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Solvent Vapor Pressures over Dilute Solutions of Tin in Mercury

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The isopiestic balance has been used to measure mercury vapor pressures over dilute solutions of tin in mercury at 523° K. These measurements were made on alloys varying in composition from 0.90774 to 0.99847 mole fraction of mercury. These results do not seem to be described by a simple mathematical function and do not approach ideal behavior in the region of measurement. Deviations from a smooth curve through the data are not greater than 0.0003 in the activity (0.3 gram cal. in the mercury partial molar free energy), and the agreement with other work is excellent.

THE ISOPIESTIC BALANCE has been used to make highly precise measurements of the cadmium vapor pressure over cadmium solutions containing small amounts of solute (*3, 4, 11*). Cadmium vapor pressures have been measured with apparent high accuracy at compositions as great as 0.9984 mole fraction. The present work extends the use of this balance to measurement of mercury vapor pressures over dilute solutions with tin as the minor component.

EXPERIMENTAL

Equipment. The general construction of the balance has been described (*2, 4*). Briefly, the isopiestic balance consists of a quartz tube contained in a furnace and suspended by a balance system. The tube consists of two vertical legs joined at their tops by a horizontal section. One leg contains the alloy, the other pure mercury condensate. The furnace surrounding the quartz tube contains four separate heaters which independently control the temperatures of each leg and of each half of the horizontal section. The top is maintained at a higher temperature than either leg, to prevent condensation. The quartz tube is mounted on a frame suspended from two fine wires and is counterbalanced so that it may pivot freely.

A side arm of the frame is attached by a third fine wire to an analytical balance. As mercury transfers from the alloy reservoir to the mercury reservoir the weights on the analytical balance must be adjusted to return the balance to its null position. The dimensions of the isopiestic balance system cause a weight shift at the analytical balance to be six times greater than the weight of mercury transferred. When no weight shift is occurring at the analytical balance, the mercury vapor pressure over the alloy and over the pure mercury condensate is the same. The alloy must necessarily be at a higher temperature than the mercury when no weight transfer is taking place. This temperature difference is measured directly with a Pt-Pt–10% Rh thermocouple pair, each junction being placed about 0.5 inch from the bottom of one of the two quartz legs. To assure nearly identical compositions the hot and cold junctions are made by cutting both types of wire and forming the two junctions at the cuts. The absolute temperature of the alloy reservoir is also measured. Copper wire is used to connect the various thermocouples to the potentiometer through a switch. All junctions between the thermocouples and the copper wire are placed side by side in an ice bath, with direct contact prevented by their individual containment in thin sleeves of plastic tubing. The relative positions of these junctions to each other are permanently fixed to eliminate spurious effects. On one of the balances these junctions are further contained in an aluminum block.

From a knowledge of mercury vapor pressure variation with temperature, the vapor pressure of the mercury over the alloy can be calculated. The composition of the alloy can be changed as desired, by condensation into or evaporation from the pure mercury reservoir. The composition of the alloy for any given measurement can be determined from the corresponding analytical balance reading.

Procedure. The original surfaces of reagent grade tin (99.9% purity by manufacturer's analysis) were removed by cutting. Then the tin was washed, first with reagent grade acetone, then with analytical reagent petroleum ether. Triple-distilled mercury was further purified by slow distillation from a tube containing uranium to remove oxide.

The isopiestic balance equilibration tube with a secondary U-tube attached was evacuated to 10^{-8} atm., flamed, then filled with argon. Tin was placed in one leg of the balance tube, mercury was loaded into the secondary tube, then the system was again evacuated to 10^{-8} atm. and flamed. The secondary tube was sealed off from the vacuum system, and part of the mercury was evaporated from the secondary tube into the horizontal section of the balance tube. Finally the balance tube was sealed off, separated from the secondary tube, and attached to the frame in the isopiestic balance. Slow distillation from the horizontal section into the alloy leg using the balance furnace completed the mercury purification. After all of the mercury had been distilled into the alloy, the sensitivity of the balance was increased by adjusting weights on the frame and on the pointer of the analytical balance until a weight shift of 0.02 mg. at the analytical balance could be detected. A balance reading was then taken.

The temperature of the mercury leg was lowered until condensation began and was held until the initial small droplets had formed into a single drop. A temperature slightly off that for pressure equilibrium was maintained until enough relatively slow transfer of mercury had taken place to create a desired alloy. Typically, the difference between the temperature held and that temperature which would give pressure equilibrium was 0.2° to 0.3° K.

Measurements were taken using the double reversal technique (*4*). After both reversals have been observed, thermocouple readings are taken and recorded for determining the absolute temperatures of the alloy and mercury reservoirs and of each half of the horizontal section. Then the temperature controller is set to maintain a temperature slightly off that for pressure equilibrium, so that the alloy composition may be changed to another desired value. When measurements have been made at a number of alloy compositions, a final analytical balance measurement is recorded. The top of the furnace is opened, leaving all heaters on, and the horizontal section is collapsed at the center with a torch. Later the amount of metal on each side is determined by weighing. From the initial and final analytical balance readings and the initial and final weights of mercury in the mercury reservoir, a factor relating the weight shift on the analytical balance to the weight of mercury transferred can be determined accurately. This factor varies slightly from tube to tube because of slight differences in dimensions.

For measuring thermocouple e.m.f.'s a Keithley 149 millimicrovoltmeter and Leeds & Northrup six-dial potentiometer combination was used with one isopiestic balance, and a Leeds & Northrup galvanometer and Wenner potentiometer combination was used with a second isopiestic balance. Both combinations had sensitivities of 0.01 μv. A double-pole, double-throw switch was used to connect the potentiometer first to the thermocouple, then to a short length of copper wire. The difference between these two readings was taken as the thermocouple potential.

Uncertainties. The precision of the isopiestic balance is high. For measurements of activity change with change in composition, the accuracy is also apparently high. Activity changes can often be detected to 1 part in 10,000 and composition changes to 1 part in 100,000. Absolute uncertainties in the activity may be reduced by extrapolating the observed results to mole fraction equal to unity (pure mercury), where the activity must also be equal to unity, to establish a thermocouple bias correction applicable to a particular run. The bias corrections for the various runs were in the range of about 3.0 ± 0.3 μv., corresponding to 0.01 ± 0.001 in the activity. The accuracy of the bias correction depends upon the correctness of the extrapolation.

Composition uncertainties are probably not a major source of error. There is only a small amount of tin (99.9%) in each alloy, so impurities in the alloy from this source would be negligible. The steps taken to purify the mercury have been discussed. Any impurities in the alloys would be expected to change the slope of the activity–mole fraction plots roughly in proportion to the fraction of impurities present. Since in the three isopiestic balance tube loadings, three different ratios of mercury to tin were introduced, similar slopes in regions of overlap between the various runs indicate no significant impurities to be present.

Although the balance system was adjusted to a sensitivity sufficient to detect weight shifts of 0.02 mg. at the analytical balance for reversal detection, the accuracy of the analytical balance with its weights was probably only ±0.2 mg. or less. Since the balance factor is approximately 6, the uncertainty in the weight of mercury transferred is ±0.03 mg. For a 3-gram sample this leads to an uncertainty of 1 part in 100,000. All weighings of tin and mercury before introduction into and after removal from the balance tube were made to 0.01 mg.

A number of factors are involved in the activity determinations. To begin with, the separation between reversals depends upon several factors: The balance sensitivity is different from measurement to measurement; heating and cooling due to mercury evaporation or condensation influence the heating rate of the samples; the sample and the thermocouple do not heat identically; and slight composition differences may exist between the bulk alloy and its surface with direction of net mercury transfer partially determining surface composition. The "double reversal" technique reduces absolute errors due to the above factors, because with this technique they tend to cancel. If the balance system is allowed to drift very far from the null position, shifting of the meniscus in each leg will appear as a weight shift at the analytical balance. To eliminate errors due to this effect, the tip of the analytical balance pointer was never allowed to drift from the null position by more than 0.05 mm.

The difference thermocouple measurements are made to the nearest 0.01 μv. Uncertainty in absolute temperatures is ±0.1° K. A bias correction, which is constant throughout a run, must be applied to all of the difference thermocouple readings. This bias is present for two reasons. First, the horizontal section of the isopiestic equilibration tube must be a few degrees higher in temperature than the legs to prevent condensation. Some heat from the horizontal section flows down the quartz tube legs. Most but not all of this heat is then drawn off by heat sinks near the top of the tube legs. There remains, however, a small temperature difference between the bottom of the tube and the thermocouple junction below it which contributes to a small temperature bias. In addition, thermocouple strains passing through temperature gradients as the thermocouple is led out of the furnace can contribute further to a thermocouple bias. These effects are essentially constant throughout a given run and may be eliminated by adding a constant correction factor to all the difference thermocouple readings.

A correction factor of 0.89 μv. was subtracted from all measured thermocouple e.m.f. readings to bring the equation (*9*)

$$E = -35.01 + 6.10222t + 0.00728131t^2 - 0.0000050249t^3 \qquad (1)$$

into agreement with more recent reference tables (*10*). For the above equation, E is in microvolts, and t is in degrees centigrade.

The vapor pressure over pure mercury was determined using the equation

$$P_{\mathrm{Hg}^{\circ}} = \exp\,(11.80812 - 7393.02/T) \qquad (2)$$

which is consistent with Hultgren's (*6*) values for mercury at temperatures in the vicinity of 523° K. The uncertainty of 13 cal. per mole in $\Delta H_{\mathrm{v},\ 298^{\circ}\,\mathrm{K.}}$ leads to an uncertainty in $(1 - a_{\mathrm{Hg}})$ and in $da_{\mathrm{Hg}}/dN_{\mathrm{Hg}}$ of less than 1 part in 1000. Corrections for differences between fugacity and vapor pressure of mercury amount to corrections in the mercury activity of 1 p.p.m. (*4*).

The major sources of uncertainty which reduce the precision of the activity measurements and the accuracy of differences between activity measurements are the uncertainty of the difference thermocouple e.m.f. (±0.05 μv.) at the time a reading is taken, and the uncertainty in the exact time at which reversal takes place, leading to an additional uncertainty of perhaps ±0.03 to 0.04 μv. in the difference thermocouple reading. Thus, the maximum uncertainty in the activity due to these effects is less than ±0.00033 in the activity, or 1 part in 3000. Usually, the errors have been less, averaging about 1 part in 10,000. An uncertainty in the bias correction leads to a greater uncertainty in the absolute value of the activity.

RESULTS

Table I gives the results of measurements on the tin-mercury system. Three isopiestic balance tube loadings were made, the first two runs being carried out in one isopiestic balance and the last run in a second balance. The activities are determined by dividing the mercury vapor pressure over the alloy by the vapor pressure of pure mercury at the same temperature. Activity is used because of its slow variation with alloy temperature and because it is determined by the temperature difference between the alloy and pure solvent reservoirs.

Figure 1 is a plot of mercury activity *vs.* mercury mole fraction. A smooth curve can be drawn through the data having no points of inflection in the range for which measurements were taken. This curve does not seem to be a simple mathematical function, so no empirical equation describing the data is given. Maximum deviations of the data from the smooth curve are not greater than ±0.0003 in the activity, the average being ±0.00012. An uncertainty of ±0.0003 in the activity corresponds to an uncertainty of ±0.3 gram cal. in the mercury partial molar free energy.

In an additional run made to determine the bias directly, 3.98906 grams of mercury were loaded into a tube and a balance factor of 6.039 was obtained from a balance reading with all mercury in one leg, and a reading with all in the other. The results for the measurements taken are shown in Table II. There is very little change in bias with change in balance weight and the average value for this run was about 0.6 μv., which is much smaller than values obtained by extrapolation. If biases of 0.6 ± 0.3 μv. were used rather than 3.0 ± 0.3, the activity curve would remain essentially unchanged in shape, but would be raised by 0.007.

DISCUSSION

At the greatest dilution measured the slope of the activity *vs.* mole fraction curve is 3.3, apparently increasing with increasing dilution. This behavior has been observed in a number of other systems in this concentration range (*3, 4, 11*). For the most dilute solution measured, the average separation of solute molecules must be less than 8.7 nearest neighbor interatomic distances. It is very possible for the influence of a solute molecule to extend further than this because of the nature of metallic bonding. Therefore, infinitely dilute solution behavior may not have yet been approached.

Table I. Vapor Pressure Measurements of Activity of Mercury Alloyed with Tin

Point No.	Balance Shift, Grams	Mercury Mole Fraction,[a] N_{Hg}	Temperature, °K.				ΔT° K.[c]	Mercury Activity,[d] a_{Hg}
			Alloy[b]	Mercury[b]	Alloy cross arm[b]	Mercury cross arm[b]		
Run I								
1	0.4246	0.99558	522.6	522.1	541.8	544.5	0.496	0.98666
2	11.3020	0.98903	523.6	522.9	542.4	545.0	0.740	0.98023
3	15.5012	0.97438	523.9	522.7	542.6	545.7	1.120	0.97021
4	17.0064	0.95085	523.8	522.2	542.7	545.0	1.638	0.95670
5	14.9356	0.97829	523.5	522.4	541.9	545.3	1.041	0.97225
6	16.2153	0.96685	523.3	522.0	541.4	544.1	1.314	0.96506
7	16.9004	0.95383	523.1	521.6	540.9	544.1	1.574	0.95826
8	16.6336	0.95996	523.1	521.7	540.9	544.1	1.447	0.96155
9	3.3293	0.99474	523.1	522.6	540.2	544.0	0.534	0.98566
10	6.2958	0.99348	523.6	523.0	541.2	544.6	0.573	0.98466
11	4.4935	0.99431	525.4	524.9	542.4	547.2	0.545	0.98551
12	17.3083	0.93975	525.4	523.6	541.9	545.5	1.818	0.95231
Run II								
13	1.5967	0.97063	526.6	525.4	544.4	547.5	1.235	0.96755
14	3.0446	0.96574	526.6	525.2	544.2	547.0	1.348	0.96461
15	4.6861	0.95776	526.3	524.8	544.5	546.9	1.516	0.96023
16	7.3262	0.93247	524.0	522.1	541.7	543.8	1.932	0.94914
17	7.7360	0.92555	523.8	521.8	541.9	544.1	2.033	0.94649
18	8.5084	0.90774	524.3	522.0	542.2	544.2	2.310	0.93951
Run III								
19	5.3399	0.99847	523.7	523.5	544.2	546.3	0.220	0.99408
20	11.3727	0.99804	523.7	523.4	543.4	545.5	0.285	0.99234
21	16.3731	0.99745	523.8	523.5	543.0	545.2	0.353	0.99052
22	18.6800	0.99703	523.9	523.5	543.2	545.4	0.382	0.98977
23	21.1557	0.99640	523.7	523.2	542.9	545.1	0.443	0.98812
24	23.7954	0.99535	524.0	523.5	544.5	546.7	0.502	0.98656

[a] Run I. Initial mercury 3.06500 grams; tin 0.00787 gram; 6.0570 gram balance shift = 1.0000 gram mercury shift. Run II. Initial mercury 1.89214 grams; tin 0.02915 gram; 6.0454 gram balance shift = 1.0000 gram mercury shift. Run III. Initial mercury 5.35814 grams; tin 0.00406 gram; 6.1160 gram balance shift = 1.0000 gram mercury shift. [b] Measured with Pt/Pt-10% Rh thermocouple against ice junction to nearest 0.1° K. [c] Measured with Pt/Pt-10% Rh thermocouple (0.001° K. precision) for temperature difference between alloy and pure cadmium using technique and equations described. All thermocouple e.m.f. values reduced by a constant 0.00270 (run I), 0.00326 (run II), or 0.00308 mv. (Run III) thermocouple correction as discussed in text. ΔT normally represents average value of two observations of distinct reversal of the direction of mercury transfer near the equilibrium point, one with the mercury reservoir temperature rising and the other falling; in a few cases only one reversal was taken and corrected for the expected reversal separation. [d] Equilibrium vapor activity relative to that over pure liquid mercury using a vapor pressure equation consistent with Hultgren's selected value.

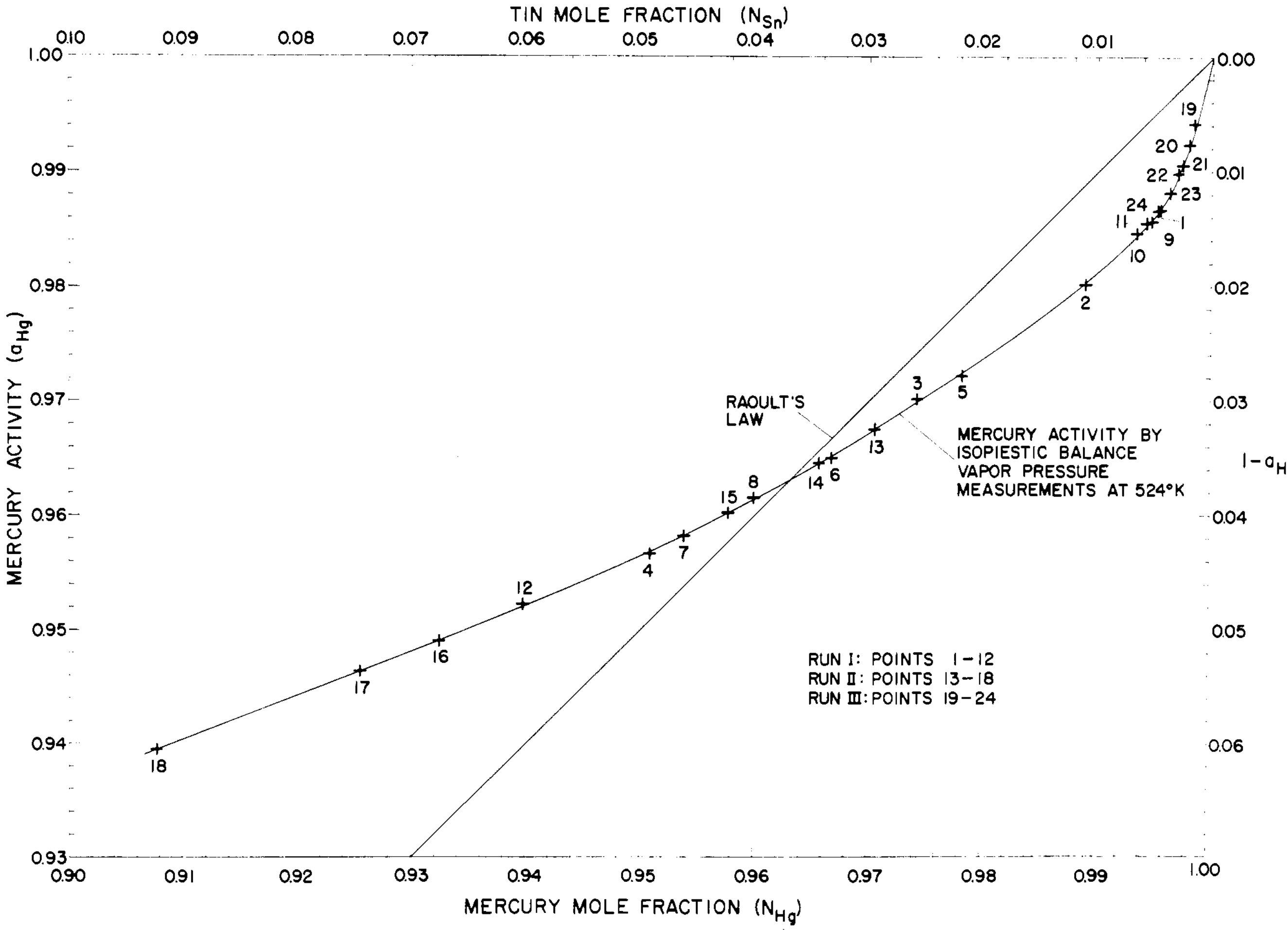

Figure 1. Mercury vapor activity relative to pure liquid mercury for solutions containing small amounts of tin

Hildebrand, Foster, and Beebe (*5*) have measured vapor pressures of mercuty over solutions of tin in mercury at 595° K., using a manometric method. The accuracy of their measurements may be indicated by comparison with other measurements on a second system (Cd-Hg) listed in the same paper. The mercury vapor pressure over cadmium-mercury solutions was measured by Pedder and Barratt (*8*) (transpiration) and by Meyer-Jungnick (*7*) (boiling point). If the various measurements are corrected to one temperature using the temperature coefficient data of Meyer-Jungnick, a smooth curve can be drawn through all of the data. Deviations from the curve are no greater than ±0.015 in the mercury activity for the concentration range 0.0 to 0.2 cadmium mole fraction, with Hildebrand's measurements slightly high. Since the cadmium mercury results show this excellent agreement for such measurements, one may have considerable confidence also in Hildebrand's manometric measurements on the tin-mercury system carried out at the same time.

Table II. Measurements Made on a Tube Containing Mercury Only

Point No.	Balance Shifts, Grams	Temperature, ° K.			Differential Thermocouple E.M.F., Mv.
		Side 1	Side 1 cross arm	Side 2 cross arm	
1	23.2565	252.6	275.9	275.7	−0.00052
2	12.9216	251.7	275.0	274.8	−0.00058
3	0.8933	251.6	275.0	274.6	−0.00067

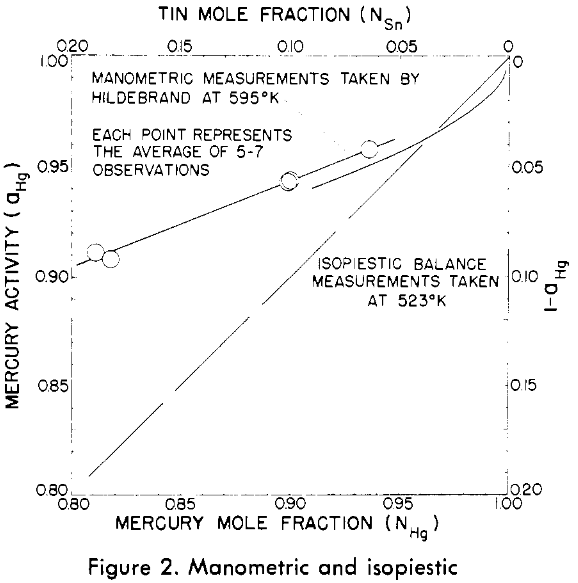

Figure 2. Manometric and isopiestic balance measurements

See text for discussion of variation of mercury activity with temperature

Figure 2 compares Hildebrand's data with those of the isopiestic balance for the tin-mercury system. From the cadmium-mercury system one would expect the error in absolute activities for Hildebrand's data to be less than ±0.015. The scatter in his data after averaging several observations is no greater than ±0.004 in the mercury

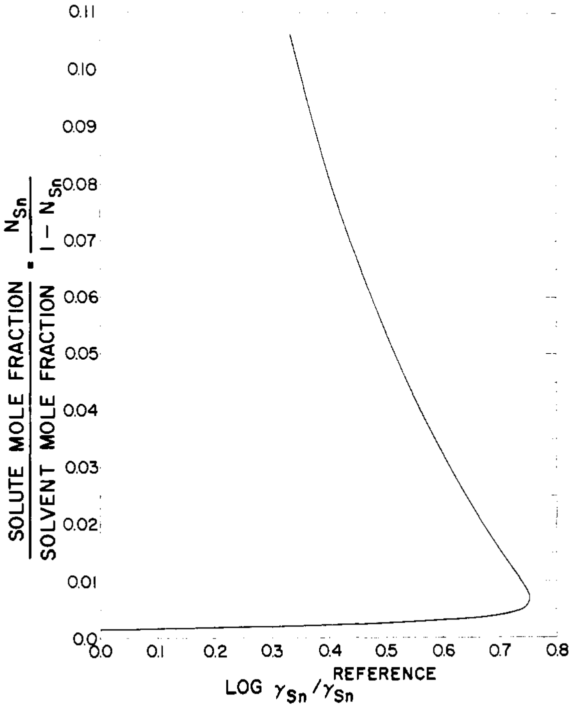

Figure 3. Duhem integration from mercury vapor pressure data

activity for the tin-mercury system. The major source of uncertainty in the isopiestic balance measurements is the extrapolation to infinite dilution. This leads to an uncertainty in the absolute mercury activity of at least 0.007. The relative uncertainty in the isopiestic balance measurements is no greater than ±0.0003, however. In the concentration range between 0.90 and 0.94 mercury mole fraction the slope of a line drawn through Hildebrand's data is the same as that using the isopiestic balance. The absolute values of the activities for this line are about 0.007 higher than those for the isopiestic balance when balance biases obtained by extrapolation are used. If the measured bias is used, there is no discrepancy between the two sets of measurements. Because of the 77° K. difference in temperatures, the activities for the two sets of data would not be expected to be identical. Since there is a lack of temperature coefficient measurements and since the possibility of structuring (*1*) prevents even the sign of the activity temperature coefficient from being known in the absence of temperature coefficient measurements, neither the direction nor amount of activity shift with temperature can be known with any certainty. Nevertheless, within the uncertainties for the two types of measurements, the data can be said to agree.

A peculiarity associated with use of the measured bias to calculate the mercury activities is that point 19 would actually have an activity equal to or greater than unity, implying a mercury vapor pressure for the alloy rising above that for pure mercury. Similar behavior has been seen on pure cadmium runs *vs.* cadmium alloy runs. Further work on the absolute bias uncertainty seemed important and is under investigation.

Figure 3 shows a Duhem integration plot of $N_{Sn}/(1 - N_{Sn})$ *vs.* log $\gamma_{Sn}/\gamma_{Sn}^{reference}$ where γ_{Sn} refers to the activity coefficient of the tin. The reference concentration was taken as that most dilute value for which a measurement had been made ($N_{Sn}^{reference} = 0.00153$). The function log $\gamma_{Sn}/\gamma_{Sn}^{reference}$ was calculated from the measured values for mercury. For this type of plot, changing reference concentration causes the curve to shift to the right or left without changing the shape of the curve. This curve emphasizes the unusual behavior of the tin-mercury system in the most dilute range for which measurements have been taken. For instance, if Henry's law is obeyed at great dilution—that is, if

$$\lim_{N_2 \to 0} \frac{da_2}{dN_2} = \text{finite constant}$$

—a plot of $N_{solute}/N_{solvent}$ *vs.* log $\gamma_{solute}/\gamma_{solute}^{reference}$ gives a finite intercept when $N_{solute}/N_{solvent} = 0$. This plot for the tin-mercury system appears at higher concentrations to be heading toward an intercept a little above 0.8; at greater dilution a new trend becomes apparent which makes it highly uncertain whether or not a finite intercept will actually be obtained.

ACKNOWLEDGMENT

This work is part of a program to measure both vapor pressure and e.m.f. for Hg-Sn solutions. The e.m.f. measurements are being carried out by Guy R. B. Elliott, and we have been in close contact during the course of the present work.

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