4	206.45	288.9	100.29
323.2	375.71	322.4	304.32	313.0	159.75
0.198 Pb		0.499 Pb		0.799 Pb	
228.5	36.12	221.5	24.95	280.1	56.61
257.4	82.42	245.1	45.62	284.0	62.48
280.6	149.69	270.0	88.96	294.1	75.98
306.7	258.28	291.5	156.84	302.6	91.91
324.7	360.38	311.0	232.70	318.1	120.91
0.300 Pb		0.600 Pb		0.892 Pb	
214.0	22.91	234.2	28.21	320.9	62.62
257.7	81.23	270.0	76.18	332.0	77.11
280.8	143.78	297.8	142.18	343.7	89.26
309.7	262.25	315.0	204.61	353.4	104.60
325.6	345.42	323.9	242.60		

[a] Atomic fraction of Pb.

The vapor-phase pressure of the still as transmitted by the inert gas was measured by a mercury manometer with one leg attached to a vacuum system. The vacuum side pressure was measured by a McLeod gage, and the manometer was read by using a cathetometer to ±0.005 mm. of Hg. The bubble point was then determined graphically by plotting temperature–time curve of a stirred liquid in the still which was heated continuously with a constant electric power input. The reported pressures have been corrected from room temperature to 0° C. The temperature was measured by a calibrated iron-constantan thermocouple with a hot-junction at 1 mm. under the metal surface and a cold-junction at 0° C.

RESULTS

Experimental data are summarized in Table I. They are in agreement with Hildebrand's data (*3*) of the same system at 324° C. by comparing activity coefficients of Hg in Tables II and III. Nine liquid compositions were determined in this work.

Since an assumption was made to use weighted charges as the liquid composition for a series of runs, measurement of mercury condensate on still wall was made for a solution containing 0.799 atomic fraction of lead. The total deposit was 0.5 gram which corresponds to about an error of 0.02 atomic %. The error depends on temperature and operation time. Therefore, results obtained at high temperature, especially the 0.9 lead fraction, may have errors larger than 0.02% and less than 0.05%. The other estimated maximum errors of temperature and pressure measurements were 0.5° C. and 2 mm. of Hg, respectively.

Table III. Activity Coefficient of Hg at 324° C.
[Calculated from data of (*3*)]

Atomic Fraction of Lead	Activity Coefficient of Hg	Atomic Fraction of Lead	Activity Coefficient of Hg
0.093	1.037	0.503	1.409
0.152	1.086	0.593	1.454
0.223	1.145	0.695	1.572
0.280	1.200	0.799	1.652
0.401	1.313	0.899	1.728

Table II. Calculation Results

Atomic Fraction of Lead	A[a]	B[a]	Av. Dev.[b], Mm. of Hg	ΔH, Cal. Per Gram Atom Vapor	γ	
					290° C.	310° C.
0.100	7.8750	−3152.56	4.30	−14,423	1.066	1.071
0.198	7.7947	−3122.34	4.58	−14,285	1.125	1.125
0.300	7.7610	−3112.42	4.03	−14,239	1.242	1.241
0.400	7.7615	−3131.32	5.15	−14,326	1.343	1.345
0.499	7.8096	−3178.38	2.12	−14,541	1.483	1.494
0.600	7.6693	−3150.93	1.61	−14,416	1.504	1.510
0.700	7.0665	−2849.78	0.87	−13,038	1.715	1.650
0.799	6,8752	−2831.44	0.76	−12,954	1.776	1.705
0.892	6.0006	−2493.94	0.95	−11,410	1.753	1.605

[a] $\log P_{\text{mm.}} = A + B/T$, ° K., vapor pressure correlation.
[b] Average deviation between measured and correlated values = $(\sum_{i=1}^{n} | t_m - t_c |)/n$.

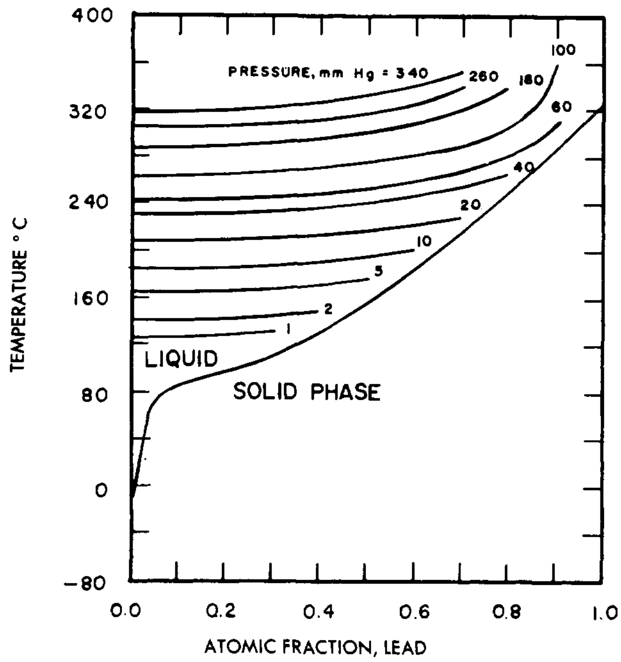

Figure 1. Isobars of liquid phase of mercury-lead system

DISCUSSION

Data were correlated by fitting them into Equation 1 with the least square method. The calculated constants *A* and *B* are shown in Table II for each liquid composition. Constant *B* is related to the differential heat of vaporization of mercury as $\Delta H = -2.3RB$. This relationship, similar to the Clausius-Clapeyron equation for a single-component system, is obtained by combining assumptions of ideal gas behavior of vapor and negligible liquid volume with a Clapeyron equation for a binary mixture shown by Dodge (*1*). The constant *B* represents $d(\log P)/d(1/T)$ according to Equation 1. The differential heat of vaporization of mercury is defined as the latent heat of vaporizing 1 gram atom of mercury from a constant composition liquid to a vapor in equilibrium with that liquid at its bubble point temperature. Since the vapor pressure of lead (*4*) is 1 mm. of Hg at 973° C., the present system at less than 350° C. can be assumed to contain only one volatile component, mercury. Therefore, the calculated differential heat of vaporization in Table II is that of mercury in liquid to pure mercury vapor.

$$\log P = A + B/T \qquad (1)$$

Isobars were plotted on the phase diagram of this liquid metal system by using the developed vapor pressure correlation. Figure 1 shows vapor pressures of various liquid metal solutions. The vapor pressure of solution is affected more by the temperature than by the composition. Table IV summarizes the vapor pressures of mixtures at their respective melting points as estimated from Equation 1.

Table IV. Vapor Pressure of Solution at Melting Point

Atomic Fraction of Lead	Melting Point, ° C.	Vapor Pressure, Mm. of Hg
0.100	84.4	0.10
0.198	100.0	0.27
0.300	113.1	0.50
0.400	134.2	1.19
0.499	156.9	2.63
0.600	187.2	6.67
0.700	220.8	19.82
0.799	250.0	29.1
0.892	283.3	33.0

Assuming ideal behavior of mercury vapor, liquid phase activity coefficient of mercury can be calculated by $\gamma = P/xp$. The vapor pressure of mercury was computed from data in (*6*). The magnitude of activity coefficients indicates the extent of deviation of metal solutions from ideal behavior. They are about 10% larger than those of mercury-tin systems under similar conditions. Mercury and lead are more closely positioned on the periodic table than mercury and tin, and yet the former deviates more from ideality than the latter.

Utilizing the general behavior of solutions of organic compounds as a guide for that of solutions of elements, one would expect that both the size and structure of atoms may cause this difference in behavior. Since lead and tin are both in group 4A and have a coordination number of six, their atomic structure mainly referring to orbit electrons is essentially the same and probably has the same magnitude of contribution to their respective mercury solutions. The remaining contributing factor is atom size. Mercury, lead, and tin have atomic radii respectively of 1.46, 1.74, and 1.40 A. (*2*). This shows that mercury and tin are more similar in atomic size than mercury and lead. Therefore, the former pair shows less deviation from ideality than the latter as indicated by these experimental data.

NOMENCLATURE

A, B = constants in Equation 1
ΔH = differential heat of vaporization of mercury
p = vapor pressure of mercury at temperature of liquid solution
P = total pressure of liquid solution
R = gas constant
x = atomic fraction of mercury in liquid solution
γ = activity coefficient of mercury in liquid solution

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