Raoult's Limiting Law and Emf Measurements on Nickel–Cadmium System

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Highly precise emf measurements have been obtained for dilute solutions of nickel in cadmium at 775°K using the cell: $W - Cd \mid CdI_2 + Cd\ (a_{Cd} = 1) \parallel CdI_2 + Cd\ (a_{Cd} < 1) \mid Cd, Ni - W$. When the mobility of cadmium dissolved in the electrolyte is assumed to be nearly the same as that for Cd^{2+}, cadmium activities may be calculated which asymptotically approach Raoult's law with increasing dilution. The measurements extend over the range 0.0009–0.0513 mole fraction of nickel with all deviations from a smooth curve through the data not greater than ±0.000005 (0.008 g/cal in $\bar{G}_{Cd}$) in the activity. The emf measurements are in good agreement with vapor pressure measurements made in this laboratory.

This work forms part of a continuing investigation at this laboratory of cadmium activities in alloys containing small amounts of solute (*3, 6–10, 12, 17*).

The evaluation of activities from emf data depends upon the value assigned to n in the equation $-nFdE = RTd \ln a_{Cd}$. The dependence of n, the average charge per mole of cadmium transferred, upon the solubility of cadmium in its iodide and upon the types, concentrations, and mobilities of the various chemical species present in the electrolyte is discussed.

If the solubility of cadmium in its iodide at 775°K is assumed to be 6.5 mol % consistent with the cooling curve measurements of Topol and Landis (*18*) and if the mobilities of the various cadmium ion species are similar as for the chloride system according to Herzog and Klemm (*11*), the Ni-Cd emf data appear to be in agreement with Raoult's limiting law. However, the experimental uncertainty associated with both the solubilities and mobilities is large.

The best test of the limiting law from the type of cells used for this work is obtained from comparisons between systems containing different solutes. Application of the above assumptions to experimental data obtained from different solute–cadmium alloys should yield the same limiting activity vs. mole fraction slope if the theory is correct. Research in this direction on Au-Cd alloys indicates no significant discrepancy between limiting slopes, indicating agreement with the theory. This discrepancy is actually independent of the assumptions just discussed.

EXPERIMENTAL

Equipment. The H-cell shown in Figure 1 has been described (*12*). The furnace surrounding the lower portion of the cell contained two heaters outside three nesting nickel-plated copper cylinders separated by air gaps. The cell was fixed rigidly to the top of the furnace and the air gap between the innermost copper cylinder, and the cell was packed with glass wool to reduce convection. Firebrick covered the point of cell exit from the furnace as well as surrounding the entire heater and cylinder arrangement. The outer cylinder was grounded to reduce stray emf effects. A Brown controller served to regulate the heaters.

The furnace rested upon a metal table which could be jacked up on one side or the other, allowing the angle of the tube containing solute pieces to be changed relative to the gravitational field. Thus, the cell could be tilted, the sidearm tapped until a single piece fell into the melt, and the cell returned to its original position without disturbing the relative position of the cell to the furnace. This rigidity was important for attainment of high precision.

The temperature was measured directly with a Pt-Pt-10% Rh thermocouple. Copper wire was used to connect the thermocouple to the potentiometer through a switch with the junctions being placed side by side in an ice bath, direct contact being prevented by their individual containment in thin sleeves of plastic tubing. The relative positions of these junctions to each other were permanently fixed by wrapping them together with copper sheet.

All emf's were measured with a Leeds and Northrup galvanometer and Wenner potentiometer combination with sensitivity of 0.01 μV. A double-pole, double throw switch was used to connect the potentiometer first to the thermocouple or cell, then to a short length of copper wire used as a reference zero potential. The difference between these two readings was taken as the potential.

Procedure. Cadmium (99.999% purity by manufacturer analysis) was slagged at 10^{-5} torr to remove oxide, then boiled with CdI_2 to free it from electrochemically important impurities. The original surfaces of reagent grade nickel (99.5%) were removed by cutting. The tungsten electrodes were cleaned electrolytically by using them to pass ac current through concentrated NaOH solution, and washing them with distilled water. Reagent CdI_2 was loaded into a side tube, boiled under vacuum until the molten CdI_2 caused no higher pressure than 10^{-5} torr to be registered beyond the cold trap, then cooled. The cell was back-filled with argon which had been purified by distillation. The cell was sealed off and removed from the vacuum system with a torch by collapsing the tubing between the stopcock shown in Figure 1 and the remainder of the cell. The cell was loaded into the furnace, the cadmium in the legs melted, and the CdI_2 fused by torch and allowed to run into the H-cell legs.

Since the upper portion of the cell was outside of the furnace so that stirring could be carried out, a constant flow of heat up the glass walls of the tube occurred. The metals at the bottom of the tubes were relatively good conductors compared to the glass, and the conduction area of the metal relative to the cross section of the tube walls was large. Thus, the pure cadmium and the alloy should have been at a uniform temperature throughout as well as the electrolyte in direct contact with the metal. However, a slight gradient across the electrolyte, especially across the crossarm containing a small amount of electrolyte, would be expected causing the permanent pure cadmium electrode to be at a slightly different temperature than the alloy electrode.

After the cell had equilibrated in the furnace for one day

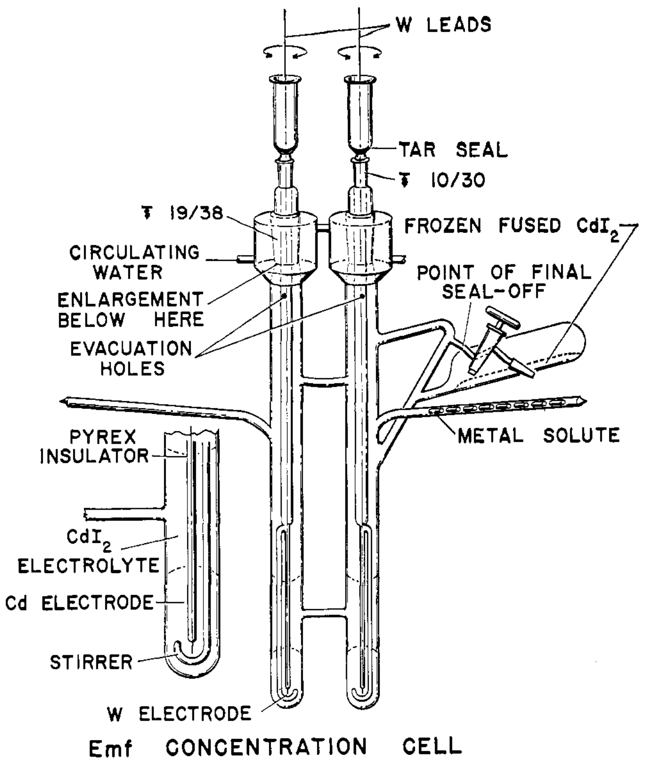

Figure 1. Emf concentration cell

Tubes below standard taper joints are drawn oversize

(pure cadmium was in each leg since no nickel had been added), the magnitude of this effect was checked by varying the position of the cell relative to the copper cylinders and noting the resulting cell emf. When the two legs were placed nearer the copper cylinders, the emf was reduced. The emf for both legs in direct contact with the inner cylinder was 0.1 μV. Since the glass of the tubes acted as good electrical insulation between the electrodes and the copper cylinder, and since the emf was generally sensitive to position in the furnace even when a large air gap separated the nested cylinders and the cell, the entire cell emf bias was evidently due to the difference in the temperatures of the alloy and permanent cadmium electrodes. This conclusion was entirely in agreement with the apparent purity of the materials.

It was assumed that slight movements of the cell relative to the copper cylinders might cause greater changes in the emf bias if the cell were extremely near the inner cylinder; therefore, the cell was centered giving the largest possible air gap between it and the cylinder. Thus, a much larger bias (56.60 μV) rather than that (0.1 μV) of direct contact was ultimately accepted with the hope that the resulting bias would remain more constant. Finally, to test the constancy of the bias in this position, the furnace was jacked up and lowered again after which both legs of the cell were stirred. The bias changed by 0.2 μV during this period. A second day was allowed to pass for the cell to further settle down before measurements on the alloys were begun. The direction of the bias change indicated that the change observed the day before was due more to the lack of cell equilibrium than to raising the furnace. Subsequent stirring on the second day showed that when the cell had finally equilibrated, the bias shift due to stirring was at most only ±0.01 or ±0.02 μV. The initial bias measured was subtracted from all subsequent emf measurements on the alloys.

Thermodynamically, the emf arising from this cell may be considered as the sum of two emf's, one arising from $Cd(T_2)$ vs. $Cd(T_1)$ and the other from $Cd(T_1)$ vs. alloy (T_1). The second emf was required for determining the activity of the cadmium at temperature T_1. Since initially no solute had been added to the alloy side, the second emf was zero, and the first was just the initial emf measured and has been referred to as the bias. Since this value is essentially constant, it must be subtracted from emf readings obtained for the alloys to obtain that value which arises from the cell $Cd(T_1)$ vs. alloy (T_1).

The emf arising from the difference in electrode temperatures was of the order of magnitude of 1 μV for each 0.001°K (*9*). Thus, the temperature difference between the two legs was less than 0.1°K, and stirring changed a given electrode temperature in the range of 10^{-5}°K after initial mechanical heating effects had been allowed to settle out.

The cell was allowed to equilibrate for two days before solute pieces were added. An initial emf bias between the two pure cadmium legs was recorded. After each piece was added, both legs of the cell were stirred and the emf observed until no further change occurred. The thermocouple and cell emf's were then recorded. The average equilibration time, with stirring required for each piece added, was about 3 hr.

Uncertainties. The precision of the experimental measurements was high. The most dilute solutions were stable to 0.01 μV in the cell emf. The thermocouple measurements were made to the nearest 0.01 μV although the uncertainty in absolute temperatures was probably as much as ±0.1°K. A correction factor of 1.37 μV was subtracted from the measured thermocouple emf to bring the equation (*14*)

$$E = -309.17 + 8.29558\,t + 0.00144103\,t^2 + 0.0000001634\,t^3$$

into agreement with more recent reference tables (*16*).

Cadmium was weighed to the nearest 0.1 mg and nickel to the nearest 0.01 mg. The CdI_2 over each leg was estimated to be about 35 grams. The uncertainty in cadmium added was less than one part in 100,000. For the most dilute nickel piece added, the uncertainty was no better than one part in 1000. However, the uncertainty in total nickel added decreased for each succeeding piece since the weighings were made on groups rather than on individual pieces after the first—i.e., after weighing the first piece, a second piece was placed on the balance pan together with the first piece, and the two were weighed together; then the third piece was added to the first two on the pan. The uncertainty in CdI_2 over each leg was not more than 5%.

RESULTS AND CALCULATIONS

Table I gives the results of measurements on the nickel–cadmium system. The experimental values of cell emf, temperature, and material added are known to a high degree of accuracy as well as precision. The calculated values for alloy composition, electrolyte composition, and activity are subject to further uncertainties, however, which result from the significant solubility of cadmium in CdI_2.

Four investigations have given rather different values for the solubility of cadmium in CdI_2. At 873°K the mole fraction of cadmium is reported as 0.061 by Von Hevesy and Lowenstein (*19*), 0.015 by Corbett et al. (*4*), 0.106 by Topol and Landis (*18*), and 0.118 by Mashovets and Poddymov (*13*). The most extensive studies were those carried out by Topol and Landis, with their decantation and cooling curve measurements being in fairly good agreement. A value of 0.065 consistent with their cooling curve measurements for the mole fraction of cadmium in CdI_2 at 775°K has been chosen for purposes of calculating the electrolyte composition in equilibrium with pure cadmium. For electrolyte in equilibrium with alloy, the solubility of cadmium was assumed proportional to the cadmium mole fraction in the alloy. This last correction is a relatively minor one for such dilute alloys.

Two other solubilities are of relatively minor importance. The reported free energies of formation (*1*) of the compounds involved in the reaction $Ni_{(soln)} + CdI_{2(soln)} = NiI_{2(soln)} +$

Table I. Activity of Cadmium Alloyed with Nickel, Emf Measurements

Point no.	Nickel, moles	Cell emf,[a] μV	Temp,[b] °K	Cadmium alloy mole fraction[c]	Cadmium activity	$\frac{1 - a_{\text{Cd}}}{N_{N_i}^{\text{alloy}}}$
1	0.0002793	32.69	774.66	0.9990844	0.9990844	0.99993
2	0.0007162	83.79	774.73	0.9976557	0.9976550	1.00030
3	0.0015440	180.38	774.79	0.9949602	0.9949584	1.00035
4	0.0029569	344.89	774.88	0.9903938	0.9903822	1.00121
5	0.0044839	522.54	774.82	0.9855066	0.9854607	1.00316
6	0.0060433	705.63	774.93	0.9805664	0.9804159	1.00774
7	0.0076413	894.08	774.89	0.9755559	0.9752453	1.01271
8	0.0092524	1086.16	774.85	0.9705570	0.9700007	1.01889
9	0.0110160	1298.00	774.95	0.9651448	0.9642533	1.02558
10	0.0128401	1521.43	775.08	0.9596116	0.9582289	1.03423
11	0.0146721	1748.55	775.00	0.9541188	0.9521305	1.04334
12	0.0165144	1981.42	775.09	0.9486598	0.9459261	1.05325

[a] All cell emf values reduced by constant 56.60 μV initial bias arising from slight temperature differences between two legs. [b] Measured with Pt/Pt-10% Rh thermocouple against ice junction. [c] 0.311432 mole of Cd and 0.0956 mole of CdI_2 were added to alloy leg. The solubility of Cd in CdI_2 was assumed to be $N_{\text{Cd}}^{\text{elec}} = 0.065\ N_{\text{Cd}}^{\text{alloy}}$.

$\text{Cd}_{(\text{soln})}$ indicate that the loss of nickel from the alloy to replace cadmium in the electrolyte is insignificant. The solubility of CdI_2 in Cd is also small, less than 0.0005 mole fraction (*12*).

A second major uncertainty involved in calculating activity concerns n in the equation $-nFdE = RTd \ln a_{\text{Cd}}$ where a_{Cd} is the cadmium activity on the alloy side. The value for n depends on the relative mobilities of the various species present in the electrolyte and will also involve the character of the dissolved cadmium species for dissolved cadmium mobility values lying between that of the Cd^{2+} ions and that of the I^-. For the cell

$$\begin{array}{l} \qquad\qquad\quad A \qquad\qquad\qquad\qquad\quad B \\ \text{Anode} \\ \text{Cd} \mid \text{CdI}_2 + \text{Cd(sat)} \parallel \text{CdI}_2(N_{\text{CdI}_2}^{\text{elec}}) + \text{Cd}(N_{\text{Cd}}^{\text{elec}}) \mid \\ \qquad\qquad\qquad\qquad\qquad \text{Ni}(N_{\text{Ni}}^{\text{alloy}}) + \text{Cd}(N_{\text{Cd}}^{\text{alloy}}) \end{array}$$

the cadmium dissolved in the electrolyte may be represented as some general species Cd_j^{i+} where i represents the charge and j the number of cadmium nuclei associated with the dissolved species. N_k^{elec} refers to the mole fraction of species k in the electrolyte. Similar to a treatment by Crawford and Tomlinson (*5*) on the Cd, CdCl_2 system, the reactions for the above cell are:

cathode

$$\frac{j}{2j - i}\ \text{Cd}^{2+}(B) + e \rightarrow \frac{1}{2j - i}\ \text{Cd}_j^{i+}(B)$$

junction

$$\begin{cases} \frac{t_1}{i}\ \text{Cd}_j^{i+}(A) \rightarrow \frac{t_1}{i}\ \text{Cd}_j^{i+}(B) \\ \frac{t_2}{2}\ \text{Cd}^{2+}(A) \rightarrow \frac{t_2}{2}\ \text{Cd}^{2+}(B) \\ t_3\text{I}^-(B) \rightarrow t_3\text{I}^-(A) \end{cases}$$

anode

$$\frac{1}{2j - i}\ \text{Cd}_j^{i+}(A) \rightarrow \frac{j}{2j - 1}\ \text{Cd}^{2+}(A) + e$$

t_1, t_2, and t_3 being the transference numbers of Cd_j^{i+}, Cd^{2+}, and I^-, respectively, as defined relative to an arbitrary frame of reference. Making use of the Gibbs-Duhem relationship, we may write

$$E = -\frac{RT}{2F} \int_A^B \frac{1}{N_{\text{CdI}_2}^{\text{elec}}} \times$$
$$\left\{1 - \frac{N_{\text{Cd}}^{\text{elec}}[(2j - i)\ N_{\text{CdI}_2}^{\text{elec}} - iN_{\text{Cd}}^{\text{elec}}]\ (u_2 - u_1)}{iN_{\text{Cd}}^{\text{elec}}(u_1 - u_2) + (2j - i)N_{\text{CdI}_2}^{\text{elec}}(u_2 - u_3)}\right\} d \ln a_{\text{Cd}}$$

where u_k is the mobility of species k with respect to the arbitrary frame of reference. The above equation depends only upon differences in mobilities and hence is independent of the frame of reference. This equation disagrees with Equation 3 listed by Crawford and Tomlinson (*5*), although their treatment including their Equations 1 and 2 leading up to Equation 3 appears to be correct. Their Equation 3 is presumed in error. For a detailed discussion treating cells of this type and including the effects of solute displacement reactions, see ref. *2*.

Herzog and Klemm (*11*) have shown that u_1 is approximately equal to u_2 for the CdCl_2 system indicating perhaps a fairly strong coupling between dissolved cadmium and Cd^{2+} ions for that system. Since metals tend to dissolve significantly in their own halides, but not in those of other metals, coupling between a metal and its own ion is probably the general cause of this dissolution. As in the chloride system, u_1 in the iodide system is likely similar to, although slightly less than u_2 because of the different ionic sizes. For this circumstance $u_2 - u_1 \approx 0$ and

$$dE = -\frac{RT}{2F} \frac{1}{N_{\text{CdI}_2}^{\text{elec}}}\ d \ln a_{\text{Cd}} \qquad (1)$$

If u_1 were a great deal less than u_2, the extreme and most unlikely case would be for cadmium coupled to the iodide ion with $u_1 \approx u_3$. This extreme where $u_2 - u_1 \approx u_2 - u_3$ gives

$$E = -\frac{RT}{2F} \ln a_{\text{Cd}} \qquad (2)$$

Any intermediate case would depend upon i and j as well as upon the mobilities. In the first case at any given concentration $N_{\text{CdI}_2}^{\text{elec}}$, n takes the value $2\ N_{\text{CdI}_2}^{\text{elec}}$, which corresponds to the two electrons for species Cd^{2+} reduced in proportion to the concentration of Cd^{2+} ions. This case then involves an integration over the concentration range between $N_{\text{Cd}}^{\text{elec}}$ and saturation. In the second case n is too greatly independent of concentration and no integration is required.

The calculations appearing in Table I are based on the assumption that $u_1 \approx u_2$ presuming the Cd, CdI_2 system behaves similarly to the Cd, CdCl_2 system. Since the experimental measurements involve slight variations in the temperature, the integration should be carried out on the function E/T to greatly reduce scatter due to the slight temperature fluctuation. This reduction in scatter is accomplished because activity is a slowly varying function with temperature. The equation for this integration is

$$\ln a_{\text{Cd}} = -\frac{2F}{R} \int_0^{\frac{E}{T}} N_{\text{CdI}_2}^{\text{elec}}\ d\ \frac{E}{T}$$

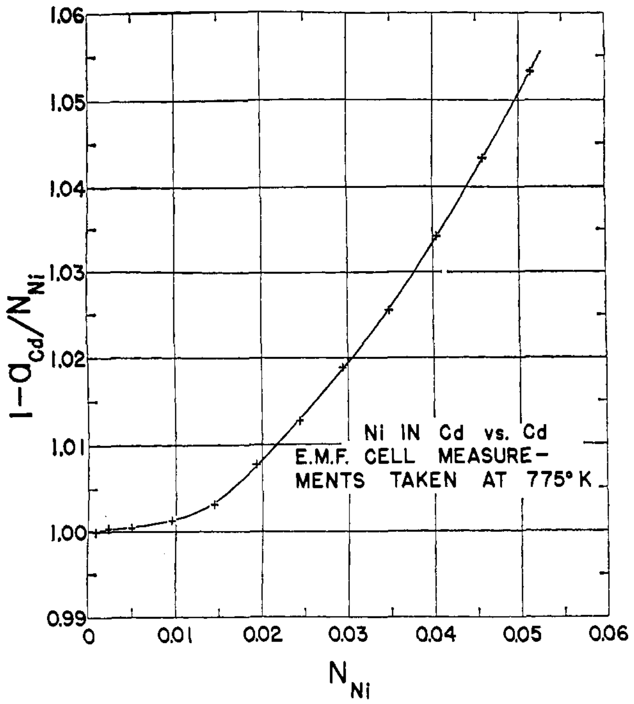

Figure 2. Dundee plot showing scatter in data

The variation of $N_{CdI_2}^{elec}$ with E/T is so slight over the range of the measurements that the trapezoid rule may be employed between the actual experimental points instead of drawing a smooth curve through the data. As a consequence, the experimental uncertainty is essentially retained in the calculated activities.

A smooth curve can be drawn through the activities having no roots in its first three derivatives. The maximum deviations from this curve are not greater than ± 0.000005 (0.008 g/cal in $\bar{G}_{Cd}$), the average deviation being ± 0.0000020. The emf readings were observed to be more stable for the more dilute measurements, and this is reflected by the decrease in scatter to an average value of ± 0.0000003 in the activity or $\pm 0.01\ \mu V$ for the first four measurements. The curve does not seem to be a simple mathematical function; therefore, no empirical equation describing the data will be given. The scatter is best illustrated by a plot of the type shown in Figure 2. Had the calculations been based upon Equation 2, this curve would remain relatively unchanged in shape but would be raised by the value 0.069.

In Figure 3 is shown a comparison of the cadmium activity determined by emf at 775°K with vapor pressure measurements (*3*) taken by isopiestic balance on the same system at 823°K. The extrapolated thermocouple biases associated with the vapor pressure measurements were reduced by 0.4 μV, increasing all plotted activities by 0.0008 compared to the data listed by Conant and Elliott (*3*). Although the emf curve is not the best one that could be drawn through the vapor pressure data, agreement seems reasonably good. Because of the temperature difference between the two sets of data, exact agreement is not required.

DISCUSSION

If the activity of a solute in a binary system has a finite slope at very great dilution, thermodynamic theory predicts that the slope of the solvent activity will approach unity when referred to its mole fraction. Experimental tests of this limiting law are difficult and require measurements of the highest precision and accuracy. The precision associated with a given experimental method is usually discernible from the scatter in the data. The problem of the accuracy to be associated with the method is not so easily solved. Few methods have even the precision required for attacking the problem of the limiting law. One of the best is that of freezing point depressions applied to aqueous solutions. Data on the KCl in H_2O system by Scatchard and Prentiss (*15*) are compared to those of this paper in Figure 4, illustrating the uncertainty associated with each type of measurement. The scatter of the data about the curve drawn through the KCl, H_2O measurements is greater than that for the Ni, Cd system. However, the uncertainty in n and the uncertainty in the Cd solubility in CdI_2 which are associated with the emf measurements make the absolute value of the intercept uncertain.

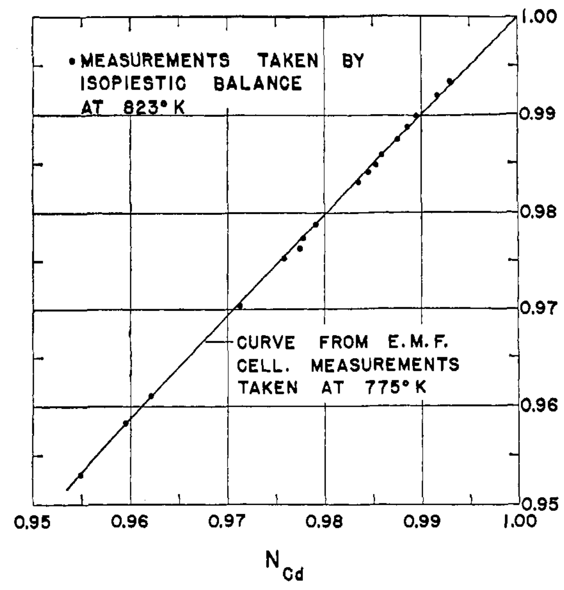

Figure 3. Comparison of vapor pressure and emf measurements

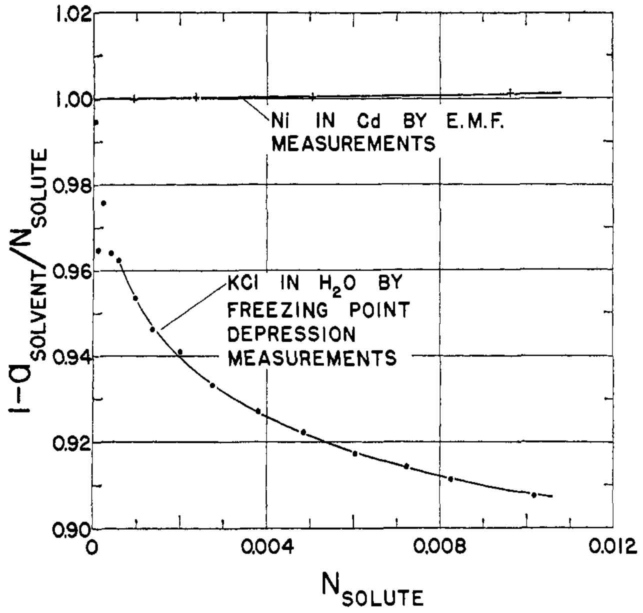

Figure 4. Comparison of approach to Raoult's limiting law by Scatchard and Prentiss freezing-point depression data and by emf data

Note added in proof: The Ni-Cd data of R. A. Schaefer and F. Hovorka [*Trans. Electrochem. Soc.*, **87,** 479 (1945)], should have been mentioned. These data do not agree with the present work, but several problems seem evident: (a) Most serious, Schaefer and Hovorka made no analysis of, or corrections for, differences in the $CdCl_2$ concentration in the Li-KCl-$CdCl_2$ electrolyte in the two H-cell legs. (b) The reported solubility of nickel in cadmium at their lowest temperature was exceeded. (c) The stabilities of NiO and CdO are close enough so that oxidative side reactions were perhaps possible.

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Vapor-Liquid Equilibrium at Atmospheric Pressure

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Vapor-liquid equilibrium of the three binary systems cyclohexane–cyclohexene, cyclohexane–1,2-dichloroethane, and cyclohexene–1,2-dichloroethane and the ternary system cyclohexane–cyclohexene–1,2-dichloroethane were measured at atmospheric pressure using an Ellis recirculation still. Experimental data were tested for thermodynamic consistency, and Wilson's equation provided a good correlation.

Published data (*1, 3*) show the two binary systems cyclohexane–cyclohexene and cyclohexane–1,2-dichloroethane inadequate in thermodynamic consistency tests. This work is an investigation of these systems plus the binary system cyclohexene-1,2-dichloroethane and the ternary system cyclohexane–cyclohexene-1,2-dichloroethane.

EXPERIMENTAL

Materials and Physical Constants. Cyclohexane, cyclohexene, and 1,2-dichloroethane were supplied as chromatography grade and used without further purification. The four-parameter equation, $\ln P_i^s = C_1 + C_2/T + C_4T + C_6 \ln T$, was used to correlate vapor pressure and temperature. The parameters C_1–C_4 were found by the method of least squares, and the best value of C_6 was obtained by trial and error. The agreement between published and calculated vapor pressure data is good. The mean absolute percentage deviation, defined as

$$D = \sum_{j=1}^{N} \left| \frac{P_j^s\ (\text{exp}) - P_j^s\ (\text{calcd})}{P_j^s\ (\text{exp})} \times 100 \right|$$

gave values ranging from 0.008 for cyclohexane to 0.043 for 1,2-dichloroethane.

The necessary physical constants were found in the literature and are reported in Table I.

Apparatus. Experimental vapor-liquid equilibrium data were determined by using a conventional glass Ellis recirculation still fully described in the literature (*2*). Pressure was regulated by a damping reservoir followed by a Cartesian monostat (*2*). Variation of pressure in the system was estimated to be, at the most, 1 mm of mercury.

Temperatures were measured by a calibrated ASTM thermometer. The probable error in the temperature is 0.05°C. The whole system was kept in a heated box, and a total load

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