point and the boiling point of the compound were determined, and the vapor-tension curve was plotted. Vapor-tension values quite different from those previously published by Schenck were obtained.

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THE RELATION BETWEEN DEVIATIONS FROM RAOULT'S LAW AND THE PARTIAL HEATS OF SOLUTION

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In the attempts which have been made to account for the deviations of liquid mixtures from Raoult's law, both chemical and physical effects have been taken into account.[1] Dolezalek and his school saw in all deviations evidence of chemical change, that is, combination between the components, or association. Although it appears to be possible by means of suitable assumptions of this kind to account for any deviation, it has been shown that in their efforts to explain all deviations in this way the exponents of this view were led to postulate effects for other reasons that were absurd or contrary to other evidence.[2] On the other hand, it has been shown that purely physical causes can give rise to deviations. Van der Waals[3] and Van Laar[4] attempted to apply the underlying ideas of van der Waals' equation of state to binary mixtures and showed that it is possible to account in this way for the various kinds of vapor-pressure curves met. More recently, Hildebrand[5] has referred deviations to differences in the internal pressures of the components. However, this theory has been developed for the purpose of giving comprehensive indications of the kind and amount of deviation over a wide field rather than a quantitative explanation of the deviations in individual cases.

It can be shown that if a binary mixture obeys Raoult's law, the heat effect of mixing the components must be zero.[6] Further, it has long been known that a general correspondence exists between the deviations from Raoult's law and the heat of mixing and also with the volume change on mixing.[7] The thermodynamical relation between the partial heat of solu-

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[1] For a complete bibliography see (a) Lecat, "L'azeotropisme," Brussels, **1918**; also (b) Hildebrand, "Solubility," Chemical Catalog Co., **1924**.

[2] Ref. 1 b, Chap. VII.

[3] Van der Waals, *Z. physik. Chem.*, **5**, 133 (1890).

[4] Van Laar, *ibid.*, **72**, 723 (1910); **83**, 599 (1913).

[5] Hildebrand, THIS JOURNAL, **38**, 1452 (1916).

[6] Schroeder, *Z. physik. Chem.*, **11**, 449 (1893).

[7] Compare Young, "Fractional Distillation," MacMillan, **1922**, p. 34.

tion Q of a component and its partial vapor pressure p over the solution is given by the Kirchhoff equation: $\frac{d\, ln\, p/p_0}{dT} = \frac{Q}{RT^2}$, where p_0 is the vapor pressure of the pure liquid.

The integration of this equation and the calculation of the partial vapor pressures when the partial heats of solution are known involve factors which are not given by thermodynamical theory.

Expressing Raoult's law in the form, $p = p_0N$, where N is the real fraction, the deviation of a component in any solution from its requirements is conveniently expressed by the quantity $ln\, p/p_0N$ or $ln\, \alpha/N$, where α is the activity.

Since most of the accurate measurements of this quantity and all the determinations of the partial heats of solution in binary mixtures have been made for liquid metal mixtures from measurements of the e.m.f.'s of concentration cells with electrodes consisting of binary liquid metal mixtures of different concentrations, it is necessary before proceeding to bring the theory of these cells into line with the expressions of Raoult's law.

According to the osmotic theory of Nernst (expressed in terms of mole fractions) the e.m.f. of a liquid metal concentration cell in which the mole fractions of the electromotively active metal at the electrodes are N_1 and N_2, respectively, is given by the formula, $\nu EF = RT\ ln(N_1/N_2)$. It has been shown that this equation holds only at infinite dilution, and to take account of the heat effect Cady[8] proposed the equation.

$$\nu EF = Q + RT\ ln\ (N_1/N_2) \qquad (1)$$

where Q is the heat of transfer of one mole of the electromotively active metal from the solution in which its mole fraction is N_2 to that in which the mole fraction is N_1. Since by definition $\nu EF = RT\ ln(\alpha_1/\alpha_2)$ and $\alpha_2 = N_2$ in the standard state, Cady's equation can be written in the form

$$ln\ (\alpha_1/N_1) = Q/RT \qquad (2)$$

where Q is now the heat absorbed in the transfer of one mole of the component concerned from the standard state to a solution in which its mole fraction is N_1.

Cady's equation has been exhaustively tested by Richards and his coworkers.[9] Using dilute amalgams these investigators concluded that although Cady's equation gives moderate agreement with the observed values in some cases, in others it does not account for the whole of the deviation from the concentration term. "On the average," they concluded, "about three-quarters of the deviations are to be explained by the heat of dilution of the amalgam according to the equation of Cady."

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[8] Cady, *J. Phys. Chem.*, **2**, 551 (1898); **3**, 107 (1899).

[9] Richards and others, *Z. physik. Chem.*, **58**, 683 (1907); **72**, 129 (1910). Carnegie Inst. Pub., Nos. **56**, **118**.

More recently a thorough investigation of concentrated thallium amalgams has been made by Richards and Daniels.[10] Making use of the data obtained in this investigation as calculated in molar quantities by Lewis and Randall,[11] it has been found that although the equality (2) does not hold, the two quantities are *nearly exactly proportional to each other* over the whole range of concentrations.

The data are given in Table I and plotted in Fig. 1. The partial heats of solution at 20° have been calculated from those given by Lewis and Randall

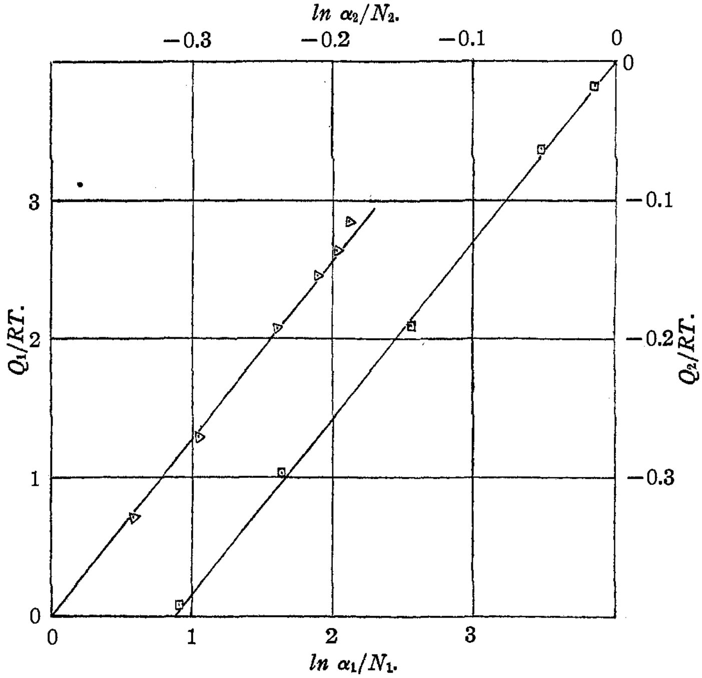

Fig. 1.—Deviations from Raoult's law and partial heats of solution of thallium and mercury in thallium amalgams. Values of $ln\ \alpha/n$ plotted against Q/RT. Thallium △ (1), mercury ◻ (2). Data of T. W. Richards and F. Daniels.

for 30° by means of the equation $Q_{20} = Q_{30} - 10\ (C'_p - C_p)$, where C'_p is the partial molar heat capacity of thallium in the given amalgam and C_p that in infinitely dilute amalgam.

The figures given in the last columns were calculated by the equation $ln\ \alpha/N = 0.78Q/RT$ for both components. It reproduces the observed values with an average error of 1.7% for thallium and 2.6% for mercury.

The fact that the same equation serves for both components is a neces-

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[10] Richards and Daniels, THIS JOURNAL, **41,** 1732 (1919).

[11] Lewis and Randall, *ibid.,* **43,** 233 (1921).

TABLE I

DEVIATIONS FROM RAOULT'S LAW AND PARTIAL HEATS OF SOLUTION OF THALLIUM AND MERCURY IN THALLIUM AMALGAMS

THALLIUM

N_2	$ln\ \alpha_2/N_2$	Q_{20}/RT, obs.	$ln\ \alpha_2/N_2$, calcd.	Difference Calcd.-obs.
0	0	0		
0.05	0.587	0.715	0.582	−0.005
.1	1.043	1.297	1.002	− .041
.2	1.605	2.078	1.621	+ .016
.3	1.889	2.457	1.917	+ .018
.4	2.025	2.640	2.06	+ .035

MERCURY

N_1	$ln\ \alpha_1/N_1$	Q_{20}/RT, obs.	$n\ \alpha_1/N_1$, calcd.	Difference Calcd.-obs.
1	0	0	0	0
0.95	−0.014	−0.017	−0.013	−0.001
.9	.051	.063	.049	− .002
.8	.144	.190	.148	+ .004
.7	.236	.297	.232	− .004
.6	.310	.392	.306	− .004

sary consequence of their expression in partial molar quantities, for since[12] $N_1\, \mathrm{d}\, ln(\alpha_1/N_1) = -N_2\, \mathrm{d}\, ln(\alpha_2/N_2)_{(N)}$, and $N_1\, \mathrm{d}\, Q_1 = -N_2\, \mathrm{d}\, Q_{2\ (N)}$

$$\therefore \frac{\mathrm{d}\, ln\ (\alpha_1/N_1)}{\mathrm{d}Q_1} = \frac{\mathrm{d}\, ln\ (\alpha_2/N_2)}{\mathrm{d}Q_{2(N)}}$$

Further data of the same kind have recently been obtained by Taylor[13] for a number of pairs of liquid metals over a range of concentrations extending from one pure liquid to the other. A plot of the data for the electromotively-active component in each case is shown in Fig. 2. The partial heats of solution of the constituents were calculated by Taylor for two or three temperature intervals in each case, but the temperature coefficient appears to be within the experimental error. The mean of the values has, therefore, been taken and the values of $ln\ \alpha/N$ are for an intermediate temperature. The accuracy of the data does not justify any further refinements. Except in the case of zinc-cadmium which diverges considerably, the maximum deviation from the linear relation scarcely exceeds the possible error in the heat of solution.[14]

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[12] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, pp. 41, 269.

[13] Taylor, THIS JOURNAL, **45**, 2865 (1923).

[14] Taylor was aware of the existence of a close proportionality between these quantities. He states "that where an alloy solution is free from compounds between the components, both the deviations from Raoult's law and the partial molar heats of mixing are proportional to the differences of internal pressure. It follows therefore that these first two quantities are closely related. For a given solute in different liquid alloy systems the partial molal heat of dilution is very nearly directly proportional to the deviation of this solute from Raoult's law." (Ref. 2, p. 2889.)

Further data of the same accuracy as those of Richards and Daniels must be available before the linear relation can be regarded as general. Such a relation would in the author's opinion be of primary importance in the theory of binary mixtures and its significance may very briefly be considered from the point of view of statistical theory. According to the statistical theory of the vaporization of binary liquids, the rate of escape of molecules from the surface is given by the product of three factors; (1) the number present in the surface layer, (2) the fraction which at any instant has sufficient energy to escape, (3) a quantity depending on the vibration frequency at the surface, the statistical constant. In this way an expression of the following form is obtained for the concentration of a substance in the vapor phase above a liquid:[15] $C = Kne^{-w/RT}$, where n is the number of molecules in the surface layer, C is the concentration in the vapor phase and

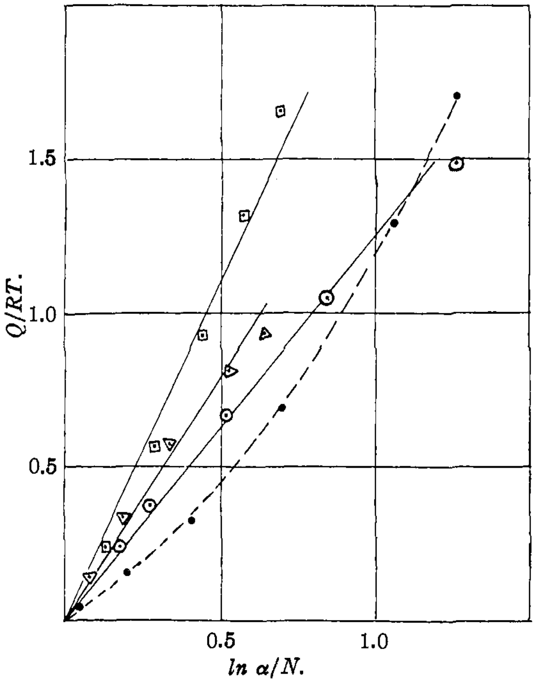

Fig. 2.—Deviations from Raoult's law and partial heats of solution of the more electropositive component of the systems:

Sn in Sn – Sn at 466° ⊡
Sn in Sn – Cd at 466° ●
Cd in Cd – Sn at 483° △
Cd in Cd – Pb at 480° ⊙

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[15] Rodebush, This Journal, **45**, 606 (1923). Butler, *Trans. Faraday Soc.*, **19**, 659 (1924). Compare especially Noyes, This Journal, **46**, 1093 (1924).

w is the work done by a molecule in escaping from the surface (per mole). If we now consider (*a*) pure liquid A for which these quantities have the values C_0, n_0, w_0; (*b*) binary liquid mixtures for which the corresponding quantities for molecules A are C_1, n_1, w_1, we obtain,

$$ln\ C_1/C_0 = ln\ (n_1/n_0) + \frac{w_0 - w_1}{RT} \tag{3}$$

Now $w_0 - w_1$, the difference in the amounts of work done by a molecule in escaping from the surface of the pure liquid and from the solution is equal to the difference between the corresponding latent heats of evaporation provided there is no heat effect in the passage of a molecule from the surface into the interior of the liquid. In this case $w_0 - w_1 = Q$, the heat of solution of pure liquid in the binary mixture and since $C_1/C_0 = \alpha$, and if the composition of the surface layer is the same as that of the bulk of the liquid, $n_1/n_0 = N$; therefore, under these conditions Equation 3 becomes $ln(\alpha/N) = Q/RT$, which is Cady's equation.

But if the whole of the heat effect does not occur in the escape of the molecule from the surface layer, if for example some portion is employed in the passage of molecules from the interior of the liquid to the surface owing to complex formation or solvation or some such effect, we should expect to find $ln\ \alpha/N < Q/RT$. The linear relation between the two quantities would be explained if the heat of solution is divided between the passage from the interior to the surface and the escape from the surface in definite proportions for each system.

Finally, it may be noted that Hildebrand[16] has shown for a number of systems that the deviation of a component from Raoult's law (expressed as $ln\ (\alpha/N)$) is also directly proportional to the difference between its partial molal volume in the solution and the molal volume of the pure liquid.

If the relation discussed in the present paper is a general one, it follows that the heat effect of solution of a component in a liquid mixture is directly proportional to the volume change which occurs.

Summary

The relation between the partial heats of solution in binary liquid mixtures and deviations from Raoult's law is discussed and it is shown that in those cases for which data exist there is a nearly exact proportionality between the deviations (expressed by $ln\ (\alpha/N)$) and the partial heats of solution. The statistical theory of binary mixtures is outlined and on certain assumptions Cady's equation is obtained. A possible explanation of the observed relation is given.

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[16] Hildebrand, THIS JOURNAL, **37**, 2459 (1915). Ref. 1 b, p. 63.