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# Further Tests of Dilute Solution Equations and Thermodynamic Relationships: The Vapor Pressure of Cadmium Over Liquid Alloys Containing Small Amounts of Lead


UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

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Printed in the United States of America. Available from Clearinghouse for Federal Scientific and Technical Information National Bureau of Standards, U. S. Department of Commerce Springfield, Virginia 22151

Price: Printed Copy $3.00; Microfiche $0.65

LA-3657
UC-4, CHEMISTRY
TID-4500

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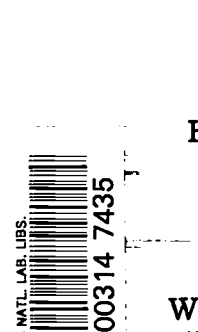
Report written: October 1, 1965
Report distributed: April 5, 1967

# Further Tests of Dilute Solution Equations and Thermodynamic Relationships: The Vapor Pressure of Cadmium Over Liquid Alloys Containing Small Amounts of Lead

by

Harold S. Swofford, Jr., and Guy R. B. Elliott




With Appendix in Reply to O' Keeffe's Comments "On the Validity of Raoult's and Henry's Laws as Limiting Laws for Dilute Solutions."

by

Guy R. B. Elliott, Harold S. Swofford, Jr., and Donald R. Conant

## Abstract

The vapor pressure of cadmium over molten lead-cadmium alloys in the dilute lead range has been measured by the isopiestic balance technique. In the range 0.004 to 0.010 mole fraction lead, the cadmium vapor pressures at 780°K obey the relationship

$$\frac{P_{Cd\ alloyed}}{P_{Cd\ pure}} = 1 - 1.63\ N_{Pb}$$

when $N_{Pb}$ is the mole fraction of lead in solution. The solvent thus shows strong negative deviation from Raoult's law in a concentration region where it is conventional to assume, based on thermodynamic arguments, that Raoult's law would be obeyed or at least closely approached. Some of the implications of this result are discussed.

At larger lead concentrations an increasing curvature becomes observable, and from 0.015 to 0.032 mole fraction lead the relationship

$$\frac{P_{Cd\ alloyed}}{P_{Cd\ pure}} = 1 - 2.04\ N_{Pb} + 33.0\ N_{Pb}^{2}$$

is obeyed, the activity becoming positive to Raoult's law at 0.9683 mole fraction cadmium.

A reply is given to the comments of M. O'Keeffe.

## Acknowledgments

We wish to acknowledge the important contributions of Joe Fred Lemons to the course of this work. For eight years he was a major force in the development and testing of the isopiestic balance, and in its subsequent use in these recent very fundamental studies.

D. R. Conant has been a co-worker and contributor to our thoughts expressed here. We wish also to acknowledge valuable discussions with L. O. Morgan without holding him responsible for any of the views expressed here.

## Introduction

The immediate purpose of the investigations reported in this paper was to test the adherence of certain colligative property measurements to "ideal" Raoult's law behavior in certain rather dilute metallic solutions. The ultimate purpose of our continuing work is to test whether thermodynamic prediction is measurably inexact for real systems.

Three equations are pertinent to our studies:

(A) A solvent equation with Raoult's law limit only if $k_A = 1$

$$\frac{P_A}{P_{A\ pure}} = 1 - k_A N_B + b_A N_B^2 \qquad (1)$$

(B) A solute equation with Henry's law limit

$$\frac{P_B}{P_{B\ pure}} = k_B N_B + b_B N_B^2 \qquad (2)$$

(C) Another solute equation

$$\frac{P_B}{P_{B\ pure}} = K N_B^{k_A} (1 - k_A N_B)^{(1-k_A)} \qquad (3)$$

P indicates pressure; A and B indicate solvent and solute, respectively; N indicates mole fraction; k, K, and b indicate constants. The interrelationships of the equations are developed in the following paragraphs.

The concept of ideal colligative properties is the basis of the prediction that, for each concentration in sufficiently dilute solution, all solutes will depress the freezing point of the solvent equally. Its use has been accepted to determine solvent purity or solute molecular weight.

The use of ideal colligative properties implies a validity to Eq. 1 with $k_A = 1$, usually with $b_A N_B^2$ either negligible or corrected for by extrapolation to greater dilution. The conclusion that $k_A = 1$ is reached from Henry's law by operating through the Duhem relationship. Likewise, Eq. 2 is the thermodynamic corollary of Eq. 1 with $k_A = 1$. Henry's law may be reached by chemical reasoning for dilute solutions. It is experimentally observed to hold in such very dilute solution studies as the solvent extraction of tracer species from one phase to another. With a $b_B N_B^2$ modification for the effect of random close approaches of two solute molecules, it is often followed closely by vapor pressures and heats of mixing.

Our reasoning, as presented in earlier references,[1-3] led us to surmise that Eq. 1 with $k_A \neq 1$ was a chemically reasonable corollary for $k_B \neq 1$.* This untested and tentative conclusion lay in opposition to the thermodynamic conclusion that $k_A = 1$ for $k_B \neq 1$. For $k_A \neq 1$ with $N_B^2$ small, Eq. 3 is the thermodynamic corollary of Eq. 1.

Experimentally for solutions of gallium in cadmium we found that the vapor pressure of cadmium obeys the relationship

$$P_{Cd}/P_{Cd\ pure} = 1 - 0.856\ N_{Ga} + 0.933\ N_{Ga}^2 \qquad (4)$$

which is in the form of Eq. 1.

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*A fundamental part of the chemical argument follows. In the Henry's law region, interactions between solute and solvent molecules which are different from the interactions between the molecules of the pure components are demonstrated by the fact that $k_B$ in Eq. 2 is not unity. That these interactions are unique to any particular solute-solvent couple is demonstrated by the $k_B$ values which are different for different couples. It would seem almost inescapable that those interactions by which the solvent molecules influence the behavior of a solute molecule neighbor would also produce a net influence on these solvent neighbor molecules as well. Such interactions would lead to Eq. 1 with $k_A \neq 1$ even in the dilute solution limit. This is contrary to the Raoult's law assumption of no net effect upon the solvent other than an ideal entropy of mixing.

These experiments with gallium-cadmium solutions demonstrated that Raoult's law with a corollary assumption of ideal colligative properties is not necessarily applicable in a composition region where it has often been assumed. Likewise these results may be coupled with heat of mixing data (see Appendix ) to show that certain accepted approximations about entropies of mixing are not necessarily valid.

Finally, the experiments confirmed our prediction of a likely form of the solvent behavior equation and thereby offered some support for our ideas of solution behavior. To this extent the data also support the idea that, when applied to real systems, thermodynamic prediction should be considered an approximation rather than an exact necessity. (It is important to reemphasize that the mathematical manipulations of thermodynamics are not in question. Gokcen's criticism[4] of our views as a violation of mathematics is not valid.) The question lies in the fundamental assumptions made when thermodynamic prediction is applied to real systems. Are the simple relationships of thermodynamics an exact description of the net result of all the very complicated processes which take place at equilibrium on a molecular scale?

Alternative proposals consistent with thermodynamics (although contrary to certain usual assumptions) could not be totally ruled out, however. First, although the gallium-cadmium data were fitted most simply and accurately by the equation we used with $k_A \neq 1$, they could also be fitted approximately by other equations (without obvious physical meaning) which were consistent with $k_A = 1$. These latter equations would require very complex entropy effects to correlate the heat of mixing and vapor pressure data. (For example, see Reference 5 and our reply in Reference 3). Second, it was possible that our reasoning from Henry's law had been incorrect though leading by accident to the proper solvent equation form. In this case Eq. 3 would describe the solute behavior when the $b_A N_B^2$ solvent terms were unimportant; if Eq. 3 is accepted, it is very difficult to offer a physical meaning to the non whole-number

exponent in $N_B^{k_A}$.*

The present experiments on lead-cadmium solutions are again a test of the ideal colligative property concept and Raoult's law. Likewise, obedience to Eq. 1 with $k_A \neq 1$ would be hard to explain as accidental, and the obedience would offer additional support for acceptance of validity in our views about thermodynamics.

## Experimental

No change in the experimental technique of operation of the isopiestic balance was made. The balance and its operation are described elsewhere.[1,2,6,7]

The lead was 99.98% Pb by manufacturer's report and by LASL spectroscopic analysis, and was of proper density. The only further purification of this lead was to cut off surface contamination and to examine the sample pieces by microscope for iron chips from the cutters.

Cadmium containing 99.999% Cd by manufacturer's report was used as source material. A secondary U-tube was initially attached to the isopiestic balance equilibration tube. The system was evacuated to $10^{-8}$ atm, flamed, and filled with argon. Lead was placed in one leg of the isopiestic balance tube, cadmium was loaded into the secondary tube, and the system was again evacuated to $10^{-8}$ atm. The secondary tube was then sealed off from the vacuum system. Part of the cadmium was evaporated from the secondary tube into the cross arm of the isopiestic balance tube, and the balance tube was sealed off and separated from the secondary tube.

The balance tube was mounted in the furnace where the cadmium was re-evaporated onto the lead sample. Cadmium in the balance tube was determined by dissolution analysis of the residue in the secondary tube and confirmed by similar analyses of the material in the balance tube legs

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*Whole numbers and simple fractions can often be ascribed a physical meaning. Thus $N_B^2$ may often be associated with the random chance that two solute molecules will be close enough to interact with each other.

after the run was completed. The metal and alloy materials in the balance tube legs were brightly metallic, and the material balance was in error by less than 0.1 mg.

Under the conditions of the experiment the vapor pressure of lead is about $10^{-10}$ atm. Even neglecting the strongly retarding effect of cadmium vapor on the transfer of lead to the reservoir, the low vapor pressure and long tube length would permit the transfer of only about 0.01 mg during the course of a run.

## Results

Table I indicates the results which are plotted in Fig. 1 as mole fraction of cadmium vs. cadmium activity, i.e. the vapor pressure of the alloy divided by the vapor pressure of pure cadmium at the same temperature. Activity is used because it is the quantity established by the

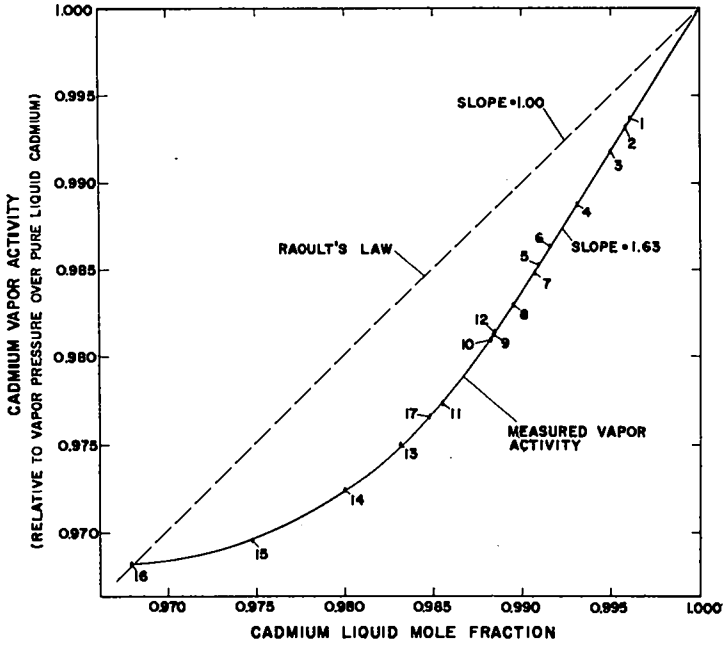


Fig. 1. Cadmium Vapor Activity for Dilute Lead in Cadmium Solutions.

Table I

The Activity of Cadmium Alloyed with Lead

| Point No. | Balance Shift (grams) | Cadmium Mole Fraction[a] | Alloy[b] | Cadmium[b] | Alloy Cross-Arm[b] | Cadmium Cross-Arm[b] | ΔT (°K)[c] | Cadmium Activity[d] |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.2870 | 0.99608 | 772.5 | 772.1 | 782.7 | 782.8 | 0.307 | 0.99368 |
| 2 | 0.7521 | 0.99583 | 773.1 | 772.8 | 783.1 | 783.2 | 0.333 | 0.99317 |
| 3 | 2.0044 | 0.99498 | 775.2 | 774.7 | 785.0 | 784.9 | 0.403 | 0.99177 |
| 4 | 3.6495 | 0.99311 | 777.6 | 777.1 | 787.4 | 787.4 | 0.555 | 0.98877 |
| 5 | 4.7157 | 0.99093 | 778.7 | 778.0 | 789.0 | 788.9 | 0.732 | 0.98525 |
| 6 | 0.4478 | 0.99159 | 776.8 | 776.1 | 788.1 | 788.1 | 0.675 | 0.98633 |
| 7 | 1.0623 | 0.99073 | 776.5 | 775.7 | 786.3 | 786.5 | 0.751 | 0.98479 |
| 8 | 1.7701 | 0.98951 | 776.3 | 775.4 | 786.1 | 786.5 | 0.842 | 0.98294 |
| 9 | 2.2800 | 0.98841 | 776.6 | 775.7 | 787.2 | 787.5 | 0.928 | 0.98123 |
| 10 | 2.3391 | 0.98827 | 776.5 | 775.5 | 787.2 | 787.2 | 0.943 | 0.98092 |
| 11 | 3.2500 | 0.98552 | 777.1 | 775.9 | 787.5 | 787.6 | 1.126 | 0.97730 |
| 12 | 2.2654 | 0.98845 | 776.9 | 776.0 | 787.4 | 787.8 | 0.923 | 0.98135 |
| 13 | 3.7963 | 0.98315 | 776.8 | 775.5 | 787.4 | 787.6 | 1.242 | 0.97496 |
| 14 | 4.3238 | 0.97999 | 777.0 | 775.6 | 787.7 | 787.7 | 1.374 | 0.97235 |
| 15 | 4.9036 | 0.97479 | 777.0 | 775.5 | 787.5 | 787.5 | 1.516 | 0.96954 |
| 16 | 5.3810 | 0.96793 | 777.4 | 775.8 | 789.5 | 789.6 | 1.586 | 0.96817 |
| 17 | 3.4335 | 0.98480 | 777.4 | 776.3 | 789.5 | 789.6 | 1.171 | 0.97642 |

[a] Points 1-5: Initial cadmium 1.32191 g; lead 0.00923 g; 6.09201-g balance shift = 1.00000-g cadmium shift. Points 6-17: Initial cadmium 1.15525 g; lead 0.01693 g; 6.12800-g balance shift = 1.00000-g 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 mV using equation of Roeser and Wenzel after subtracting a constant mV bias correction for each run. Points 1-5 reduced by 0.0029 mV; points 6-17 reduced by 0.0037 mV. 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. For a discussion of usage of the Roeser-Wenzel equation see Ref. 7.

[d] Vapor activity relative to that over pure liquid cadmium using equation consistent with Hultgren[8] value, namely $P^{o}_{Cd} = \exp(-13{,}119/T + 19.950 - 1.05676 \ln T)$.

temperature difference between the alloy and the cadmium reservoir and, further, because it is little affected by small changes in the alloy temperature.

The point numbers indicate the order in which the measurements were made, points 1-5 representing measurements with the first balance tube while the remaining points were made with a second tube.

These results may be described analytically, except for a narrow transition region, by two equations. The first equation,

$$\frac{P_{Cd \text{ in solution}}}{P_{Cd \text{ pure}}} = 1 - 1.63\, N_{Pb \text{ in solution}}, \qquad (5)$$

applies in the range 0.004 to 0.010 mole fraction lead. Near 0.012 mole fraction lead, the transition region is observed. For the range 0.015 to 0.032 mole fraction lead, the data may be described by the equation

$$\frac{P_{Cd \text{ in solution}}}{P_{Cd \text{ pure}}} = 1 - 2.04\, N_{Pb \text{ in solution}} + 33.0\, N_{Pb}^{2} \text{ in solution}. \qquad (6)$$

This is shown by the Dundee plot in Fig. 2 where the data are plotted as $(1 - a_{Cd}) / N_{Pb}$ vs. $N_{Pb}$. Obedience to the form of Eq. 1 leads to linearity on this plot with the slope determined by $b_A$, the coefficient of the $N_{Pb}^{2}$ term.

## General Discussion

As discussed before[1,2] the isopiestic balance is particularly well suited for measuring changes in activity and composition simultaneously. The analytical balance connected to the equilibrium tube is adjusted to sense about 0.05 mg shift in apparent weight. This sensitivity, because of lever arm amplification, corresponds to 0.05 x (1/6) or about 0.01 mg of actual cadmium transferred. When using a 1-gram sample, one can thus measure about one part in 100,000 change in cadmium present in the alloy.

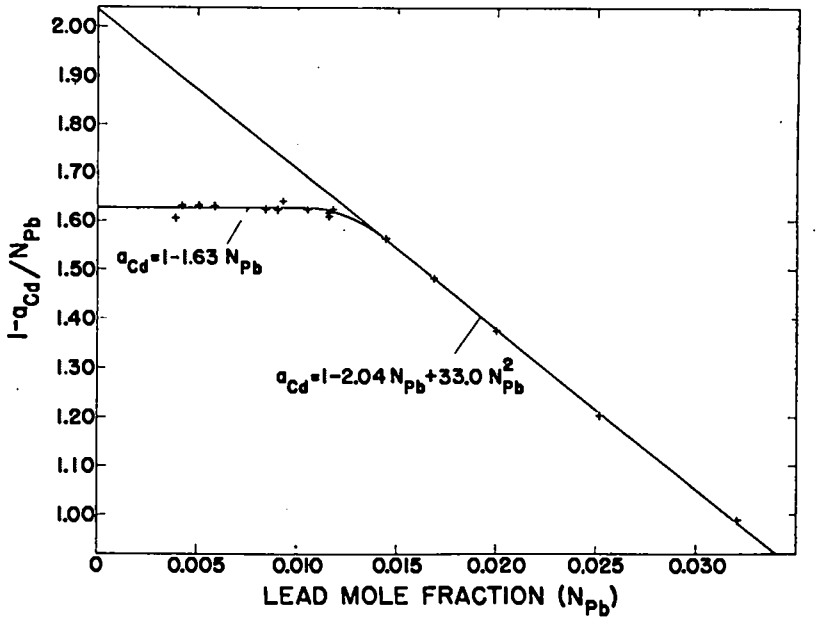


Fig. 2. Dundee Plot to Show the Fit of the Data to the Equation Form Used.

For measuring the cadmium activity the temperature is maintained uniformly constant by concentric massive copper cylinders (nickel plated), and changes in the temperature difference are measured to about 0.005°K. Because the cadmium vapor pressure is altered only 2% per degree,[8] shifts in activity are observed to one part in 10,000 corresponding to 0.2 calorie in the cadmium partial molal free energy.

When the system (alloy plus reservoir cadmium) is at pressure equilibrium, there is no tendency for material to transfer, and the null weight for the balance is constant. If the cadmium in the reservoir is too cool for equilibrium, cadmium transfers from the alloy; if it is too hot, into the alloy. When the alloy temperature is held constant while the reservoir warms slowly toward pressure equilibrium, the material transfer will at first remove cadmium from the alloy, then cease at that temperature which is consistent with pressure equilibrium, and finally reverse and

return cadmium to the alloy. An analogous phenomenon can be observed on cooling the reservoir. As the balance was operated, a distinct reversal of the direction of cadmium transfer could be observed at $0.010^{\circ}$ to $0.015^{\circ}K$ beyond the equilibrium point whether the reservoir was being heated or being cooled. In Table I each experimental point (except the last) is the average of two temperatures, one heating and the other cooling, at which such a reversal was observed. In Fig. 1, for purposes of reproduction, we have drawn the data bars roughly consistent with the two reversal temperatures. Actually, the averages appear to fall consistently within $0.005^{\circ}K$ of the equilibrium value.

These average values are independent of whether the alloy was initially accepting cadmium or evaporating it (i.e. liquid diffusion is shown to be adequate to prevent data bias) and are reproducible whether the rate of reservoir temperature change approaching equilibrium is as much as $0.008^{\circ}K$ per minute or as little as $0.001^{\circ}K$ per minute.

Previous papers[1-3] demonstrate the unimportance of small corrections for the difference between the fugacity and the pressure of the cadmium vapor, for $\overline{V}dP$ changes in the partial molal free energy of the cadmium in the liquid resulting from changes in the pressure of the vapor upon it, for uncertainty in the temperature coefficient of cadmium vapor pressure, for the effect of differences in the alloy temperature at which measurements were made, and for differences in thermocouple compositions within any thermocouple wire.

Because cadmium oxide is more stable than lead oxide,[9] the lead must remain metallic. The evacuation and loading techniques, and the relative volatilities of CdO[10] and Cd,[8] would trap any oxygen traces as oxide mostly outside the isopiestic balance tube in the secondary U-tube which is used only in loading. Any slight failure of the outer cadmium to trap oxygen traces would be further corrected by reaction of CdO in the isopiestic balance tube cross arm with the $SiO_2$ container material, hence it would be unavailable to the solution under test. A final confirmation of the absence of oxygen in solution with consequent depression of the

cadmium activity lies in the agreement of data from solutions with different starting compositions.

The reproducible behavior of these lead-cadmium data, of earlier confirmed data on gallium-cadmium solutions[2] ($k_A$ = 0.856), and of other dilute solution data on nickel-cadmium[11] ($k_A$ = 1.06), on gold-cadmium[12] ($k_A$ = 2.80), and on copper-cadmium[11] ($k_A$ = 2.85) indicate an absence of any apparent systematic error resulting from the manner in which the measurements were made and show a real inconsistency with Raoult's law.

Finally, there seems little reason to question the fundamental validity of the isopiestic balance technique since its results received extensive confirmation by different techniques. (See, for example, Reference 13.)

## Other Measurements

Early vapor pressure data[14] on lead-cadmium solutions show positive deviations from Raoult's law in the midregions, and recent work[15] confirms this trend but scatters too much in our composition region to offer any test of our results. Although the deviations are initially negative, they are followed by positive deviations beyond 0.9683 mole fraction cadmium in agreement with other investigators.

Emf and heat of mixing data have been extrapolated to infinite dilution to give a lead partial molal enthalpy of +3720 calories.[8] Because cadmium dissolves to some unknown extent in the $CdCl_2$-LiCl-KCl molten electrolyte solutions of the emf cells, it is difficult to know what value of n to use in relating $\Delta F$ to $n\mathcal{F}\mathcal{E}$. We will therefore not attempt to compare our vapor pressure results with emf measurements. Furthermore, the change in cadmium vapor pressure behavior at 0.012 mole fraction lead invalidates the extrapolation to infinite dilution for both types of data.

## Interpretation of Results

Raoult's Law and Thermodynamic Prediction - Equation 5, with $k_A = 1.63$ instead of 1.00, has been shown to be valid in the most dilute solutions measured. The uncertainty in this number is very small. Therefore, Raoult's law is not applicable in this case, i.e. when there is as little as one part in 250 of lead solute in the cadmium solvent.

Since the solvent activity is linear in the solute (not solvent) mole fraction, we conclude that each solute atom contributes equally in its effect upon the cadmium solvent. It seems corollary to us that each lead solute atom would also contribute equally to the solute behavior, i.e., that Henry's law would be obeyed by the lead solute. This is contrary to the thermodynamic requirement that Raoult's law be obeyed if Henry's law is obeyed.

In the absence of experimental data on the activity of the solute, it is not possible to state that there is a thermodynamic contradiction involved. However, the reasonableness of Henry's law combined with the preciseness of these experiments leads us to consider that alternative along with the other possible explanations.

The principal basis for accepting Raoult's law is that solutions do follow Henry's law closely; and, if the Duhem relationship is exact when applied to real systems, this leads to Raoult's law. We have pointed out,[2] that many experimental tests of the Duhem relationship have failed to support the usual contention that it is exact for real system activities. Even the classic studies of von Zawidzki (which are so often cited as "proof" of the validity of the Duhem relationship for real systems), in fact, frequently contradict the Duhem vapor pressure correlation in the end regions of composition. And it is in the end regions where we would expect the assumptions of applied thermodynamics to be least satisfactory.

Solution Structure - Structural implications of the change of behavior of the solution at 0.012 mole fraction of lead will be discussed

in a later paper. Other similar solution behavior has also been covered.[11,12,16,17]

Positive Heats, Negative Vapor Pressure Deviations - Although the calorimetry in our concentration range has not yet been done for the lead-cadmium system, it seems worthwhile to discuss such measurements in light of our views on thermodynamics.

It seems possible to us, that positive heats of mixing may be associated with negative deviations from Raoult's law by the vapor pressures. First consider the identical atom metallic bonds of pure lead and of pure cadmium. In our view much of the strength of these metallic bonds is a result of resonance stabilization of electron energy levels relative to those of the isolated (gaseous) atoms. Since resonance is greatest between identical atomic levels with the atoms at identical positions, the addition of any impurity into the pure metals will reduce the resonance near the impurity.

When a small amount of lead is dissolved in a large amount of cadmium, the resonance of pure lead is destroyed and the resonance of cadmium is weakened. These factors would tend to require a large heat absorption in the mixing process.

A factor which could tend to evolve heat would be the direct interaction between lead solute atoms and their cadmium solvent neighbors.

It seems possible to consider that the mixing would involve a net heat absorption because of the loss of resonance (for both lead and cadmium) but that the local bonding of cadmium to lead would be strong enough to reduce the cadmium vapor pressure below that for ideal mixing. In this analysis the resonance in the pure lead does not influence the cadmium vapor pressure but does influence the heat of mixing.

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## Appendix

### Reply to O'Keeffe "On the Validity of Raoult's and Henry's Laws as Limiting Laws for Dilute Solutions."

by

Guy R. B. Elliott, Harold S. Swofford, Jr., and

Donald R. Conant

O'Keeffe[1a]* has suggested an alternative interpretation of the meaning of our data[2a] on the vapor pressure of cadmium over dilute gallium in cadmium solutions. O'Keeffe emphasizes possibly important changes in the Fermi energy, $\Delta E_F$, as the electron concentration changes with solution composition. We welcome this type of discussion, and we recognize that his communication raises a reasonable question.

Changes in the Fermi energy would be reflected in the heat of mixing gallium with cadmium which Kleppa[3a] has measured. Kleppa has chosen the form $\Delta H^M = A\ N_{Ga} + B\ N_{Ga}^2$ to describe his data. The upper curve of Fig. 1a shows that the equation fits his data well in the region of interest to us.

From Kleppa's equation we have evaluated $\Delta \bar{H}_{Ga}$ as shown by the middle curve. The equation form used by Kleppa is frequently interpreted in the following way: Except for the effect of random close approaches of solute atoms to each other, the atoms of a homogeneous solution mix with a

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*When O'Keeffe's correspondence was published, we sent him and submitted to the Journal of Physical Chemistry a slightly different version of the present appendix. O'Keeffe agreed that our reply showed that his comments were not applicable to the gallium-cadmium system, and he submitted a clarification of his original correspondence to show that his ideas were, however, appropriate for other systems. The clarification was published, but our reply was not published because it questioned thermodynamic correlations for real systems. For that reason we are taking this unusual method of publicizing our reply.

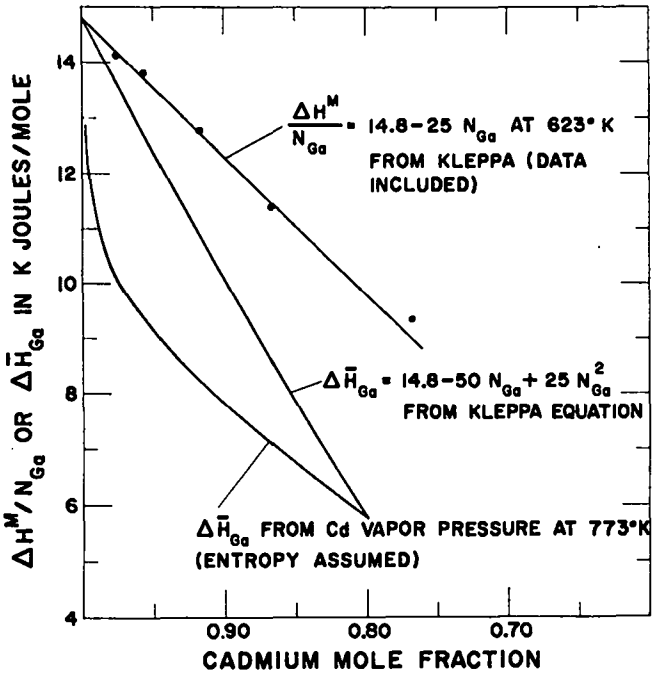


Fig. 1a. A Thermodynamic Contradiction for $\Delta\bar{H}_{Ga}$ Using Heat of Mixing or Cadmium Vapor Pressure Data Plus Usual Entropy Assumptions.

constant heat per atom in dilute solution. The correction for these random close approaches is made by the addition of a term in the square of the solute concentration. Our vapor pressure equation is of a similar form.

In the development of the equations O'Keeffe presents, the equating of the change in the chemical potential of the electrons to the change in the Fermi energy requires the assumption that there is negligible entropy effect associated with changes in the electron concentration. For the solute (which he treats as ionic) an ideal entropy of mixing is assumed.

The lower curve of Fig. 1a is a second evaluation of $\Delta\bar{H}_{Ga}$ using these same entropy assumptions. We have Duhem integrated the cadmium vapor pressure equation to find the changes in gallium activity. We then evaluated $\Delta\Delta\bar{H}_{Ga}$ in the region 0.20 to 0.005 mole fraction gallium using

the idealized entropy assumptions above, and accepted $\Delta\bar{H}_{Ga} = 5.8$ kJ/mole as the starting point for plotting purposes.

The discrepancy between the two evaluations of $\Delta\bar{H}_{Ga}$ indicates that the assumption of changes in the Fermi energy along with idealized entropy assumptions is not thermodynamically consistent with the equations derived from the data. This discrepancy exists both in the regions of our own data[2a] (0.008 to 0.037 mole fraction gallium) and those of Predel's[4a] measurements (beyond 0.11 mole fraction gallium).

Thermodynamic consistency would require the conclusion that, if the heat of mixing and either or both of the two interconsistent groups of vapor pressure measurements are accepted, then the entropy changes are quite unlike the idealized values postulated.

We will return to the entropy discussion, but first we will describe the vapor pressure of cadmium over several other solutions. In the most dilute solutions measured, the behavior of all the systems is of the same form as that for gallium solutions

$$\frac{P_{Cd}}{P_{Cd\ pure}} = 1 - k_1 N_{solute} + b N^2_{solute}. \qquad (1a)$$

Values of $k_1$ and b are listed in Table Ia. (This $k_1$ is also $\partial \ln a_B / \partial \ln N_B$ in the solute activity equation which is thermodynamically corollary. Note that $k_1$ for the Ga-Cd system is 0.856 rather than a value between 1 and 2 as in O'Keeffe's proposal.)

Table Ia

Values of $k_1$ and b in Equation 1a for Various Solutes in Cadmium at the Most Dilute Solution Measured.

| Solute | Reference | $k_1$ | b | Most Dilute Solute Mole Fraction |
|---|---|---|---|---|
| Ni | 5a | 1.06 | ~ 0 | 0.007 |
| Au | 6a | 2.88 | ~ 0 | 0.003 |
| Cu | 5a | 2.85 | ~ 0 | 0.002 |
| Ga | 2a | 0.856 | 0.943 | 0.008 |
| Pb | 7a | 1.63 | ~ 0 | 0.004 |

Except for the gold data, all measurements have been repeated one or more times on different starting alloys using different isopiestic balance tubes.

By chemical reasoning presented elsewhere,[2a,8a,9a] we had been led to suspect that, even in the limit of infinite dilution, obedience to Henry's law by the solute would not lead to a unit slope in the activity-mole fraction relationship (Raoult's law). If this suspicion proved correct, then it would have to be recognized that thermodynamics can offer only an approximate correlation of the properties of real systems. (This correlation is clearly very close to correct in many cases.) The question of exact correlation is connected with the atomic character of matter--. Does the idealized situation described by the simple mathematics actually correspond exactly with the net result of the very complex interactions in a real solution?

The experiments whose results are presented in Table Ia were designed to test certain conclusions which have been considered (by a combination of chemical and thermodynamic reasoning) to be inevitable. Thus Lumsden[10a] on page 245 of his book calculated the activity of lead as determined by its freezing point in equilibrium with its liquid alloys containing small amounts of cadmium. By the implied assumptions of Henry's law to describe the cadmium behavior, Raoult's law for the lead, and ideal entropy estimates, he could arrive at a heat of fusion of lead. He stated, "It will be noticed that not one of the calorimetric determinations made during the present century can be reconciled with this calculated value of the heat of fusion." He then discussed "how such large errors can arise" in the calorimetric values. Later measurements by Douglas and Dever[11a] showed that several of the rejected calorimetric values had been essentially correct. These measurements cannot be reconciled with thermodynamic calculations using customary assumptions.

Our measurements again show that this common type of "thermodynamic" calculation is not valid. The activities of cadmium in our dilute solutions do not follow Raoult's law.

The very important remaining question is this: Does the discrepancy between experiment and customary prediction result (A) from wrong assumptions about the entropy of these systems, or (B) from a more fundamental error in assuming that the results of thermodynamic calculations apply exactly to real systems?

If we accept (A), then the forms of the solute and solvent equations in the gallium-cadmium system lead on dilution to a rapidly increasing distribution ratio of gallium in the vapor to gallium in the liquid. Ordinarily one would anticipate that the distribution ratio would become essentially constant in dilute solution (Nernst's Distribution Law). Since the distribution ratio at moderate dilution strongly favors the liquid, a trend toward complete rejection of the gallium by the liquid at infinite dilution seems to us to be chemically unreasonable. This is the thermodynamic prediction from the cadmium vapor pressure equation, however. Statistically we would anticipate that the variation with concentration of the gallium partial molal entropy would be larger than for an ideal solution. Thermodynamic calculation from the cadmium vapor pressure equation and Kleppa's enthalpy equation leads to a smaller variation, however.

The above reasons, among others, lead us to find (B) more attractive, but we recognize the need for direct experiments which do not involve entropy assumptions. These we are undertaking.

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