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THE CONSTITUTION OF CERTAIN LIQUID AMALGAMS.

BY JOEL H. HILDEBRAND.

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When two homogeneous liquid amalgams containing a metal less noble than mercury are connected by an electrolyte containing the ion of the dissolved metal, there exists a difference of potential between the amalgams usually calculated by the familiar formula

$$E = \frac{RT}{nF} \ln \frac{c_1}{c_2}, \qquad (1)$$

where E denotes the difference of potential, R the gas constant, T the absolute temperature, n the valence of the ion of the metal, F the Faraday equivalent, and c_1 and c_2 the concentrations (variously expressed) of the concentrated and dilute amalgams, respectively.[1] This equation has been subjected to exceptionally rigorous experimental verification in the Harvard[2] and Princeton[3] laboratories. The general result of these investigations has been to show that the equation holds more accurately the greater the dilution, but that an increasing deviation is found as the amalgams become more concentrated. With cadmium, indium and thallium amalgams the observed differences of potential are greater than are given by the above formula, while zinc, lead and tin amalgams show

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[1] For the history of this formula and a very full bibliography on this subject, cf. Richards and Forbes, *Pub. Carnegie Inst. Wash.*, 56; *Z. physik. Chem.*, 58, 683 (1907). Also, Richards, Wilson, and Garrod-Thomas, *Pub. Carnegie Inst. Wash.*, 118; *Z. physik. Chem.*, 72, 129, 165 (1909).

[2] *Loc. cit.*

[3] Hulett and DeLury, THIS JOURNAL, 30, 1812 (1908); Crenshaw, *J. phys. Chem.*, 14, 158 (1910).

differences of potential less than those indicated by the formula. Similar deviations had been earlier observed by Cady,[1] who proposed a modification of the formula by adding a term to include the heat of dilution, U, as follows:

$$E = \frac{RT}{nF} \ln \frac{c_1}{c_2} + \frac{U}{nF}. \qquad (2)$$

This formula was able to account for part, but not all, of the deviation from the simpler formula, and Richards and his co-workers have discussed, at some length, the possible reasons for the discrepancies and mentioned the need for a study of the osmotic side of the problem.

Several years earlier Haber[2] had published a paper calling attention to the relation between the e. m. f. of such a cell and the constitution of the amalgam, and showed how the simple formula would have to be modified in order to take this into consideration. However, he also made clear the uncertain character of such a modification on account of the fact that the gas laws had been assumed to hold for the osmotic pressure of the metal dissolved in the mercury. It therefore becomes very uncertain how much of the deviation from our simple formula is to be ascribed to the formation of compounds and how much to the inaccuracy of the gas laws themselves in concentrated solutions. He then showed that according to our present knowledge an exact formula can be given only in terms of vapor pressure, and gave the following formula by analogy with the equation of Dolezalek[3] for the lead accumulator:

$$E = \frac{RT}{nF} \left(w_2 \ln p_2 - w_1 \ln p_1 - \int_{w_1}^{w_2} \ln p\,dw + m \ln \frac{p_2}{p_1} \right).$$

In this equation w_1 and w_2 denote the number of mols of solvent mercury in a concentrated and dilute amalgam, respectively, p_1 and p_2 denote the corresponding vapor pressures of mercury over the amalgams, and m is the number of atoms of combined mercury forming the general compound MHg_m. Lack of data on the vapor pressure of amalgams prevented the application of this equation, and, apparently, the determination of the value of m.

The present writer, in a communication on "The Relation between the Potential of Liquid Amalgam Cells and the Constitution of the Amalgam,"[4] has shown that the term containing m in Haber's equation should be eliminated, and that the formula can be simplified to the following, which was derived directly by a process of isothermal distillation:

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[1] *J. phys. Chem.*, **2**, 551 (1898).

[2] *Z. physik. Chem.*, **41**, 399 (1902).

[3] *Z. Elektrochem.*, **4**, 349 (1899).

[4] *Orig. Com. 8th. Intern. Congr. Appl. Chem.*, **22**, 139; also *Trans. Am. Electrochem. Soc.*, **22**, 335 (1913).

$$nEF = RT\int_{N_1}^{N_2} Nd \ln p. \qquad (3)$$

In this formula N denotes the number of mols of mercury in the amalgam per mol of solute metal.

In order to integrate the right-hand member of this equation it is necessary either to determin experimentally the relation between N and p, or else to make some assumption regarding it. At the present stage of development of the theory of solutions the natural assumption to make is that the vapor pressure of the mercury is proportional to its mol-fraction in the amalgam. In the form of an equation this becomes

$$p = p_0X, \qquad (4)$$

where p_0 is the vapor pressure of pure mercury and X its mol-fraction in the amalgam. For an ideal solution

$$X = \frac{N}{N + 1}. \qquad (5)$$

For other solutions X depends also upon the solvation or association of the solute, and must be expressed accordingly. Thus where the solute forms a compound MHg_m the equation becomes

$$p = p_0 \frac{N - m}{N - m + 1}. \qquad (6)$$

The experimental determination of the relation between N and p has been made by the writer in the case of zinc amalgams.[1] It was shown that the vapor-pressure law could be brought into accord with experiment by assuming an association of zinc, varying according to the law of mass action. In applying the resulting relation between N and p to integrate the e. m. f., formula (3), however, a simplifying assumption was made which gave the integrated expression an approximate character only. The mathematical difficulties involved in an exact integration of the expression have now been overcome, and it is the purpose of this paper to show how this can be done, not only for zinc, but for certain other distinct types. The results allow some interesting conclusions to be drawn regarding the constitution of the amalgams whose potentials have thus far been measured with sufficient accuracy.

Zinc Amalgams.

In the paper just referred to it has been shown that the application of the vapor-pressure law indicated the existence of the following equilibrium in zinc amalgams:

$$2Zn = Zn_2.$$

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[1] "The Vapor Pressure of Zinc Amalgams," *Orig. Com. 8th Intern. Congr. Appl. Chem.*, **22**, 147; also *Trans. Am. Electrochem. Soc.*, **22**, 319 (1913). See this paper for discussion and references on the vapor-pressure law and on the constitution of amalgams.

If we take 1 mol of zinc in N mols of mercury, and represent the amount of Zn_2-mols formed by α, then the Zn-mols remaining would be $1 - 2\alpha$, and the total number of mols in the amalgam $N + 1 - \alpha$. Applying the law of mass action, using mol-fractions in place of concentrations, we have

$$K\left(\frac{1 - 2\alpha}{N + 1 - \alpha}\right)^2 = \frac{\alpha}{N + 1 - \alpha}. \qquad (7)$$

(In this expression K is the reciprocal of the constant in the previous paper, resulting in a slight simplification.) If this equation is solved for α we find that

$$\alpha = \frac{A + N - \sqrt{N^2 + 2AN + A}}{2A}, \qquad (8)$$

where we put

$$4K + 1 = A. \qquad (9)$$

Since the vapor-pressure law becomes, in this case,

$$p = p_0 \frac{N}{N + 1 - \alpha} \qquad (10)$$

we have, substituting the above value of α,

$$p = p_0 \frac{2AN}{2AN + A - N + \sqrt{N^2 + 2AN + A}}. \qquad (11)$$

If we use this to get $Nd \ln p$, a complicated expression results, the prospect of whose integration appeared rather discouraging at the time the former paper was published, so that an approximation was made by writing equation (7) simply as

$$K = \alpha N.$$

It has since been found, however, that equation (11) can be used directly to give an integrable form of $Nd \ln p$ if the following substitution is made:

$$x = N + \sqrt{N^2 + 2AN + A}.$$

The presentation here is simplified by making this substitution in (11) before getting $Nd \ln p$ in terms of N, which gives

$$p = p_0 \frac{x - A}{(x + 1)^2}.$$

From this we find that

$$Nd \ln p = \frac{dx}{x + 1},$$

and therefore,

$$nEF = RT\int_{N_1}^{N_2} Nd \ln p = RT\int_{x_1}^{x_2} \frac{dx}{x + 1} = RT \ln \frac{x_2 + 1}{x_1 + 1}.$$

On replacing N for x we get as the integrated equation,

$$nEF = RT \ln \frac{1 + N_2 + \sqrt{N_2^2 + 2AN_2 + A}}{1 + N_1 + \sqrt{N_1^2 + 2AN_1 + A}}. \qquad (12)$$

If we take for F 96540 coulombs, for R 8.316 joules, and convert logarithms to the base 10, the equation becomes:

$$E = 0.00019834 \frac{T}{n} \log \frac{1 + N_2 + \sqrt{N_2^2 + 2AN_2 + A}}{1 + N_1 + \sqrt{N_1^2 + 2AN_1 + A}}. \qquad (13)$$

We will apply this equation first to the measurements of Richards and Forbes.[1] Using their data for the series comprizing amalgams Nos. 1, 7, 2 and 20, we first calculate the number of mols of mercury per mol of zinc, N, in each.[2] The results are given in the third column of Table I. In the fourth column are given the measured differences of potential at 23.01° between each amalgam and the most dilute. In the fifth column are the corresponding values derived from formula (13) by substituting the valence of the zinc ions, $n = 2$, the absolute temperature corresponding to 23.01°, and letting $A = 11.6$. This value of A corresponds to $K = 2.65$ in equations (7) and (9). It will be seen that the observed and calculated values of E agree within the limit of experimental error.

It is interesting to compare these differences of potential with those that should be obtained if the zinc were not associated. In such a case, according to the vapor-pressure law,

$$p = p_0 \frac{N}{N + 1}, \text{ we find that } N d \ln p = \frac{dN}{N + 1}$$

and on integration and substitution of the ordinary values,

$$E = 0.00019834 \frac{T}{n} \log \frac{N_2 + 1}{N_1 + 1}. \qquad (14)$$

This same equation results if $K = 0$, and therefore $A = 1$ in equation (13). It is not given here for the first time, having been used by Richards, Wilson and Garrod-Thomas.

The potential differences calculated from this formula are given in the sixth column of the table. In the seventh column are given the differences between the values in the sixth column and those in the third, and which indicate the deviation of the observed values of e. m. f. from those for an ideal solution at the various values of N. Since the potentials of actual and ideal solutions are still somewhat different when $N = 711$, this difference must be added to the values in the sixth column to get the total deviation. The deviation at $N = 711$ is found by subtracting formula (13) from formula (14) letting $N_1 = 711$, and taking N_2 so large that A is negligible in comparison. This is calculated to be 0.09

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[1] *Loc. cit.*

[2] There is evidently a mistake in the figures in the original for the weight of mercury added in making amalgam No. 20. A private communication from Dr. Forbes states that it should be 19.617 gr.

millivolts, which is accordingly added to all the values in the seventh column to get those in the eighth. These last are plotted in Fig. 1 against log N. The curve represents the difference between the two formulas, (14) and (13), where A = 11.6, at varying values of log N_1 when N_2 is very large. It is evident that the deviations of the observed potentials from those for an ideal solution coincide very closely with the curve as calculated.

TABLE I.—ZINC. Richards and Forbes.

Amalgam No.	% Zn.	N.	E (millivolts) at 23.01°. Observed.	Calc. (13).	Ideal.	Deviations. from N=711.	Total.
1	0.893	36.270	35.15	36.17	37.58	—1.43	—1.52
7	0.435	74.836	27.85	27.82	28.53	—0.68	—0.77
2	0.150	217.09	14.91	14.88	15.07	—0.16	—0.25
20	0.046	711.2	0.00	0.00	0.00	0.00	(—0.09)

Turning now to the measurements of Crenshaw on the same amalgams, we find that there is an unfortunate lack of agreement with the work of Richards and Forbes. In Table II are given the results of Crenshaw's work, the potentials being all reckoned from the most dilute amalgam given. The ideal potentials and the deviations are also given as before, and the latter are plotted in Fig. 1.

TABLE II.—ZINC. Crenshaw.

$\frac{\text{Gr. Zn}}{\text{Gr. Hg}}$.	N.	E (millivolts) at 25°. Observed.	Ideal.	Deviations.
2.2/100	14.72	65.01	68.50	—3.49
2/100	16.34	64.12	67.24	—3.12
1.8/100	18.16	63.18	65.96	—2.78
1.4/100	23.35	60.75	62.88	—2.13
1/100	32.69	57.21	58.72	—1.51
$5/10^3$	65.37	49.38	50.02	—0.64
$2/10^3$	163.4	38.23	38.37	—0.14
$1/10^3$	326.9	29.53	29.52	+0.01
$1/10^4$	3269.0	0.00	0.00	0.00

Although these deviations are not very far from those corresponding to the measurements of Richards and Forbes and to the formula (13), the difference, according to Fig. 1, is nevertheless far greater than the maximum error claimed by the experimenters. Moreover, it is evident that no value can be given to A which will bring the measurements of Crenshaw into harmony with the present theory. If these represent the true potentials of zinc amalgams, then we must assume that the amalgams contain molecules more complex than Zn_2, for which case the formula would be much more complicated, and so has not yet been worked out. Against such an assumption are the following considerations: First, the measurements of the vapor pressure of zinc amalgams at 300° indicate the presence of Zn_2. At lower temperatures we should expect a different value for the equilibrium constant rather than a change in the nature of the equilibrium. Second, the work of Richards and Forbes was repeated by Richards and Garrod-Thomas[1] giving results in entire accord with those of the earlier investigation. Third, the break in the curve for Crenshaw's deviations at log N = 2.51 is hard to understand from any theoretical standpoint, and gives ground for suspicion of some experimental error. The writer is unable to detect any source of error in the procedure published from either laboratory, and will therefore rest with the statement of the above facts. It would be most desirable to have the work repeated by the method used by Crenshaw, in which a two-phase amalgam was used for comparison. It would be especially desirable, from the standpoint of this paper, to have the work done at higher temperatures and greater concentrations.

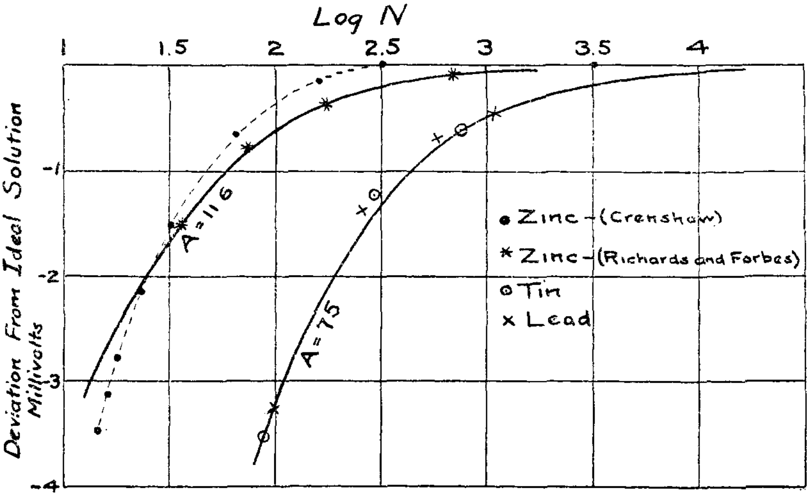

FIG. 1.

Temperature Coefficient of the Zinc Amalgam Cells.

By means of the present considerations it is possible to treat the temperature coefficient of these cells in connection with the heat of the reaction:

$$2Zn = Zn_2 + Q.$$

Richards and Garrod-Thomas have made careful measurements of the temperature coefficient of certain zinc amalgam cells, from which can be calculated the heats of dilution of the amalgams by means of the equation of Helmholtz,

$$U = nEF - nFT\frac{dE}{dT}. \qquad (15)$$

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[1] *Loc. cit.*

Now the heat of dilution should be due mainly to a certain portion of the heat Q of the above reaction. The value of Q can therefore be easily determined as follows: By using formula (8) it is possible to calculate the extent to which zinc is associated, 2α, for any value of N. Suppose that the fraction associated in the more concentrated amalgam is $2\alpha_1$, and in the other, $2\alpha_2$, then on dilution from N_1 to N_2 the heat of dilution U is a fractional part of Q as given by the relation

$$-U = (2\alpha_1 - 2\alpha_2)Q. \qquad (16)$$

(The minus sign is due to the fact that U is of opposit sign from Q.)

We will consider the amalgams in cups 1, 3 and 4 of the above experimenters. N is calculated from the per cent. zinc in each case, and from this 2α, using A = 11.6 as determined in the previous section. The results are seen in Table III:

TABLE III.

Cup.	% Zn.	N.	2α.
1	0.913	35.45	0.114
3	0.0998	327.0	0.0156
4	0.0302	1082.0	0.0048

TABLE IV.

Cups.	E at 29.96° (millivolts).	dE/dT.	U.	$2\alpha_1-2\alpha_2$.	Q.
1–3	27.036	0.09342	—246.8	0.098	2500
1–4	42.529	0.14463	—251.0	0.109	2300
3–4	15.502	0.05144	—16.4	0.0108	(1500)

In Table IV are given the values of e. m. f. and its temperature coefficient for pairs of these same amalgams. In the fourth column are the heats of dilution calculated by the Helmholtz equation; in the fifth, the fraction of the total heat of reaction producing the amount U; and in the last column the heat of reaction calculated by (16). The value of U calculated between cups 3 and 4 is a small difference between two large quantities and hence greatly subject to experimental error, so that the value of Q calculated from it deserves little weight. We will take for Q the mean between the first two values, 2400 joules, and write accordingly,

$$2Zn = Zn_2 + 2400 \text{ joules.}$$

This enables us to determin the temperature coefficient of the equilibrium constant K, and consequently that of A, and we are then able to give an expression for the temperature coefficient of the e. m. f. of the above pairs of amalgams.

Applying the well-known equation of van't Hoff to the temperature coefficient of an equilibrium constant, we write

$$\frac{d \ln K}{dT} = \frac{-Q}{RT^2}, \quad \text{or} \quad \frac{dK}{dT} = \frac{-KQ}{RT^2}. \qquad (17)$$

Since $4K = A - 1$,

$$\frac{dA}{dT} = \frac{-4KQ}{RT^2}. \tag{18}$$

If we differentiate with respect to temperature the formula for the e. m. f. of zinc amalgams, (12), we obtain the equation

$$\frac{dE}{dT} = \frac{R}{nF} \ln \frac{1 + N_2 + \sqrt{N_2^2 + 2AN_2 + A}}{1 + N_1 + \sqrt{N_1^2 + 2AN_1 + A}} + \frac{RT}{nF}\left[\frac{(N_2 + 0.5)/\sqrt{N_2^2 + 2AN_2 + A}}{1 + N_2 + \sqrt{N_2^2 + 2AN_2 + A}} - \frac{(N_1 + 0.5)/\sqrt{N_1^2 + 2AN_1 + A}}{1 + N_1 + \sqrt{N_1^2 + 2AN_1 + A}}\right]\frac{dA}{dT}.$$

The second term of the right-hand member of this equation is much smaller than the first, so that it may be simplified with sufficient approximation by putting $N + A$ for $\sqrt{N^2 + 2AN + A}$, and dropping the 1 and the 0.5. If we make also the usual substitutions and include the values of Q, A, K, and dA/dT by (18), we find, when $t = 30°$,

$$\frac{dE}{dT} = 0.0_4 9917 \log \frac{1 + N_2 + \sqrt{N_2^2 + 2AN_2 + A}}{1 + N_1 + \sqrt{N_1^2 + 2AN_1 + A}} + 0.00435\left[\frac{N_1}{(N_1 + 12)(2N_1 + 12)} - \frac{N_2}{(N_2 + 12)(2N_2 + 12)}\right]. \tag{19}$$

Using this formula to calculate the temperature coefficients given in Table IV, we find, as shown by Table V, that the calculated and observed results agree within the limit of experimental error. In the fourth column of Table V are given the same coefficients calculated from the equation

$$\frac{dE}{dT} = \frac{R}{nF} \ln \frac{c_1}{c_2}, \tag{20}$$

which was used by previous investigators and was gotten by combining the equations of Cady and Helmholtz, (2) and (15). It will be seen that this equation is much inferior to the one here derived, (19).

TABLE V.

	dE/dT (millivolts).		
Cups.	Calc. (19).	Observed.	Calc. (20).
1-3	0.0936	0.0934	0.0954
1-4	0.1448	0.1446	0.1469
3-4	0.0513	0.0514	0.0515

The significance of the lack of agreement shown by (20) is evident if it is gotten by direct differentiation of the ordinary formula, (1), which gives

$$\frac{dE}{dT} = \frac{R}{nF} \ln \frac{c_1}{c_2} + \frac{RT}{nF}\,\frac{c_2}{c_1}\cdot\frac{\partial(c_1/c_2)}{\partial T}.$$

From this it is seen that formula (20) will be correct in no case where the actual concentration is affected by the temperature, in other words, in no case where association or solvation exists depending on the dilution and accompanied by a heat effect.

To summarize the foregoing conclusions, we may say that there seems to be complete accord between experiment and theory. There are probably few solutions whose constitution we may assert with such confidence. We are prepared to state the reaction occurring within the amalgam, its equilibrium constant, and the heat it liberates, so that the effect of temperature on the reaction can be determined. It may be interesting to have added, as is done in Table VI, the degree of association at 23° calculated from equation (8), using A = 11.6 as indicated by the Harvard work.

TABLE VI.

N.	10.	100.	1000.
% zinc	3.16	0.33	0.33
% association	26.5	4.75	0.52

It may be asked, finally, how the degree of association calculated at 23° compares with that indicated by the vapor-pressure measurements at 300°. The equilibrium constant at 300° can be calculated from that at 23° by integrating the van't Hoff equation (17). In this instance we must assume that the heat of reaction Q is constant. This assumption makes the resulting calculation only an approximation where such a large temperature interval is involved. The integrated equation is then

$$\log \frac{K_1}{K_2} = \frac{Q}{19.15}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

If $K_1 = 2.65$ when $t_1 = 23°$, then the equation gives $K_2 = 1.66$ at 300°, using $Q = 2400j$. The value of K_2 derived from vapor-pressure measurements at 300° was 2.0. This agreement is quite all that could be expected in a calculation over such a wide temperature interval.

Lead Amalgams.

The e. m. f. measurements of Richards and Garrod-Thomas on lead amalgams indicate a deviation from an ideal solution of the same nature as that found with zinc amalgams, but much greater. The writer finds that the same formula as was used with zinc expresses the behavior of lead amalgams if the constant A is put equal to 75. The values so calculated are shown in Table VII, compared, as before, with the observed and ideal values. The total deviation of the observed potentials from those of an ideal solution are also given in the last column, and plotted against log N in Fig. 1. The deviation at N = 1100 is gotten by calculation, being the difference between formulas (13) and (14) when N_2 is very large. The values for N are not very accurate, as the original data do not admit of their calculation as accurately as was the case with zinc. In view of this circumstance the agreement of the observed with the calculated values, as shown both by the table and the curve, is very satisfactory.

TABLE VII.—LEAD AMALGAMS.

% Pb.	N.	E (millivolts) at 30°. Calc. (13).	Observed.	Ideal.	Total deviations.
1.02	100.5	28.25	28.25	31.08	—3.25
0.404	253.8	17.97	18.11	19.08	—1.39
0.180	570.4	8.23	8.27	8.55	—0.70
0.0932	1100.0	0.00	0.00	0.00	(—0.42)

The temperature coefficient can be treated in the same way as with zinc. The uncertainty in the values for N, however, and the apparent inferiority of these measurements to those with zinc, cause the results to be less satisfactory, and this paper need hardly be prolonged for their presentation.

The per cent. association of the lead in the amalgams can be calculated, as before, by means of formula (8). The results are shown in Table VIII for several values of N. The figure for N = 10 of course involves a considerable extrapolation.

TABLE VIII.

N.	10.	100.	1000.
% association	59	22	3.5
% lead	9.4	1.0	0.1
% tin	5.6	0.6	0.06

Tin Amalgams.

In the original publication from the Harvard laboratory it was shown that lead and tin amalgams are practically identical in their electrical behavior, the deviation from equation (1) being the same for both. This indicates that the differences of potential are to be calculated by the same formula. In Table IX, accordingly, are shown the potentials and deviations calculated exactly as those given in Table VIII for lead. The difference between the calculated and observed values is hardly more than that indicated by the experimental errors shown by the curve in the original. The deviations are represented in Fig. 1, and the per cent. association is shown in Table VIII along with those for lead.

TABLE IX.—TIN AMALGAMS.

Amalgam.	N.	E (millivolts). Calc. (13).	Observed.	Ideal.	Total deviations.
H 1	89.07	24.95	25.00	27.90	—3.51
H 2	293.7	11.64	11.82	12.44	—1.22
H 3	763.1	0.00	0.00	0.00	(—0.60)

Thallium Amalgams.

Thallium amalgams, contrary to those thus far considered, give potential differences greater than those calculated for an ideal solution. This is naturally attributed to the formation of compounds with the mercury. The formula for such a case has been derived in the preceding paper by the writer[1] by using equation (6) to integrate equation (3). The integration need not be repeated here. The resulting formula is

$$E = 0.00019834\,\frac{T}{n}\left[m \log \frac{N_2 - m}{N_1 - m} - (m - 1) \log \frac{N_2 - m + 1}{N_1 - m + 1}\right] \quad (21)$$

where m is the number of atoms of mercury in the compound MHg_m supposed to be formed with the dissolved metal M. In Fig. 2 are plotted deviations of this formula from that for ideal solutions (14) using for m the values 1, 2, 4 and 6. The observations of Richards and Wilson, given in Table X, are represented in this figure, and are seen to be very close to the curve corresponding to $TlHg_6$. There is an indication, more apparent if the e. m. f. is calculated between N = 193.3 and N = 54.25, that at greater concentrations $TlHg_6$ breaks down gradually into some simpler compound. This may be $TlHg_2$, which has been shown by Kurnakow[2] to exist in the solid state. This is confirmed by some unpub-

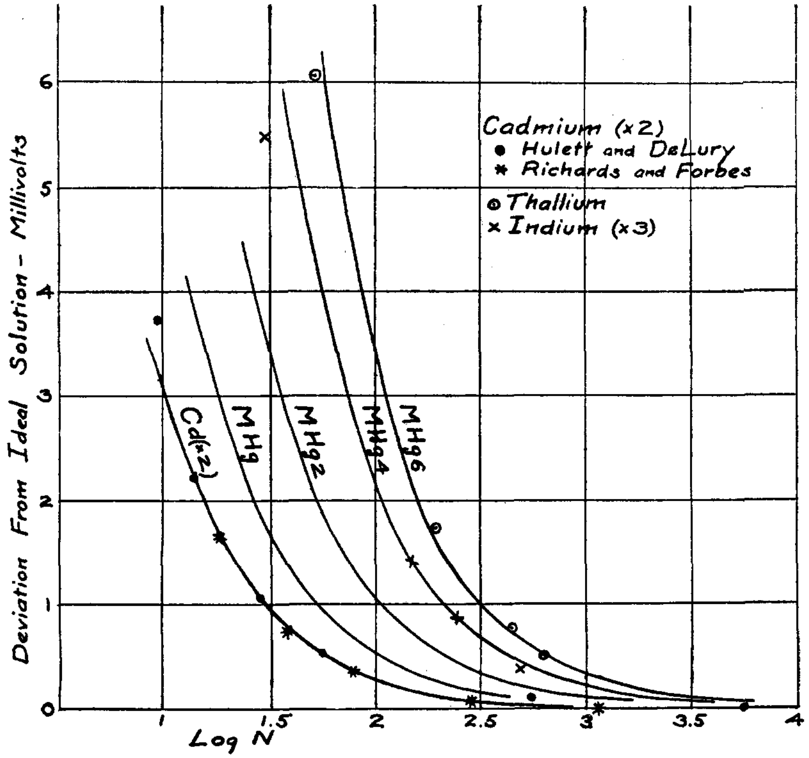

FIG 2

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[1] *Loc. cit.*

[2] *Z. anorg. Chem.*, 30, 86 (1902).

lished data on very concentrated amalgams very kindly communicated privately to the writer by Professor Richards. Further consideration of these amalgams may be postponed until these latest measurements in the Harvard laboratory have been published. It should be mentioned that the large heat of dilution calculated from the temperature coefficients by Richards and Wilson indicate an equilibrium between two solutes accompanied by a considerable heat of reaction.

TABLE X.—THALLIUM AMALGAMS.

% Tl.	N.	E (millivolts) at 30°. Calc. $TlHg_6$.	Observed.	Ideal.	Total deviations.
1.846	54.25	69.88	69.83	64.27	6 06
0.5249	193.3	32.48	32.70	31.43	1.77
0.2294	443.6	10.05	10.09	9.82	0.77
0.1575	646.6	0.00	0.00	0.00	(0.50)

Indium Amalgams.

The behavior of indium amalgams is similar to that of thalium amalgams, except that the higher compound, on applying formula (21), seems to be $InHg_4$, which breaks down into some simpler compound. Just what the latter is can be determined only by e. m. f. measurements with much more concentrated amalgams or by thermal analysis. For the present the results will merely be given as in Table XI, and the observed deviations from the ideal solution indicated in Fig. 2. The deviations are multiplied by three before plotting so as to make the trivalent metal indium compare with the univalent thallium.

TABLE XI.—INDIUM AMALGAMS.

Amalgam.	N.	E (millivolts) at 30°. Calc. $InHg_3$.	Calc. $InHg_4$.	Observed.	Ideal.	Deviations.
E1	29.22	25.99	26.58	26.30	24.59	1.83
E2	149.6	10.41	10.50	10.52	10.17	0.47
E3	238.9	6.22	6.27	6.29	6.11	0.29
E4	483.5	0.00	0.00	0.00	0.00	(0.12)

Cadmium Amalgams.

It is very gratifying to find that the measurements with cadmium amalgams by Hulett and DeLury[1] agree very closely with those of Richards and Forbes. On calculating the deviations of the actual from the ideal potentials, multiplying by two to make them compare with a univalent metal, and plotting in Fig. 2, it was found that they are much less than those indicating complete formation of CdHg. The natural assumption is that this compound is formed partially, to an extent depending on the relative amounts of the two metals. If this is true, we should expect the following equilibrium:

$$\begin{array}{ccccc} Cd & + & Hg & = & CdHg. \\ 1-\alpha & & N-\alpha & & \alpha \end{array}$$

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[1] THIS JOURNAL, 30, 1812 (1908).

Beneath each substance is written the amount present at equilibrium, starting with 1 mol of cadmium and N mols of mercury. Since the total number of mols present is then $N + 1 - \alpha$, we can write, applying the law of mass action as in the case of zinc,

$$\left(\frac{1 - \alpha}{N + 1 - \alpha}\right)\left(\frac{N - \alpha}{N + 1 - \alpha}\right) = K \frac{\alpha}{N + 1 - \alpha},$$

or,

$$(1 - \alpha)(N - \alpha) = K\alpha(N + 1 - \alpha)$$

from which we find that

$$2\alpha = N + 1 - \sqrt{(N + 1)^2 - 4BN} \tag{22}$$

where

$$B = \frac{1}{K + 1}.$$

The vapor-pressure law is to be written in this case

$$p = p_0 \frac{N - \alpha}{N + 1 - \alpha}.$$

Substituting the value of α given by (22),

$$p = p_0 \frac{N - 1 + \sqrt{(N + 1)^2 - 4BN}}{N + 1 + \sqrt{(N + 1)^2 - 4BN}}.$$

Before proceeding further we will substitute x for N by means of the equation

$$\sqrt{(N + 1)^2 - 4BN} = x - N,$$

which gives

$$p = p_0 \frac{x - 1}{x + 1}.$$

Using this to integrate formula (3), we find that

$$nEF = RT\int_{N_1}^{N_2} N d \ln p = RT\int_{x_1}^{x_2} \frac{dx}{1 + x - 2B} = RT \ln \frac{1 + x_2 - 2B}{1 + x_1 - 2B},$$

and substituting N for x

$$nEF = RT \ln \frac{N_2 + 1 - 2B + \sqrt{(N_2 + 1)^2 - 4BN_2}}{N_1 + 1 - 2B + \sqrt{(N_1 + 1)^2 - 4BN_1}}. \tag{23}$$

It was found that this formula expresses the behavior of cadmium amalgams very closely when $B = 2/3$, in which case, making also the usual substitutions, the formula becomes,

$$E = 0.00019834 \frac{T}{n} \log \frac{N_2 - {}^1/_3 + \sqrt{N_2^2 - {}^2/_3 N_2 + 1}}{N_1 - {}^1/_3 + \sqrt{N_1^2 - {}^2/_3 N_1 + 1}}. \tag{24}$$

The curve for cadmium in Fig. 2 represents the difference between this formula and the one for an ideal solution, the differences being multiplied by two to reduce to a univalent basis. In Table XII the measurements of Richards and Forbes are compared with this equation, and in Table XIII those of Hulett and DeLury. The agreement is excellent in both cases.

TABLE XII.—CADMIUM AMALGAMS.

Richards and Forbes.

		E (millivolts) 23°.			
Amalgam.	N.	Calc. (24).	Observed.	Ideal.	Deviations.
1	18.47	52.58	52.51	51.74	0.77
5	38.34	43.16	43.10	42.77	0.33
2	76.88	34.24	34.23	34.06	0.17
3	286.7	17.42	17.40	17.40	0.04
8	1124.0	0.00	0.00	0.00	0.00

TABLE XIII.—CADMIUM AMALGAMS.

Hulett and DeLury.

		E (millivolts) at 25°.			
$\frac{\text{Gr. Zn}}{\text{Gr. Hg}}$.	N	Calc. (24).	Observed.	Ideal.	Deviations.
5.902/100	9.522	111.81	112.10	110.23	1.87
4/100	14.05	106.75	106.73	105.61	1.12
2/100	28.10	97.71	97.66	97.13	0.53
1/100	56.20	88.73	88.73	88.46	0.27
$1/10^3$	562.0	59.12	59.16	59.10	0.06
$1/10^4$	5620.0	29.56	29.56	29.56	0.00
$1/10^5$	56200.0	0.00	0.00	0.00	0.00

The amount of the compound CdHg present in these amalgams can be calculated by the aid of formula (22), the results being given in Table XIV. It will be noticed that the equilibrium is of such nature that it is not much affected by the further dilution of a dilute amalgam. This fact accounts for the small heat of dilution calculated by Richards and Forbes from the temperature coefficient of e. m. f., for even if the heat of formation of CdHg is large only a small part of it is absorbed in further diluting a dilute amalgam. The calculation of this heat of formation as was done in the case of zinc amalgams will consequently require measurements with very concentrated amalgams where α varies more rapidly:

TABLE XIV.

N.	1.	10.	100.
% Cd in amalgam........................	36.0	5.32	0.56
% of Cd as CdHg........................	42.3	64.5	66.5

Discussion.

There are several points regarding the validity of the deductions made in this paper which should be discussed in conclusion. It may be thought that any formula capable of such variation as the fundamental one here employed is too empirical to be of final value, and that the conclusions reached are always involved in the premises. It is important, therefore, to see just what hypotheses are invoked, and at what points.

First of all, the initial formula, (3), was derived by equating the electrical work done in the transfer of one mol of solute from one amalgam to another to the exactly equivalent work of the same transfer by isothermal distillation of the solvent. The two processes are both reversible and therefore maximum and so involve the same change in total energy, which therefore should not appear in the equation.[1] The only assumption beyond the ordinary ones of thermodynamics used in the derivation of our equation is that the vapor of the solvent obeys the gas laws, N being defined as the number of mols of *vapor* which, when condensed, dissolve one mol of solute.

If the vapor does not obey the gas laws with sufficient accuracy, the formula still holds rigidly if p represents the ideal pressure, *i. e.*, the pressure that would be exerted if the vapor did obey the gas laws. This may be well expressed by using the function proposed by G. N. Lewis,[2] "fugacity," ψ. This is connected with the "activity," ξ, similar to what is frequently called active mass, by the relation

$$\psi = \xi RT.$$

By employing these terms we may write equation (3) either

$$n\mathrm{EF} = \mathrm{RT}\int_{\mathrm{N}_1}^{\mathrm{N}_2} \mathrm{N}d \ln \psi, \qquad \text{or} \qquad n\mathrm{EF} = \mathrm{RT}\int_{\mathrm{N}_1}^{\mathrm{N}_2} \mathrm{N}d \ln \xi.$$

There is hardly room for questioning this relation in either form, and where the activity can be independently measured, as was done fairly closely in the case of zinc amalgams, we should find complete agreement. Although the vapor-pressure law was assumed in expressing the vapor pressure of zinc amalgams, the measurements are independent of the law and might have been expressed by some more empirical equation. The course of the curve for the potentials of these amalgams can therefore hardly be much different from that represented in Fig. 1 unless the vapor pressures are in error.

In the case of the other amalgams we have introduced an additional assumption, which cannot be regarded as rigid, but which will be subjected to a rigid and much needed study by this means of investigation.

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[1] For the same reason it is hard to see in the equation of Cady anything more than a provisional expression. If the heat of dilution is not zero it is still involved in the electrical work and so appears on both sides of the equation. The fault with the simple concentration formula (1) lies, not in the lack of a heat term but in the fact that RT ln c_1/c_2 is not an expression of the osmotic work of expanding the solute. The true expression must result from the correction of this term and not in the addition of another. It should be mentioned that Professor Cady was evidently deterred from following the present line of reasoning only through lack of the correct law for vapor pressure.

[2] *Proc. Am. Acad.*, **43**, 259 (1907); *Z. physik. Chem.*, 61, 129 (1908).

This assumption is that the activity, or vapor pressure, is proportional to the mol fraction, X, whence we write

$$nEF = RT\int_{N_1}^{N_2} N d \ln X.$$

It is quite probable that this equation is not altogether rigid, although we know nothing at present of the nature of the modifying factors, something which it is of the utmost importance to learn if we are to extend our knowledge of solutions. It may be pointed out that this equation may be applied to alloys in general, where the vapor pressure cannot be conveniently measured; further, that with our extended knowledge of the constitution of solid alloys as a necessary check, it is thus possible to study this important problem in a very searching way.

It may have been noticed that we have considered the molecule of mercury, in all the above cases, to be the same both in the liquid and the vapor state. Some justification of this should be presented. Measurements of the surface tension of mercury by Siedentopf[1] gave a temperature coefficient of molecular surface energy much less than the ordinarily accepted value 2.12. This has been taken to indicate a high degree of association. The lack of an adequate theory for this relation, however, should cause us to be cautious in accepting its results on a liquid having such different properties from those used in deriving the coefficient 2.12.

Trouton's Rule is another relation largely used to distinguish normal and associated liquids. This may best be used in the modified form proposed by Nernst:[2]

$$\frac{\lambda}{T_b} = 9.5 \log T_b - 0.0007\, T_b, \tag{25}$$

where λ denotes the molecular heat of vaporization, and T_b the absolute boiling point. Mercury boils at 357°, so that the right-hand member of the equation becomes 22.2. The heat of vaporization has been determined by Kurbatoff,[3] who gives the value 67.8 cals. at the boiling point. This corresponds to 21.5 for λ/T.

Since associated liquids give values for this quotient greater than those calculated by equation (25), the evidence thus adduced is decidedly against association.[4]

A further evidence that mercury is not associated in the liquid state is the success in accounting for the vapor pressure of zinc amalgams when the zinc is assumed to be associated but the mercury unassociated.[5]

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[1] *Wied. Ann.*, **61**, 235 (1897).

[2] *Theoret. Chem.*, **5**, Aufl. 329.

[3] *Z. physik. Chem.*, **43**, 104 (1903).

[4] See also Bingham, THIS JOURNAL, **28**, 723 (1906).

[5] Cf. Dolezalek, *Z. physik. chem.*, **64**, 727 (1908); **71**, 191 (1910).

If a metal can be found whose amalgam obeys the ideal vapor pressure law, (4) and (5), this evidence will be still more conclusive. Such a case is now being sought in this laboratory.

We feel justified, therefore, in considering mercury, at least provisionally, as unassociated in the liquid state.

The possible objection mentioned at the beginning of this discussion that the mode of treatment here used can be twisted into any shape desired to suit the facts, is not peculiar to this case. It applies equally well to all colligative properties. If the rule of Avogadro does not hold in any particular case we do not hesitate to postulate dissociation or association and then proceed to calculate its extent by means of the deviation from our law. Such a law must therefore always have a hypothetical nature, requiring other hypotheses when deviations arise. The only limitation required is that the results must be consistent with those derived from other methods.

Summary.

The formula given in a previous publication for the electromotive force of liquid amalgam concentration-cells, is here integrated exactly by the aid of the vapor-pressure law and applied to those amalgams which have thus far been investigated with sufficient accuracy with the following results:

1. The results of e. m. f. and vapor-pressure measurements with zinc amalgams are shown to be in very good agreement. In the light of the vapor-pressure law this is shown to indicate that in these amalgams the zinc exists uncombined with the mercury but associated according to the equation:

$$2Zn = Zn_2 + 2400 \text{ joules.}$$

The equilibrium constant of this reaction, and accordingly the degree of association at different dilutions, is given and shown to be in excellent agreement with the measurements of e. m. f. and its temperature coefficient.

2. With lead and tin amalgams the same formula relating e. m. f. with constitution as was deduced for zinc is shown to apply, but with a different constant, corresponding to a much greater degree of association.

3. The measurements on thallium amalgams are shown to correspond to the formula derived for the cases where combination exists between the solute and the mercury. The compound indicated in this case is $TlHg_6$, which gives evidence of breaking up into some simpler compound, probably $TlHg_2$ in the more concentrated amalgams.

4. Indium amalgams, on applying the same formula, seem to contain $InHg_4$ breaking down into some simpler compound in the more concentrated amalgams.

5. Cadmium amalgams seem to contain both free Cd and the compound

CdHg, in proportions depending on the law of mass action. The e. m. f. formula is derived from this case and shown to give the observed values of e. m. f. very closely. The per cent. of the cadmium as CdHg is calculated. In the most dilute amalgams $^2/_3$ of the cadmium is combined to form CdHg.

The validity of the fundamental formula is discussed and its value is pointed out in determining the constitution of metallic solutions and as a means of investigating the present unknown factors influencing the vapor pressure of solutions.

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THE CALCULATION OF EQUIVALENT CONDUCTANCE AT INFINIT DILUTION.

BY STUART J. BATES.

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1. Introduction.

For the full interpretation of the results of any investigation upon the properties of solutions of electrolytes, it is necessary to know the concentrations, both of the ions and of the undissociated molecules with a considerable degree of accuracy. The calculation of these concentrations is based upon the degree of ionization, γ. This is most satisfactorily given by the relation,

$$\gamma = \frac{\Lambda}{\Lambda_0} f\left(\frac{\eta}{\eta_0}\right),$$

where Λ is the equivalent conductance of the solution in question, Λ_0 the equivalent conductance of an infinitly dilute solution of the electrolyte and $f(\eta/\eta_0)$ is some function of the relative viscosity of the solution which in sufficiently dilute solution may be taken as unity.

Evidently if the concentrations of the various constituents are to be accurately known, the value of Λ_0 must be determined with considerable precision. Thus an error of but 0.1% in the value of this constant for potassium chloride at 18° causes an error of over 1.7 per cent. in the value calculated for the concentration of the unionized molecules at 0.01 normal, and an error of over 4.7% at 0.001 normal. Hence it is of importance to examin various methods of calculating Λ_0 values, and to discuss, with the aid of the available experimental data, the most probable values for these constants.