Vapor Pressure of Liquid Metal Solutions: Mercury–Tin

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Experimental measurements of bubble point temperature of a stirred liquid mixture under helium atmosphere at a controlled pressure were made to obtain vapor pressures of binary liquid solutions of mercury and tin. Thermodynamic functions such as liquid-phase activity coefficients and heat of vaporization were calculated and presented.

WITH THE ADVENT of nuclear reactors and high temperature technology, liquid metals have found an increasing number of applications. Also, they represent a unique class of relatively simple solutions of atoms and their agglomerates. Therefore, a study of their vapor pressures and related thermodynamic properties is of interest from both theoretical and practical grounds.

Behavior of metal solutions may be studied by measuring electric potentials between the liquid metal solution of interest and a reference electrode or by measuring vapor pressure of solutions. Usual methods of measuring vapor pressure require an elaborate set-up and are time-consuming. The present work used a simple apparatus (*1*) and shortened the experimentation time (*4*). A slight decrease of precision is therefore expected. Maximum errors in measured temperature and pressure here are respectively 0.5° C. and 2 mm. of Hg. These errors are caused mainly by pressure fluctuations of solution in the neighborhood of its bubble point.

The binary system studied in this work consists of a volatile component (mercury) and a relatively non-volatile component (tin). Vapor pressure data of this system at 324° C. are available (*2*) but that at other temperatures are not. This work presents experimental data at temperatures below 324° C. and shows temperature effect on solution behvavior or deviation from ideality.

EXPERIMENTAL

Materials. Mercury (F.W. Berk and Co.) was triple distilled and had the following maximum impurities:

non-volatile	0.001%
insoluble in HNO_3	0.000
base metal	0.000

Tin (J.T. Baker Chemical Co.) had the following maximum impurities:

As	0.000005%
Cu	0.0005
Fe	0.0005
Pb	0.001
Zn	0.0005

Equipment. The equilibrium still in Figure 1 is made of 304 stainless steel and contains a thermocouple well and a stainless steel stirring rod which is not shown in Figure 1. The lower end of this rod was bent to a hoop shape to stir liquid and the upper end was welded to a stainless steel tube which contains a soft iron core and is inside the glass adapter. A solenoid slipped on the glass adapter causes the mixing rod to oscillate vertically within a distance less than 1 cm. and thus to agitate liquid. The lower part of the still, about four inches, was heated by an electric furnace.

The use of a magnetic stirrer diminishes liquid phase temperature gradient from about 1° C./mm. (without stirring) to less than 0.1° C./mm. as measured by thermocouple travel. This is essential for an accurate measure-

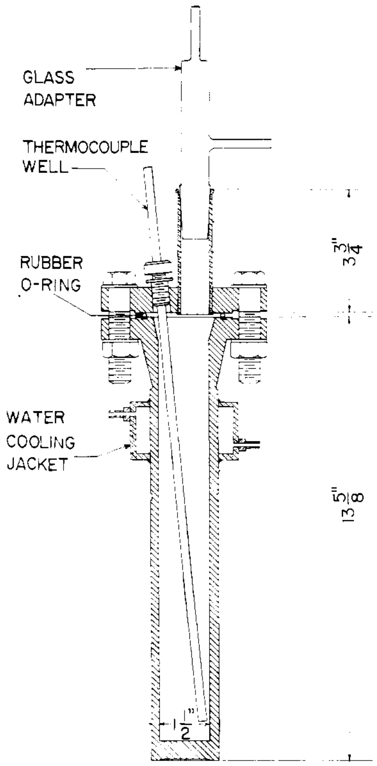

Figure 1. Equilibrium still

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ment of bubble point. During regular runs, the thermocouple junction was always adjusted to about 2 mm. below the interface. Other advantages of this stirring rod are speeding up preparation of a homogeneous solution and having no possible leakage of air into the system in comparison with other mechanical driving devices.

The metal vapor pressure inside the still was transmitted by helium gas to a mercury manometer with the other leg connected to a vacuum pump and a McLeod gage which gives the absolute pressure on one side of the manometer. Differential mercury levels of the monometer were measured with a cathetometer with a precision of ±0.05 mm. The sum of readings of the monometer and McLeod gage gave the absolute pressure of the still.

The still was enclosed in a hood and a small fan drew air from this hood continuously to a water scrubber. This prevented hazards of poisoning from possible metal vapor leaked from the still.

Procedure. Approximately 200 grams of metals were weighed and charged to the still. Then the whole system was pumped to a pressure less than 50 microns, leaks were checked and the system was refilled with helium. Two or three such cycles were performed to eliminate air and moisture which will react with metals at an elevated temperature.

These metals were heated under helium for melting and complete dissolution with the aid of the stirring rod. About thirty minutes was spent on stirring after melting which was indicated by a heating curve from a temperature recorder. The still was then cooled and pressure was lowered to a chosen level which was subsequently maintained by using a Cartesian manostat and a slow purge of helium.

The temperature controller was then turned to a high temperature setting so that liquid metal solution was continuously heated under a constant pressure. Temperatures of furnace, metal solution and their difference were logged on a recorder and the power input to the furnace could be changed by adjusting a resistor connected in series with the heating elements of the furnace. Approach of bubble point was indicated by a slight change of slope of the difference-temperature curve. When this was observed, the thermocouple in still was switched from the recorder to a high precision potentiometer and mild stirring was initiated. Temperature was then measured every two minutes and pressure reading was also checked. The bubble point was subsequently determined graphically by plotting temperature *vs.* time (i.e. a heating curve). The bubble point of the solution is the intersecting point between two extrapolated lines of different slopes and usually between two consecutive points less than 1° C. apart.

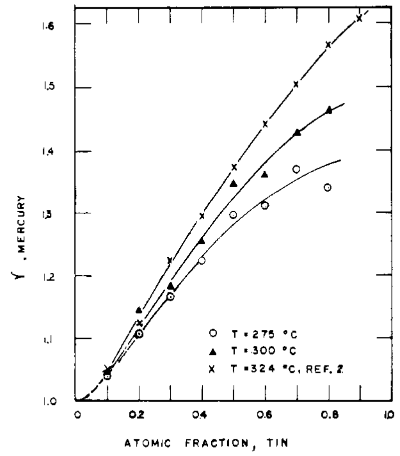

Figure 2. Liquid phase activity of coefficients of mercury

Table I. Experimental Data

t° C.	Pressure Mm. of Hg	t° C.	Pressure Mm. of Hg
0.100 Sn[a]		0.500 Sn	
255.1	79.28	268.6	76.90
265.7	104.39	276.0	93.67
271.4	120.39	288.0	123.73
283.9	159.02	304.2	181.75
295.4	208.10	310.7	204.89
309.7	288.68	322.8	311.78
0.200 Sn		0.599 Sn	
254.1	73.50	235.6	25.13
262.7	89.59	253.2	40.49
271.6	112.99	265.4	57.65
296.2	203.51	278.0	78.10
314.0	304.77	304.2	142.60
		318.7	205.92
0.300 Sn			
267.5	94.08	0.700 Sn	
273.6	120.02		
290.5	169.32	238.1	21.44
301.0	206.42	265.0	41.86
317.1	299.99	287.8	80.50
		320.1	163.15
0.400 Sn			
264.0	76.93	0.798 Sn	
273.6	100.80	269.7	32.50
290.2	145.59	289.7	54.18
304.0	205.34	311.9	99.07
324.7	311.78	315.6	103.38

[a] Atomic fraction of tin.

After a measurement was made, pressure was reset to a level higher than the previous one. Periodic measurements of temperature and pressure were repeated to obtain a new bubble point. A repetition of this precedure thus yielded a set of vapor pressure *vs.* temperature data at a constant liquid composition. Then, the still was cooled to room temperature under helium and additional metal was added to change composition of the solution and the above procedure was repeated.

Calibration of thermocouple was made by comparing experimental bubble points of pure mercury with calculated temperatures from the mercury vapor pressure correlation (*3*). The maximum correction to the standard millivolts table of the Alumel-Chromel couple used here was less than 2° C. All manometer readings were also corrected for room temperature effect on density change of mercury.

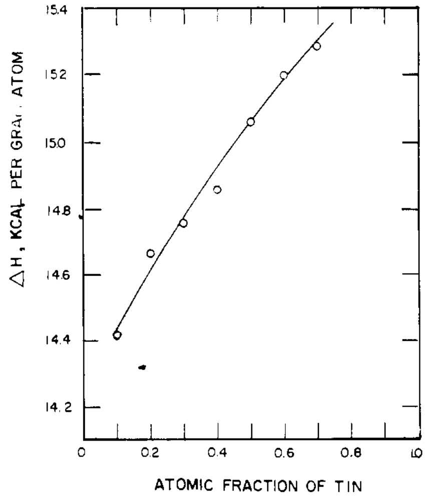

Figure 3. Differential heat of vaporization