Solute-Solvent Interactions in Liquid Alloys

Vapor Pressures over Dilute Solutions of Gold or Silver in Mercury, and Dilute Solutions of Silver in Cadmium

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The isopiestic balance has been used to measure solvent vapor pressures over dilute mercury and cadmium alloys containing gold or silver. The cadmium alloy measurements were carried out at 773° K., while those for mercury were at 523° K. Measurements on two of the systems may be described by the simple equations

$$P_{\text{Cd alloyed}}/P_{\text{Cd pure}} = 1 - 1.1477\ N_{Ag},\ N_{Ag} = 0.008 \text{ to } 0.020$$

$$P_{\text{Hg alloyed}}/P_{\text{Hg pure}} = 1 - 2.0092\ N_{Ag},\ N_{Ag} = 0.003 \text{ to } 0.008$$

Data of the Au-Hg system are best described by a smooth curve which is not a simple mathematical function and which does not approach ideal behavior in the region of measurement, N_{Au} = 0.008 to 0.039. Deviations of the data from the respective curves are not greater than 0.00017 activity units (0.17 gram-cal. in $\bar{G}_{\text{solvent}}$).

THE ISOPIESTIC balance is a sensitive instrument capable of measuring changes of vapor pressure with composition to a high degree of precision (*2, 4, 5, 9*). This high precision has enabled members of this laboratory to observe abrupt changes of activity with composition for many systems and to observe deviations from Raoult's law at fairly great dilution ($N_{\text{solute}} = 1.5 \times 10^{-3}$).

The present measurements are not extensive for any system, but they seem very accurate in indicating changes of activity with composition for dilute solutions. Since there seems little likelihood that further work will be done on these systems in the near future, the present results are made available.

EXPERIMENTAL

All measurements were made using the "double reversal" technique discussed previously (*5*). Because of the relatively higher vapor pressures of mercury at 250° C. compared with cadmium at 500° C., the temperature differences between the two legs during distillation were necessarily kept smaller in the case of mercury, to avoid formation of small droplets on the legs above the main bulk of the metal.

The silver and gold were of 99.95% purity by manufacturer's analysis. The surfaces of these metals were cleaned by washing first with reagent grade acetone, then with analytical reagent grade petroleum ether. Cadmium of 99.999% purity, as analyzed by the United Mineral and Chemical Corp., was used as a starting material and purified using usual procedures (*2*). Triple-distilled mercury was further purified by slow distillation from a tube containing uranium to remove oxide.

A Leeds and Northrup galvanometer and Wenner potentiometer combination which had a sensitivity of 0.01 μv. was used to measure the platinum–10% rhodium to platinum thermocouple e.m.f.'s. For a temperature around 500° or 250° C., one of two correction factors, 1.37 or 0.89 μv., was subtracted from the measured thermocouple e.m.f. to bring the respective equation (*7*)

$$E = -309.17 + 8.29558\ t + 0.00144103\ t^2 + 0.0000001634\ t^3 \quad (1)$$

or

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

into agreement with the more recent reference tables (*8*). For the above two equations, E is in microvolts and t is in degrees centigrade.

The silver-cadmium run, which was carried out in one of two balances available, had a thermocouple bias of 0.0025 mv., determined by extrapolation. Both the gold-mercury and silver-mercury runs were carried out in the other isopiestic balance, which had an extrapolated bias of 0.0027 mv.

RESULTS

Tables I and II give results for the silver-cadmium, gold-mercury, and silver-mercury systems. The activities are determined by dividing the solvent vapor pressure over the alloy by the vapor pressure of pure solvent at the same temperature. Activity is used because it varies slowly with alloy temperature and is determined by the temperature difference between the alloy and pure solvent reservoirs. The vapor pressure over pure cadmium was determined using the equation

$$P^\circ_{Cd} = \exp\left(-13{,}119/T + 19.950 - 1.05676 \ln T\right) \quad (3)$$

which is consistent with Hultgren's values (*6*). The 150-cal. per mole uncertainty in $\Delta H_{v.,298^\circ K.}$ indicated by Hultgren corresponds to an uncertainty of 1 part in 200 in the slope of activity *vs.* mole fraction (*5*). The same uncertainty also applies to the function $(1 - a_{Cd})$. The actual uncertainty in a_{Cd} due to uncertainties in $\Delta H_{v.,298^\circ K.}$ is much smaller. The vapor pressure over pure mercury was determined using the equation

$$P^\circ_{Hg} = \exp\left(11.80812 - 7393.02/T\right) \quad (4)$$

This equation is consistent with Hultgren's values for mercury at temperatures in the vicinity of 523° K. The uncer-

Table I. Activity of Cadmium Alloyed with Silver

Point No.	Balance Shift in Grams	Cadmium Mole Fraction[a]	Temperature, °K.				ΔT, °K.[c]	Cadmium Activity[d]	Deviation from Calculation[e]
			Alloy[b]	Cadmium[b]	Alloy crossarm[b]	Cadmium crossarm[b]			
1	0.7066	0.99170	775.1	774.6	797.0	795.5	0.469	0.99044	–0.00003
2	1.0650	0.99110	775.6	775.1	797.8	796.2	0.498	0.98985	+0.00007
3	2.1888	0.98851	774.5	773.9	796.5	795.0	0.650	0.98676	–0.00005
4	3.7756	0.98049	776.0	774.9	797.3	795.8	1.107	0.97762	+0.00001

[a] Initial cadmium 0.99336 gram; silver 0.00704 gram; 6.04360 gram balance shift = 1.00000 gram cadmium 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 to 0.005° K. temperature difference between alloy and pure cadmium, but average value of approaches from different composition directions carried to 0.001° K. for calculation purposes. Distinct reversal of cadmium transfer observed 0.010 to 0.015° K. beyond equilibrium values. ΔT calculated from millivolts using equation of Roeser and Wenzel, after subtracting a constant 0.002518-millivolt bias correction. Bias established by finding that constant correction necessary for each run to make the data extrapolate linearly to unit activity at pure solvent; these bias corrections are roughly constant between runs for any thermocouple. [d] Vapor activity relative to that over pure liquid cadmium, using equation consistent with Hultgren's (*6*) value, namely $P^{\circ}_{\mathrm{Cd}} = \exp(-13{,}119/T + 19.950 - 1.05676 \ln T)$. [e] Calculated using equations in text.

Table II. Activity of Mercury Alloyed with Gold and with Silver

Point No.	Balance Shift, Grams	Mercury Mole Fraction[a]	Temperature, °K.				ΔT,° K.[c]	Mercury Activity[d]	Deviation from Calculation[e]
			Alloy[b]	Mercury[b]	Alloy crossarm[b]	Mercury crossarm[b]			
					Gold				
1	0.6105	0.99172	524.6	524.0	545.5	545.1	0.620	0.98346	–0.00002
2	2.9876	0.98745	524.4	523.6	545.5	544.8	0.782	0.97918	+0.00005
3	4.7636	0.97960	524.2	523.2	544.5	543.4	1.011	0.97312	–0.00016
4	5.5307	0.97206	524.2	523.0	544.6	543.5	1.197	0.96824	+0.00017
5	6.0003	0.96388	524.3	522.9	544.5	543.6	1.419	0.96246	–0.00004
6	6.1007	0.96146	524.3	522.8	544.5	543.6	1.478	0.96093	+0.00005
					Silver				
1	3.5096	0.99593	524.1	523.8	544.2	548.0	0.309	0.99172	–0.00010
2	11.9646	0.99346	523.9	523.4	543.8	547.6	0.491	0.98686	+0.00001
3	21.6608	0.97844	523.7	522.7	543.1	547.1	1.023	0.97276	+0.00028
4	22.7963	0.97052	523.6	522.4	542.7	546.5	1.244	0.96693	–0.00007
5	22.9240	0.96925	523.6	522.4	542.5	546.2	1.269	0.96627	+0.00014
6	0.4114	0.99642	522.4	522.1	541.5	545.5	0.266	0.99281	...
7	5.6516	0.99550	522.3	522.0	542.0	546.4	0.332	0.99104	+0.00009

[a] 6.03960 gram balance shift = 1.00000 gram mercury shift. Au run: Initial mercury 1.24944 grams; gold 0.00942 gram. Ag run: Initial mercury 4.27106 grams; silver 0.00811 gram. [b] Measured with Pt-Pt-10% Rh thermocouple against ice junction to nearest 0.1° K. [c] Measured with Pt-Pt-10% Rh thermocouple to 0.005° K. temperature difference between alloy and pure mercury, but average value of approaches from different composition directions carried to 0.001° K. for calculation purposes. Distinct reversal of cadmium transfer observed 0.010° to 0.015° K. beyond equilibrium values. ΔT calculated from millivolts using equation of Roeser and Wenzel, after subtracting a constant 0.0027- or 0.00264-millivolt bias correction for each run, respectively. Bias established by finding that constant correction necessary for each run to make the data extrapolate linearly to unit activity at pure solvent; these bias corrections are roughly constant between runs for any thermocouple. [d] Vapor activity relative to that over pure liquid cadmium, using equation consistent with Hultgren's (*6*) value, namely, $P^{\circ}_{\mathrm{Hg}} = \exp(11.80812 - 7393.02/T)$. [e] Calculated using equations in text.

tainty of 13 cal. per mole in $\Delta H_{\mathrm{v.,298^\circ K.}}$ leads to an uncertainty in $(1 - a_{\mathrm{Hg}})$ and in $da_{\mathrm{Hg}}/dN_{\mathrm{Hg}}$ of less than 1 part in 1000.

Usually, the balance factor relating the weight of solvent shifted from one leg to the other to the balance shift is determined experimentally for each tube loading, since the balance factor can vary slightly from tube to tube. For the silver-mercury system, the balance factor was not thus obtained, so a balance factor equal to that for the gold-mercury run was chosen.

The four figures present the data for these systems as functions of the solute mole fraction, with point numbers indicating the order in which the measurements were taken.

Figure 1 is a plot of cadmium activity *vs.* cadmium mole fraction for the silver-cadmium system. The data can be described analytically by the equation

$$\frac{P_{\mathrm{Cd\ in\ soln.}}}{P_{\mathrm{Cd\ pure}}} = 1 - 1.1477\, N_{\mathrm{Ag\ in\ solution}} \tag{5}$$

The lack of significant curvature to the data in this concentration range is better shown in the plot (Figure 2) of $(1 - a_{\mathrm{Cd}})/N_{\mathrm{Ag}}$. Obedience to the form of Equation 5 leads to a horizontal line on this plot. A squared term in the solute mole fraction for describing the activity would lead to a straight line with nonzero slope.

Figure 3 is a plot of mercury activity *vs.* mercury mole fraction for both the gold-mercury and silver-mercury systems. These results may be described analytically by two equations. The first equation

$$\frac{P_{\mathrm{Hg\ in\ soln.}}}{P_{\mathrm{Hg\ pure}}} = 1 - 2.0092\, N_{\mathrm{solute}} \tag{6}$$

applies in the range 0.003 to 0.008 solute mole fraction. From 0.008 to 0.039 solute mole fraction, the data can be described by a smooth curve which is illustrated best in Figure 4. This curve corresponds to a strictly empirical five-parameter equation

$$\frac{P_{\mathrm{Hg\ in\ soln.}}}{P_{\mathrm{Hg\ pure}}} = 1 - 3.1038\, N_{\mathrm{solute}} + 181.57\, N^2_{\mathrm{solute}} - 6709.3\, N^3_{\mathrm{solute}} + 121{,}470\, N^4_{\mathrm{solute}} - 859{,}800\, N^5_{\mathrm{solute}} \tag{7}$$

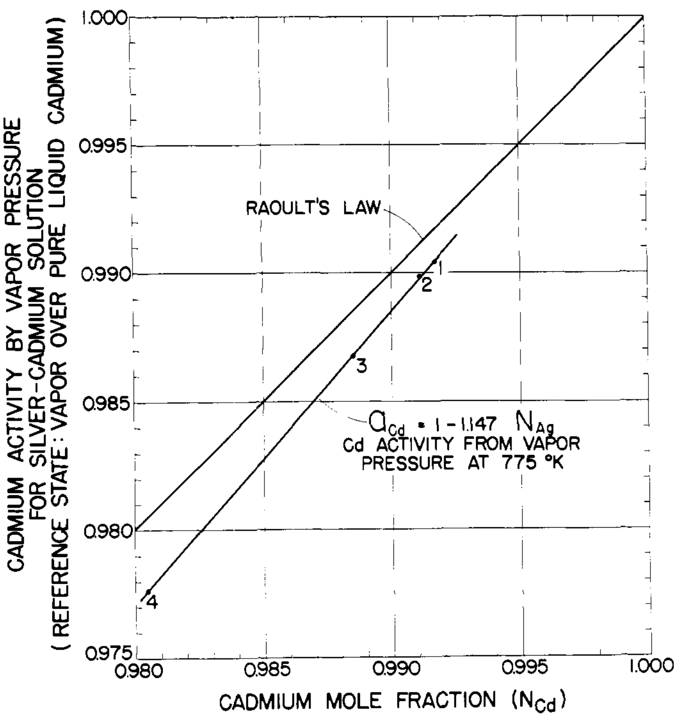

Figure 1. Cadmium vapor activity relative to pure liquid cadmium for solutions containing small amounts of silver

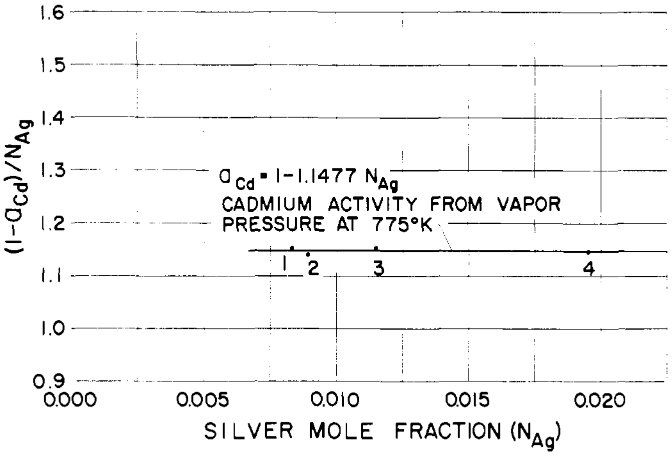

Figure 2. Dundee plot for cadmium solutions containing small amounts of silver

A polynomial with fewer terms does not give a good fit to the data. This equation appears to be adequate for purposes of interpolation, but is very likely inadequate for purposes of extrapolation. For instance, the coefficient multiplying N_{solute} is not assumed to be the limiting slope for the actual system itself at infinite dilution. The equation form used to fit the data does imply, however, that in the region of the measurements there is no tendency for approach to Raoult's limiting law, but rather a tendency away from Raoult's law with increasing dilution. The sizes of the deviations of the data from the above curve are consistent with those of isopiestic measurements on other systems (9). In Figure 4, the plot of $(1 - a_{\text{Hg}})/N_{\text{solute}}$ *vs.* N_{solute} clearly illustrates the difference in behavior over the two concentration ranges. Deviations from these equations are listed in Table II. Deviations of 0.00015 activity units correspond to 0.29 cal. per mole deviation in the precision of the partial molar free energy.

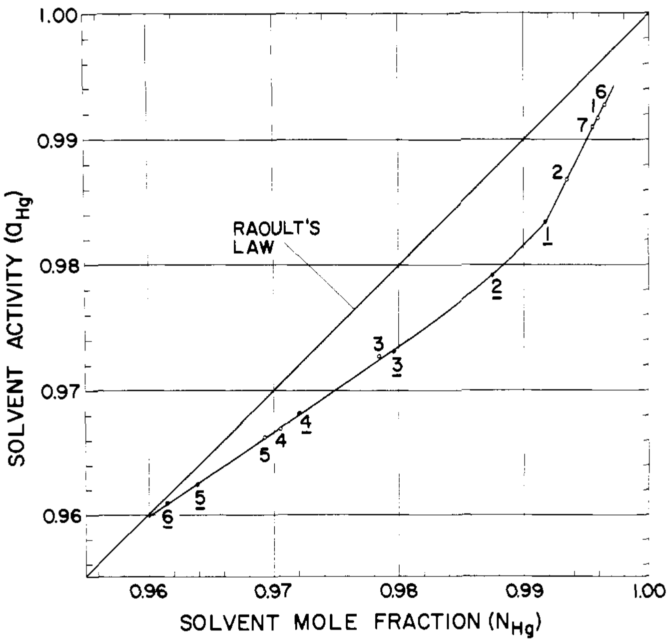

Figure 3. Mercury vapor activity relative to pure liquid mercury for solutions containing small amounts of gold or silver at 523° K.

Solid circles refer to the gold-mercury system; open circles refer to the silver-mercury system

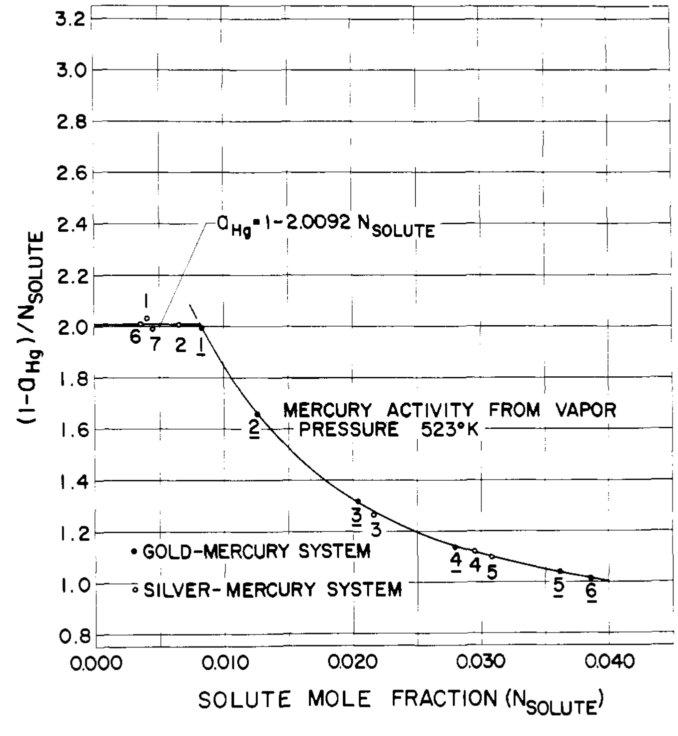

Figure 4. Dundee plot for mercury solutions containing small amounts of gold or silver

As a check on the consistency of the bias used for each system, an additional experiment was carried out in which compositions of gold-mercury alloys were compared against those of silver-mercury alloys when they were allowed to equilibrate through the vapor at 523° K. A quartz container with four legs was used for this experiment. The legs were arranged in positions corresponding to the corners of a square. Two legs on diagonally opposite corners were charged with 0.00111 mole of silver each. The other two legs were charged with 0.00111 mole of gold. About 0.218 mole of mercury was vaporized into the tube under vacuum and the tube was sealed off. Different amounts of mercury were contained in the four legs at the time the tube was placed in the furnace. A week later the tube was removed. Within a 5% uncertainty, each of the four legs contained the same volume of metal—i.e., the final composition of each leg was $N_{Hg} = 0.980 \pm 0.001$. Evidently the mercury vapor pressure over 2 mole % silver in mercury is nearly the same as that over 2 mole % gold in mercury, in agreement with the isopiestic balance results.

DISCUSSION

Alloy vapor pressure measurements made at this laboratory have been on alloys more concentrated than 0.001 solute mole fraction. Determining the slope of the solvent activity with concentration at infinite dilution by any presently known method of measurement appears impossible; thus, Raoult's limiting law for infinite dilution is not directly subject to test. One can only look for trends in activity behavior at such concentrations for which adequate measurements can be made, searching for indications of approach to the limiting law with increasing dilution.

All systems for which vapor pressures have been measured at this laboratory have shown no tendency to approach Raoult's law as dilution is increased. A few of these systems (*2, 4, 5, 9*) have been discussed in publications. The systems appearing in the present paper are illustrative of the preceding discussion.

For the silver-cadmium system, the data lie on a line that, within the uncertainty of the data, seems to be straight, with a nonunit slope.

The gold-mercury and silver-mercury systems apparently have nearly the same activity at the same concentration between 97 and 98%, and at 99.2% mercury. Clearly, the behavior of the silver-mercury system must undergo a marked change at some solute concentration greater than 0.7%. Whether the silver-mercury system behaves similarly to the gold-mercury system in the concentration range from 98 to 99.2% is not clear, because data are lacking. For the gold-mercury system, either of two rather different types of behavior could easily be followed for solutions more dilute than 0.8 mole % of gold; these cannot be distinguished from the present data. The gold-mercury curve might continue smoothly out toward infinite dilution, as does that for the tin-mercury system (*1*), or it might undergo a marked change in behavior at or below 0.8% gold, yielding a line similar to that for silver-mercury. Similar behavior of the lead-cadmium system has been published (*5*).

The similarity in the data for both mercury systems does not seem unreasonable, considering the atomic size and chemical similarity of the two solutes.

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Equilibrium Hydrogenations of Multi-Ring Aromatics

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Chemical equilibria were determined for the naphthalene-hydrogen, indene-hydrogen, acenaphthene-hydrogen, and fluorene-hydrogen systems. Measurements were made over ranges of temperature and pressure appropriate to a totally vaporized system. Equilibrium constants and heats of hydrogenation are given.

PUBLISHED equilibria for hydrogenation of multi-ring aromatic hydrocarbons are limited to the naphthalene-hydrogen (*3, 5, 7, 11*), diphenyl-hydrogen (*5*), and phenanthrene-hydrogen (*5*) systems. A previously reported technique (*5*), modified to assure more accurate temperature measurements, has been used to determine the equilibria in the indene-hydrogen, acenaphthene-hydrogen, and fluorene-hydrogen systems, as well as to redetermine and extend the temperature range for the naphthalene-hydrogen system.

EXPERIMENTAL

Fluorene, indene, acenaphthene, and naphthalene were desulfurized with Raney nickel in methanol and were either redistilled or recrystallized. Purity, as determined by gas chromatography, was 99.0 mole % or better. Electrolytic hydrogen (Liquid Carbonic Division of General Dynamic Corp.), certified to be 99.9% pure, was used without further purification.

The apparatus and techniques to establish equilibrium and to withdraw material for analysis have been described (*5*), except that a Pd-on-charcoal catalyst (Matheson, Coleman, and Bell) was used in the present experiments. The

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