Isopiestic Balance Measurements of Solvent Vapor Pressures over Dilute Liquid Solutions of Nickel in Cadmium

DONALD R. CONANT and GUY R. B. ELLIOTT
University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M. 87544

The activity of cadmium vapor over 17 alloys containing 0.008 to 0.045 mole fraction of nickel at 823° K. has been measured using an isopiestic balance. The measured cadmium activities may be described by the single equation $P_{\text{Cd alloyed}}/P_{\text{Cd pure}} = 1 - 1.06\, N_{\text{Ni}}$ where P is the cadmium pressure over the alloy or over pure cadmium at the same temperature and N_{Ni} is the mole fraction of nickel in the liquid solution. The largest deviation of an experimental point from the value calculated by this equation corresponds to 0.0007 in activity units or 1 gram cal. in the cadmium partial molal free energy.

THE ISOPIESTIC BALANCE is capable of high precision in measuring solution vapor pressures and compositions simultaneously. Recently, the technique has been applied to various liquids, including Au-Cd (*4*), Ga-Cd (*8*), Pb-Cd (*13*), Ag-Cd (*2*), Sn-Hg (*1*), and Ag-Hg (*2*). Some of these systems show abrupt changes with composition in the vapor activity-mole fraction relationships, and similar effects have been shown in the activity as measured by electromotive force in Au-Sn (*6*); evidence of these shifts in behavior appears also in electrical conductivity measurements (*4*). The present Ni-Cd system is more like Ga-Cd, Ag-Sn (*6*), and Cu-Sn (*6*), in that it has not shown such changes of behavior within the precision of the measurements.

EXPERIMENTAL

This balance (*7*) may be used to determine vapor pressures over solutions in which only one component is significantly volatile. Briefly, it consists of a two-legged quartz tube mounted in a furnace and suspended by a balance system. One leg contains the alloy and the other contains pure cadmium condensate. Each is heated independently, and nesting copper cylinders provide a high level of temperature uniformity locally. The horizontal section connecting the legs is heated to prevent condensation there. The frame on which the tube is mounted is suspended outside the furnace from two fine wires and is counterbalanced so that the system may pivot freely. A side arm of the frame is attached by a third fine wire to an analytical balance. Cadmium transfer from the alloy to the pure cadmium leg changes the center of mass of the system; to return the balance to null position the weights must be adjusted, and this is a measure of the composition shift for the alloy.

When no weight shift is occurring at the analytical balance, the vapor pressure of cadmium over the alloy and over the pure cadmium condensate is the same; the temperature difference between the two legs is a measure of the cadmium activity in the alloy, evaluated from pressure-temperature relationships for pure cadmium (*10*). The temperature difference is measured with a specially prepared (*7*) Pt-Pt-10% Rh thermocouple pair, each junction placed about 0.5 inch from the bottom of one of the two quartz legs.

More recent modifications in technique have been discussed (*8*). Further changes of procedure were made in the present work to test and to attempt to improve the balance operation. (Commercial models may be obtained through Los Alamos Thermodynamic Equipment, P.O. Box 1796, Santa Fe, N. M.).

The "double reversal" technique (passing forward and back through that temperature at which the cadmium in the reservoir exhibited the same vapor pressure as the hotter alloy) was not used in this case. Instead, after a suitable alloy composition had been created (by holding appropriate alloy and reservoir temperatures for a day or so), the reservoir temperature was shifted to the temperature for pressure equilibrium between alloy and reservoir (as detected by the absence of transfer of cadmium). The cadmium temperature regulator and its variable autotransformer were then manually adjusted so as to hold the system very close to the equilibrium conditions for several hours.

Cadmium, 99.999% pure by the manufacturer's report, was cleaned by cutting off surface oxide. To purify the cadmium more effectively than had been done in the past, 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. Reagent grade nickel (99.5%) 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. (During the evaporation process the cadmium in the secondary tube served as an oxygen "getter" for any traces of oxygen not removed by the vacuum pumps before the seal-off.)

Table I. Activity of Cadmium Alloyed with Nickel

Point No.	Balance Shift, Grams	Cd Mole Fraction,[a] N_{Cd}	Temperature, ° K.				ΔT, ° K.[c]	Cadmium Activity,[d] a_{Cd}	Deviation from Calculation[e]
			Alloy[b]	Cadmium[b]	Alloy crossarm[b]	Cadmium crossarm[b]			
				RUN I					
1	2.1456	0.98954	821.1	820.5	837.1	832.7	0.605	0.98906	+0.00015
2	3.3466	0.98758	821.5	820.7	837.3	832.9	0.739	0.98665	−0.00018
3	4.0792	0.98597	821.4	820.6	837.1	832.6	0.829	0.98504	−0.00009
4	2.7864	0.98858	821.1	821.1	837.3	832.8	0.667	0.98796	+0.00007
5	4.9155	0.98355	821.7	820.2	836.9	832.7	0.984	0.98226	−0.00030
6	6.4689	0.97575	821.9	820.5	837.8	833.1	1.428	0.97439	+0.00010
7	7.6559	0.96201	821.6	819.4	837.1	831.8	2.232	0.96020	+0.00047
				RUN II					
8	2.6286	0.99300	823.1	822.7	840.6	845.4	0.416	0.99251	−0.00007
9	13.2342	0.95481	824.0	821.2	841.2	844.8	2.710	0.95213	+0.00003
10	13.0129	0.95943	823.7	821.3	840.8	844.4	2.406	0.95738	+0.00038
11	12.1221	0.97126	823.7	822.0	840.9	844.8	1.712	0.96950	−0.00004
12	10.9806	0.97908	823.8	822.5	841.0	845.4	1.233	0.97795	+0.00013
13	9.2094	0.98529	823.9	823.1	841.2	845.5	0.889	0.98407	−0.00034
14	11.2898	0.97742	823.9	822.6	841.2	845.4	1.378	0.97540	−0.00067
15	9.4834	0.98458	823.9	823.0	841.6	846.3	0.934	0.98327	−0.00038
				RUN III					
16	0.2527	0.99169	825.8	825.3	845.9	849.7	0.492	0.99120	−0.00001
17	3.6792	0.97778	825.7	824.3	845.7	849.0	1.324	0.97645	0.00000

[a] Points 1 to 7. Initial cadmium 1.53151 grams; nickel 0.00658 gram; 6.31400 grams balance shift = 1.00000 gram cadmium shift. Points 8 to 15. Initial cadmium 2.32584 grams; nickel 0.00707 gram; 6.48773 grams balance shift = 1.00000 gram cadmium shift. Points 16 to 17. Initial cadmium 0.92242 gram; nickel 0.00386 gram; 6.15760 grams 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 using thermocouple junctions from abutting pieces of thermocouple supply wire so that junction compositions are essentially identical. ΔT calculated from millivolts using equation of Roeser and Wenzel (*7*) after subtracting a constant millivolt correction (see "Accuracy of the Data") for each run. Points 1 to 7 reduced by 0.0023 mv.; points 8 to 15 reduced by 0.0013 mv.; points 16 and 17 reduced by 0.0015 mv. [d] Vapor activity relative to that over pure liquid cadmium using a vapor pressure equation consistent with value selected by Hultgren, Orr, Anderson, and Kelley (*10*). [e] Calculation using $a_{\mathrm{Cd}} = 1 - 1.06\,N_{\mathrm{Ni}}$.

The balance tube was mounted in the furnace, where the cadmium was re-evaporated onto the nickel 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 after the run was completed. The metal and alloy materials in the balance tube legs were brightly metallic.

RESULTS

Seventeen measurements in three runs (three separate balance loadings) were carried out, with the results shown in Table I. The cadmium activities may be described by the single equation

$$P_{\mathrm{Cd\,in\,alloy}}/P_{\mathrm{Cd\,pure}} = 1 - 1.06\,N_{\mathrm{Ni}} \qquad (1)$$

No measured cadmium activity is more than 0.0007 activity unit from the value calculated from this equation; in terms of the partial molal free energy of the cadmium, this amounts to a deviation calculated as $RT\ \ln(a_{\mathrm{obsd}}/a_{\mathrm{true}}) = 4.575(823)\log 1.0007 = 1$ gram cal.

For runs II and III two compositions were established independently of the balance analysis—i.e., from the material added and the final composition analysis. For run I, because of experimental difficulties, the points were evaluated by assuming a value for the balance factor which would bring the data into line with runs II and III.

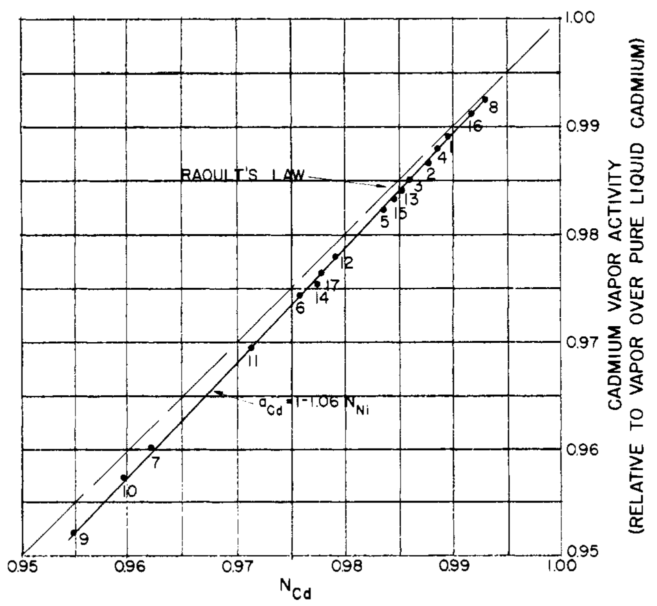

Figure 1. Cadmium vapor activity over liquid nickel-cadmium solutions at 823°K.

ACCURACY OF DATA

Figure 1 shows the precision of the results. Now consider the compositions. When the tube is loaded, much more cadmium than nickel is present. Thus, the nickel impurities are a small part of the total metal present and would normally appear as an error in the slope of the activity–mole fraction relationships; 0.5% impurity of the same molecular weight as nickel and obeying Raoult's law or $0.005 \times 0.06 = 0.0003$ from the 1.06 listed. Heavier impurities obeying Raoult's law would have a proportionately smaller effect.

The cadmium was of reported high purity and oxygen was probably the main contaminant. This oxygen would have remained as oxide on vaporization of the cadmium, producing an extremely pure material. This source of error may be considered negligible.

Analysis of the initial and final composition, as in runs II and III, is highly accurate, since it involves only before and after weighings of the glass tubes from which the cadmium or cadmium-nickel alloys are dissolved.

The composition for run I was set by the secondary, but fairly precise, technique of assigning a composition at point 7, which makes run I consistent with the line to point 9. The line of data must agree with the slope set by the five known compositions and their vapor pressures. An error in the final composition assigned to run I would create an artificial curvature in the activity–mole fraction plots. (This is because the balance monitors the moles of cadmium removed rather than the moles present. The fractional error in one does not equal the fractional error in the other.) Thus, the over-all linearity of the whole group of data is a further indication that the composition of point 7 is assigned properly.

The sensitivity of the balance is about ± 0.05 mg. in 0.3 to 1 gram of alloy present. In addition, the lever arm relationship between the analytical balance and the isopiestic balance tube leads to another factor of 6 favorable to the detection of composition changes. The interpolation to intermediate compositions is not a major source of uncertainty.

In the vapor pressures assigned, there is much more serious uncertainty. First, there is the observed scatter. Because the vapor pressure of cadmium changes about 1.5% per degree at this temperature, an uncertainty of 0.010° K. in ΔT amounts to 0.015×0.01 or 1.5 parts in 10^4. This is the average deviation, but several points fall more than twice as far from the line (Table I).

This scatter is larger than is usually obtained using the "double reversal" method and is ascribed to the difficulty in detecting cadmium transfer into or out of the alloy when miniscus hysteris is randomly influencing the lever arm at which the liquids sit in the legs of the equilibrator tube. (With the double reversal method, the direction of movement of the balance is more constant, the errors are more reproducible, and they are largely cancelled when the reversal is taken from both too hot and too cold a reservoir. The technique used for Ni-Cd is no longer used.)

There is also an absolute error in the apparent activity because of the thermocouple bias (*8*). This affects all measurements equally in a run, but varies by about the equivalent of 0.1° from run to run. This introduces an uncertainty of about 0.2% in the absolute activity.

If the bias on all points is set so they will extrapolate to unit activity at infinite dilution as has been done here, the absolute accuracy is probably much better, but chemical intuition has now been superimposed upon the measurements.

There are no data from other sources to compare directly with these data. However, there are a number of experiments from which isopiestic balance techniques can be compared with other precise vapor pressure techniques. Since no other techniques of measuring vapor pressures are as precise as the isopiestic balance, however, the checks must reflect that lack of precision.

Some of the very best differential manometer studies of alloys have been made on Hg-Sn (*9*) and these agree with isopiestic balance results (*1*) within the claimed uncertainties after adjustment for the temperature difference between the two experiments.

Isothermal isopiestic equilibrations give activities in the Ga-Cd system (*11*) which agree with the isopiestic balance results (*8*).

Isothermal isopiestic equilibration of mercury solutions containing gold and silver have also checked the isopiestic balance (*2*), and the isopiestic balance measurements with Au-Cd solutions have been compared with other vapor pressure work (*4*).

Finally, a very high accuracy in relative compositions was shown by the isopiestic balance with the discovery of microphases in solids (*5*) and their subsequent confirmation by x-ray diffraction studies (*12*). This work confirms our belief that it is possible to obtain a very high level of compositional accuracy.

DISCUSSION

Recent work (*1–3, 6, 8, 13*) has shown that Raoult's law is not necessarily asymptotically approached by alloys at levels of dilution where it has been customary to assume this approach. Therefore, we are not surprised to find apparent deviation with nickel-cadmium solutions. However, the deviations are not large and the scatter of data was such that we did not attempt to establish the temperature coefficient for the deviations and thereby the partial molal enthalpies and entropies for this system.

LITERATURE CITED

(1) Conant, D.R., "Solvent Vapor Pressures over Dilute Solutions of Tinin Mercury," unpublished data, 1967.

(2) Conant, D.R., Swofford, H.S., Jr., unpublished data.

(3) Elliott, G.R.B., Conant, D.R., Swofford, H.S., Jr., Houseman, B.L., Chapt. 28, 3rd International Symposium on High Temperature Technology, D.D., Cubicciotti, ed., Asilomar, Calif., September 1967, IUPAC, Butterworths, London, 1968.

(4) Elliott, G.R.B., Herrick, C.C., Lemons, J.F., Nordine, P.C., Los Alamos Scientific Laboratory, Rept. **LA-3526** (1966).

(5) Elliott, G.R.B., Lemons, J.F., *Advan. Chem. Ser.*, No. **39**, 144–52, 153–69 (1964).

(6) Elliott, G.R.B., Lemons, J.F., *J. Electrochem. Soc.* **114**, 935 (1967).

(7) Elliott, G.R.B., Lemons, J.F., *J. Phys. Chem.* **64**, 137 (1960).

(8) Elliott, G.R.B., Lemons, J.F., Swofford, H.S., Jr., *J. Phys. Chem.* **69**, 933 (1965).

(9) Hildebrand, J.H., Foster, A.H., Beebe, C.W., *J. Am. Chem. Soc.* **42**, 545 (1920).

(10) Hultgren, R., Orr, R.L., Anderson, P.D., Kelley, K.K., "Selected Values of Thermodynamic Properties of Metals and Alloys," pp. 64–5, Wiley, New York, 1963.

(11) Predel, B., *Z. Metallk.* **49**, 226 (1958).

(12) Roof, R.B., Elliott, G.R.B., *Inorg. Chem.* **4**, 691 (1965).

(13) Swofford, H.S., Jr., Elliott, G.R.B., *Inorg. Chem.* **7**, 666 (1968).

RECEIVED for review February 15, 1968. Accepted April 8, 1968. Division of Inorganic Chemistry, 151st Meeting, ACS, Pittsburgh, Pa., March 1966. Work done under the auspices of the U. S. Atomic Energy Commission.