Abrupt Changes in Cadmium Activity with Composition for Dilute Copper and Gold Alloys

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Evidence of very narrow and abrupt changes in the activity *vs.* mole fraction behavior for dilute liquid alloys of Au-Cd and Cu-Cd is reported. Detailed isopiestic balance measurements on pure cadmium show an unexpected change in thermocouple electromotive force bias with weight shift. The alloy data are discussed in the context of possible solution structuring. The pure cadmium data suggest that the shifting bias results from the physical chemistry of the system isolated within the balance equilibration tube.

The isopiestic balance is very sensitive to variations of vapor pressure with composition (*1-3, 6, 9*), allowing abrupt changes of activity with composition to be observed. The earliest reported literature concerning this phenomenon is the work of Elliott *et al.* (*4, 5*). Because of improvements in balance design and experimental technique, clearer evidence for such abrupt changes has been obtained and is the subject of this paper. The behavior of the activity *vs.* mole fraction curve for both the Au-Cd and Cu-Cd alloys is unexpected for the following reasons:

The abrupt shifts occur at great dilution (4% or less solute).

The transition region is very narrow (changes in mole fraction of 0.003 or less).

The transition region for such dilute liquid alloys has an unusual shape; the general form is two steep straight lines of activity *vs.* mole fraction, connected by a region of apparently almost constant activity. This form is reminiscent of a "two-phase gap" or transition region between two immiscible phases.

Experimental work carried out in this laboratory concerning dilute alloys of tin in mercury indicated a smooth increase in the slope of the curve of activity *vs.* mole fraction with increasing dilution (*1*).

A possible explanation for this observed behavior might be a change in temperature bias as a result of material transfer; direct measurements on pure mercury proved this not to be the case. Nevertheless, since investigations involving dilute alloys of gold in cadmium showed a similar activity *vs.* mole fraction behavior with increasing dilution, it was decided that measurements on pure cadmium were in order and they are here reported. An effect was observed and the necessary corrections have been made to the Au-Cd and Cu-Cd data.

EXPERIMENTAL

The isopiestic balance used for obtaining the cadmium vapor pressure measurements consists of a quartz tube with two legs suspended by a balance system and surrounded by a furnace. For alloy systems, one leg contains the alloy and the other the pure cadmium condensate. The leg and cross arm temperatures are separately controlled.

Cadmium of 99.999% purity as analyzed by the United Mineral and Chemical Corp. was cleaned by cutting off surface oxide. Gold metal 99.95% pure by manufacturer's report and electrolytic copper with an assay minimum of 99.9%, as reported by Matheson, Coleman and Bell, were used without further purification. The gold and copper metals were introduced directly into the balance tubes. However, the cadmium was vaporized into the tube under an initial vacuum of 10^{-8} atm from an attached U-tube. Half of the cadmium originally loaded into the U-tube remained in the tube after completion of the evaporation.

The temperatures for equilibrium between a particular alloy and the reservoir were determined by slowly shifting the reservoir temperature until cadmium transfer ceased, then reversed. Reversal points were approached from both higher and lower temperatures relative to the equilibrium temperature.

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 cadmium transferred is ±0.03 mg. For a 1-gram sample this leads to an uncertainty of 3 parts in 100,000. All weighings of the metals before introduction into and after removal from the balance tube were made to 0.01 mg.

The thermocouple measurements for measuring the temperature difference between the two legs are made to the nearest 0.01 μv. Uncertainty in absolute temperatures is $\pm 0.1^\circ$K. A correction factor of 1.37 μv was subtracted from all measured thermocouple electromotive force readings to bring the equation

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

into agreement with more recent reference tables (*8*). For Equation 1, E is in microvolts, and t is in degrees Celsius.

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

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$$P^\circ_{Cd} = \exp(-13{,}119/T + 19.950 - 1.05676 \ln T) \quad (2)$$

which is consistent with Hultgren's values (7). 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 (6).

More extensive descriptions of the experimental apparatus, techniques, and uncertainties are available (2, 3, 6, 9).

In connection with the pure cadmium work, two different isopiestic balance systems were used by two different investigators and the method for introduction of the balance equilibration tubes was standardized using templates. Use of templates combined with careful centering of the legs within the copper furnace cylinders improved the reproducibility of technique and results between the two balances and the individual investigators.

RESULTS

The data tabulated in Table I for Au-Cd alloys at 777° and 742° K, and for Cu-Cd alloys at 772° K, are depicted graphically in Figures 1, 2, and 3, respectively. These data have all been corrected for a changing temperature bias related to the amount of cadmium transferred between the reservoirs. The experimental details of this temperature bias are discussed with the presentation of the pure cadmium data. The abrupt changes in activity as a function of composition for the alloy are obvious from Figures 1, 2, and 3 and have midpoints at mole fractions Cd 0.9925, 0.9937, and 0.9630, respectively.

The surprising results of the pure cadmium investigations are illustrated in Figure 4. Two separate balance equilibration tubes were loaded with pure cadmium. Pure cadmium tube 1 was run by Conant (run 1 in Figure 4) in balance

Table I. Activity of Cadmium Alloys

			Temperature, °K					
Point No.	Balance Shift, Grams	Cadmium Mole Fraction[a]	Alloy	Cadmium	Alloy crossarm	Cadmium crossarm	ΔT, °K	Cadmium Activity
				GOLD RUN 1				
1	2.7198	0.99550	777.3	776.7	787.8	784.9	0.608	0.98769
2	0.2081	0.99671	776.7	776.2	787.4	787.3	0.441	0.99104
3	1.1544	0.99634	777.4	776.9	787.5	787.9	0.499	0.98989
4	2.3937	0.99570	777.5	776.9	787.8	787.8	0.575	0.98836
5	3.5372	0.99489	777.8	777.2	788.6	789.1	0.682	0.98621
6	4.4275	0.99400	778.2	777.4	788.7	788.6	0.802	0.98383
7	5.4965	0.99243	777.8	777.0	787.6	788.1	0.834	0.98318
8	5.2432	0.99287	778.4	777.6	790.3	790.3	0.825	0.98337
9	5.6108	0.99221	778.0	777.1	788.0	788.8	0.828	0.98331
10	6.5981	0.98961	778.4	777.4	789.6	789.7	0.931	0.98126
11	7.4458	0.98545	778.5	777.2	789.1	789.5	1.299	0.97395
12	6.7467	0.98906	778.2	777.3	788.9	789.6	0.975	0.98036
13	5.7336	0.99196	778.7	777.9	789.0	789.6	0.832	0.98326
14	4.3028	0.99414	778.8	778.0	789.3	790.0	0.777	0.98435
15	3.9075	0.99455	779.2	778.5	791.7	792.9	0.720	0.98552
				GOLD RUN 2				
1	0.2877	0.99601	742.5	741.9	764.1	762.3	0.587	0.98694
2	0.6027	0.99584	741.6	741.0	763.7	761.8	0.606	0.98648
3	0.9525	0.99564	742.4	741.7	763.7	762.0	0.629	0.98601
4	1.4187	0.99535	741.8	741.1	763.2	761.9	0.671	0.98505
5	1.8246	0.99506	741.7	741.0	762.9	761.5	0.708	0.98424
6	2.8822	0.99409	741.3	740.5	763.0	761.2	0.771	0.98282
7	3.5168	0.99330	742.1	741.3	763.4	762.1	0.763	0.98304
8	4.1558	0.99227	742.8	742.0	763.4	761.8	0.791	0.98254
9	4.6846	0.99114	742.7	741.8	763.3	762.1	0.843	0.98130
10	5.4440	0.98877	741.7	740.7	762.2	761.0	0.960	0.97867
11	5.9315	0.98645	744.1	743.0	764.9	763.4	1.084	0.97611
12	5.0612	0.99010	741.7	740.8	762.5	761.7	0.899	0.98002
13	4.2028	0.99218	741.6	740.8	762.3	761.2	0.791	0.98239
14	3.6507	0.99311	741.3	740.5	762.1	760.9	0.764	0.98298
				COPPER RUN				
1	1.9052	0.97803	773.9	772.5	795.5	794.9	1.478	0.97004
2	2.2110	0.97587	774.2	772.6	796.6	796.0	1.590	0.96783
3	2.4112	0.97421	774.0	772.3	795.9	795.1	1.677	0.96608
4	2.9290	0.96862	773.8	771.9	795.6	794.6	1.954	0.96055
5	3.3412	0.96209	773.8	771.5	795.3	794.3	2.225	0.95518
6	3.5037	0.95870	773.7	771.3	795.0	794.0	2.394	0.95185
7	3.5895	0.95666	773.4	770.9	795.1	793.8	2.500	0.94973
8	3.1762	0.96501	774.0	771.8	796.3	795.3	2.132	0.95704
9	3.2885	0.96307	774.0	771.7	796.1	795.1	2.216	0.95538
10	3.2918	0.96301	773.9	771.7	795.9	794.9	2.215	0.95540
11	3.3212	0.96247	773.5	771.3	795.8	794.7	2.213	0.95540
12	3.5662	0.95723	774.3	771.8	796.4	795.2	2.471	0.95039
13	3.4188	0.96055	774.9	772.6	796.7	795.6	2.305	0.95375

[a] Au run 1. Balance factor = 6.1439, initial cadmium = 1.55143 g, gold = 4.46×10^{-5} mole. Au run 2. Balance factor = 6.0265, initial cadmium = 1.37058 g, gold = 4.72×10^{-5} mole. Cu run. Balance factor = 6.0868, initial cadmium = 0.86186 g, copper = 1.097×10^{-4} mole.

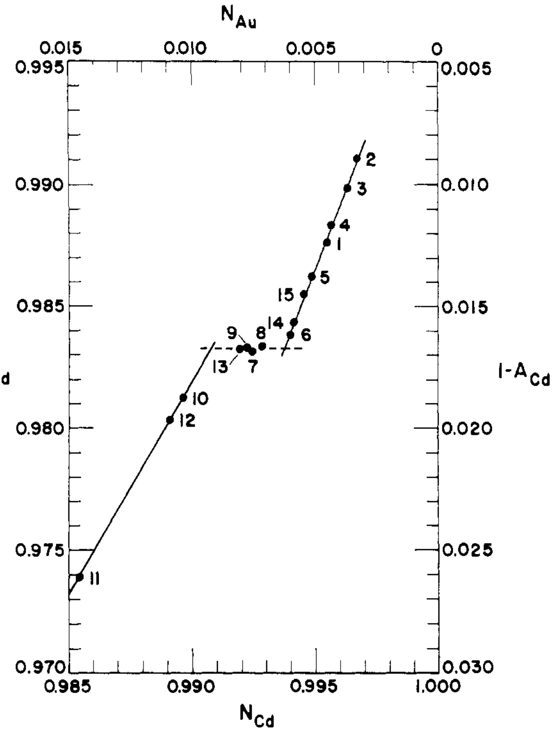

Figure 1. Au-Cd, 777° K

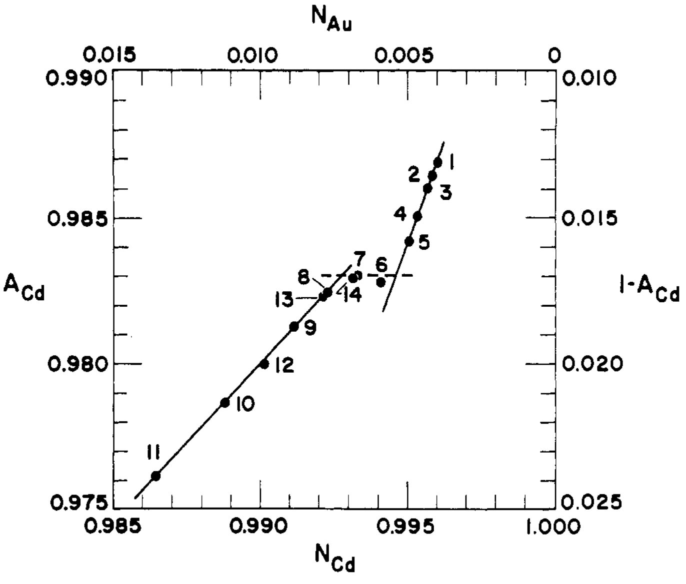

Figure 2. Au-Cd, 742° K

1 prior to a general overhaul of both balances. After the overhaul, Conant carried out measurements on tube 1 (run 2) and tube 2 (run 3) in balance 1, while Swofford carried out measurements on tube 1 (run 4) and tube 2 (run 5) in balance 2. To ascertain the effect of the bias change on dilute alloys, Swofford also carried out measurements on a very dilute Au-Cd alloy in balance 2 (run 6). The line drawn through these latter data is that for pure cadmium.

The thermocouple electromotive force—that is, the temperature bias—is not constant, but is a linear function of the weight of cadmium transferred between the two reservoirs. The reference point for the tabulated weight shifts was set equal to zero for equal amounts of cadmium in both legs. An empirical expression which fits the data is given by Equation 3:

$$\text{Thermocouple emf} = -(0.075 \pm 0.007) \times \text{bal. shift} + \text{constant} \quad (3)$$

On a separate loading of a third equilibration tube with pure cadmium by Conant, attempts were made to change the slope of the thermocouple electromotive force bias curve by cocking the equilibration tube within the legs of the copper furnace cylinders, creating a large differential temperature between the two overheats, lowering the temperature of both overheats to within a few degrees of the

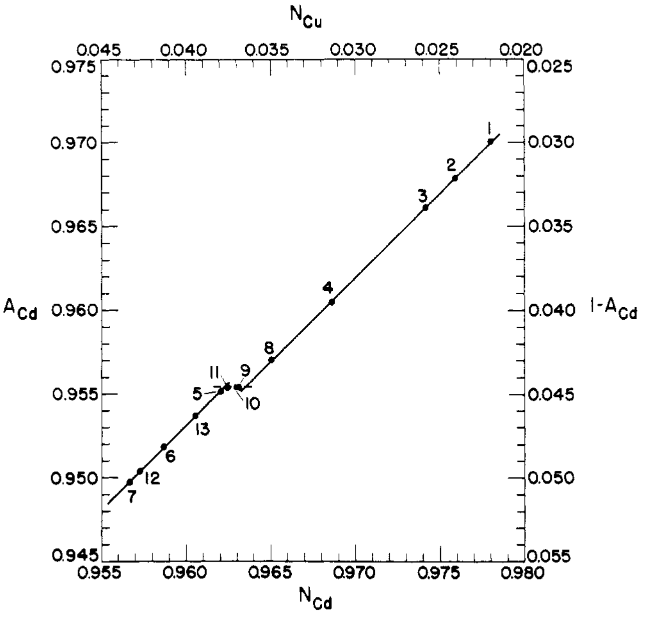

Figure 3. Cu-Cd, 772° K

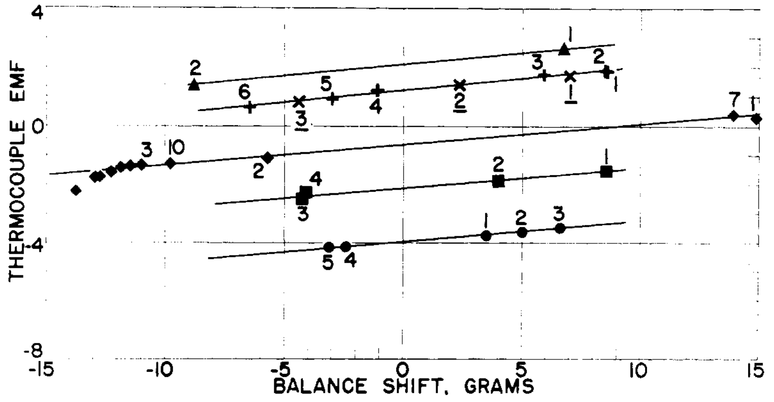

Figure 4. Pure Cd and dilute Au-Cd

furnace legs, and finally using an off-center null point on the analytical balance to record the reversals. These radical departures from "normal" balance equilibration tube loadings did not appear to change the slope significantly, but as in the two previously reported pure cadmium loadings, a shift in the absolute bias was observed. The total bias shift, for equal amounts of cadmium in both legs, was 1.3 μv between extremes.

DISCUSSION OF RESULTS

The possible implications of the abrupt changes in cadmium activity with composition in the gold and copper alloys, without further investigations, are not entirely clear. The data suggest that over the more dilute concentration range, for any given system, one type of solution behavior is predominant, while in the more concentrated regions a rather different type of behavior results, with a very abrupt region of transition connecting the two. One possible explanation might involve two types of liquid structure which are incompatible, thus requiring a narrow composition range for transition.

An explanation for the observed behavior of pure cadmium is not available at this time. Work with pure mercury (*1*) and our many investigations presented above indicate that the observed phenomenon does not originate as an experimental artifact from the isopiestic balance. It would seem that any explanation must be derived from the physical chemistry of the system isolated within the balance tube. Although this matter has been pondered at great length in this laboratory, our thoughts are speculative and no definitive statement is warranted.

It is obvious from the data involving very dilute gold in cadmium that in the concentration range investigated it is impossible to differentiate between the behavior of the alloy and pure cadmium. Because of the uncertainties in the measurement of the slope of the thermocouple electromotive force bias, it is not possible to determine accurately the slope of the plot of activity *vs.* mole fraction for the most dilute gold-cadmium measurements (run 6).

The sloping thermocouple bias found in the pure cadmium investigations is significant only when large amounts of cadmium are transferred—i.e., very dilute alloy measurements. The measurements tabulated in Table I and illustrated in Figures 1, 2, and 3 are not significantly altered by this effect, although a correction has been applied.

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Binary Freezing Point Diagrams for Some Methyl Ketones and Their Complete Solubilities in Acetone, Methanol, Benzene, and Carbon Tetrachloride

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In the course of our investigations into the development of correlation procedures for the solubilities of long chain homologous and analogous compounds, the following highly pure methyl ketones were prepared: 2-tridecanone, 2-heptadecanone, and 2-nonadecanone. Since the methyl ketones are important in many chemical reactions and since mutual solubilization is very pronounced in most long-chain homologous compounds, an investigation into the mutual solubilization effects of the methyl ketones was undertaken. The investigation was extended to include the solubility behavior of the methyl ketones in two polar solvents—acetone and methanol—and two nonpolar solvents—benzene and carbon tetrachloride.

EXPERIMENTAL

The pure methyl ketones were recrystallized samples of fractionally distilled materials. The pure stearic acid was a recrystallized material prepared from the fractionally distilled methyl ester. The acetone, methanol, and carbon tetrachloride were reagent grade solvents freshly distilled. The benzene used was a reagent grade material dried over sodium wire and distilled through a packed column.

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