drolyzed by sodium hydroxide, the alcohol portion ether extracted and a part of it treated with α-naphthyl isocyanate. The allyl α-naphthylcarbamate[3] thus obtained, after two recrystallizations from ligroin, melted at 108°.

Pyrazole.—A vinyldiazomethane solution (0.53 g. in 100 cc. of ether) was set aside for two days, then evaporated. The crystalline residue of pyrazole weighed 0.72 g. This indicates that an appreciable isomerization of the vinyldiazomethane occurs during synthesis in the distillation process. After being twice recrystallized from ether, it melted at 68°. It was identified as pyrazole by converting 0.1 g. of it to pyrazole picrate, m. p. 160°.

Summary

The synthesis and some of the properties of allylnitrosourethan and vinyldiazomethane are discussed.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 21, 1935

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(3) Neuberg and Kansky, *Biochem. Z.*, **20**, 446 (1909), reported m. p. of 109°.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

The Constitution of Liquid Zinc Amalgams

BY HERMAN A. LIEBHAFSKY

Cells in which the electrodes are zinc amalgams of different concentrations, and the electrolyte is an aqueous solution of a zinc salt, have been investigated frequently during the past fifty years.[1] In three of these investigations,[1,2,3] exceptional care has been employed and the accuracy consequently attained has been so great that the problem of determining the electromotive forces of such cells near room temperature appears to be closed, with these two experimental results definitely established. First, dilute zinc amalgams, even in the absence of oxygen, tend increasingly to lose zinc as they become more dilute,[2a] so that the resulting uncertainties in composition constitute the chief stumbling blocks in obtaining the electromotive forces of zinc amalgam cells to within, say, 0.001 millivolt. And, second, these electromotive forces are actually smaller than the ideal values corresponding to the Nernst equation, so that[4]

$$E_{\mathrm{act}} + \Delta E = E_{\mathrm{id}} = 0.09922T\log[\Sigma(\mathrm{Zn})_1/\Sigma(\mathrm{Zn})_2] \quad (1)$$

ΔE, the departure from ideality, is positive and decreases with the concentration of the more concentrated amalgam in the cell. Richards and Forbes[1] pointed out that this departure from ideality qualitatively indicated a partial polymerization of the zinc. Hildebrand[5] contributed greatly to the problem from the experimental side[5b] when he proved that the vapor pressures of zinc amalgams at 300° exhibit deviations from ideality corresponding to ΔE; and from the theoretical side when he showed, in accord with the ideas of Dolezalek,[6] that both types of deviations could, within certain limits, be *quantitatively* explained on the assumption that

$$\mathrm{Zn}_2 \overset{K_2}{\rightleftharpoons} 2\mathrm{Zn};\ K_2 = (\mathrm{Zn})^2/(\mathrm{Zn}_2) \quad (2)$$

was the only equilibrium existing in these amalgams. More recently the *activities* of zinc amalgams have been calculated from the electromotive force data[2b,3] and the interpretation of ΔE in terms of molecular species (a *concentration* treatment) has lost ground—a state of affairs easy to comprehend if, as Crenshaw[2b] states, the best experimental results for these amalgams agree better with each other than they do with Hildebrand's equation

$$E = 0.19834\,\frac{T}{n}\log\frac{1 + N_2 + \sqrt{N_2^2 + 2AN_2 + A}}{1 + N_1 + \sqrt{N_1^2 + 2AN_1 + A}} \quad (4)$$

where $n = 2$, the N's are the number of moles of mercury for one mole of zinc in amalgams 1 and 2, and $A = 4/(K_2^N + 1)$(see Footnote 4).

It is our purpose here to show that the positive values of ΔE for the zinc amalgams can be quantitatively accounted for without recourse to an activity treatment if we assume the equilibrium

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(1) Richards and Forbes, *Z. physik. Chem.*, **58**, 683 (1907).

(2) Crenshaw, (a) *J. Phys. Chem.*, **14**, 158 (1910); (b) *ibid.*, **34**, 863 (1930).

(3) Pearce and Eversole, *ibid.*, **32**, 209 (1928). For a complete historical summary and additional references, see Ref. 1.

(4) The summation sign, Σ, prefixed to a concentration term indicates that all the zinc in an amalgam is meant; thus, $\Sigma(\mathrm{Zn}) = (\mathrm{Zn}) + (\mathrm{Zn}_2) + (\mathrm{Zn}_3) + \ldots$. Four concentration units have been employed in the investigations referred to above: *viz.*, (1) g. Zn/100 g. Hg, here denoted (as it has just been) by ( ); (2) g. Zn/100 g. amalgam; (3) the units of Richards and Forbes, which we shall designate by $(\mathrm{Zn})^v$—namely, g. Zn/100 g. amalgam for the most concentrated amalgam only; for any other amalgam, this unit with the density change compensated which occurs when the amalgam is prepared by dilution from the most concentrated; (4) the mole fraction of zinc, equal to $1/(1 + N)$, where N is the number of moles of mercury for one mole of zinc; equilibrium constants expressed in this unit will be distinguished by a superscript; thus K_2^N. Electromotive forces will usually be expressed in *millivolts*.

(5) Hildebrand, (a) THIS JOURNAL, **35**, 501 (1913); (b) *Trans. Am. Electrochem. Soc.*, **22**, 335 (1913).

(6) Dolezalek, *Z. physik. Chem.*, (a) **64**, 727 (1908); (b) **71**, 191 (1910).

$$\mathrm{Zn_3} \underset{}{\overset{K_3}{\rightleftharpoons}} 3\mathrm{Zn};\ K_3 = (\mathrm{Zn})^3/(\mathrm{Zn_3}) \qquad (3)$$

to exist in addition to Reaction 2. This means in effect that we assume solutions of Zn, Zn_2, and Zn_3 in mercury at room temperature to be ideal over the entire range of composition.

The Experimental Data

Before proceeding with our interpretation of the experimental data, however, we shall have to re-examine these carefully for the following two reasons. First, all the finally accepted data of Richards and Forbes have never yet been compared with the other accurate experimental results; and, second, although several comparisons have been made, the results thereof are by no means in agreement.[7]

Richards and Forbes measured many combinations of cells at a number of temperatures in the neighborhood of 23° and thus proved beyond doubt that all their final results are concordant; but they did not, as was done in the subsequent investigations, actually measure the electromotive force of every other amalgam against the most concentrated. They did conveniently summarize all their final results, however, when they gave for each value of $(\mathrm{Zn})^{\nu}$ the deviation from ideality (analogous to ΔE, but for which we shall retain their symbols $D\pi$) that they would have obtained had they measured each of the other amalgams against No. 3, the most concentrated. Now, $D\pi$ will not be significantly affected by small changes either in the temperatures of the cells or in the concentrations of the amalgams, and the calculations of E_{act} and ΔE for the data of Richards were based on this fact.[8]

The most serious inaccuracies in these electromotive force investigations are encountered with dilute amalgams since these exhibit the greatest tendency to lose zinc. Crenshaw, and Pearce and Eversole measured all their other amalgams at 25° against the saturated amalgam, for which $\Sigma(\mathrm{Zn}) = 2.2200$, as a common reference electrode. We are therefore doubly justified in adopting a method of comparison which places the greatest weight, not upon an arbitrarily chosen dilute amalgam, but upon the most concentrated one in each series. To do this, we modify the procedure of Richards and Forbes slightly by plotting ΔE(Eq. 1) against log $[2.2200/\Sigma(\mathrm{Zn})]$, as in Fig. 1. Their data are for 23.09° (296.2°K.), and have been brought to the same scale as the others (which are for 25°) by adding 2.600 to the ordinate and log 2.2200/0.9173 to the abscissa; this procedure arbitrarily places the point for their No. 1 amalgam on the curve; but it does not similarly constrain the results for their other amalgams, so that the points for these will not agree with the curve unless the corresponding measurements are also in agreement.

An examination of Fig. 1, in which the circles have diameters corresponding to only 0.05 millivolt, immediately reveals that the agreement among all three sets of results is excellent at the higher, and good at the lower, concentrations. The downward deviations for the two most dilute amalgams (Crenshaw's) are undoubtedly caused by loss of zinc,[9] and thus do not indicate a real departure from the horizontal line which ΔE reaches in dilute solution; most of the downward deviations for the other points probably also have their origin in a loss of zinc, so that the actual values of $\Sigma(\mathrm{Zn})$ are less than those employed in

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(7) Hildebrand, and Pearce and Eversole have concluded that Crenshaw's measurements, made over the largest possible concentration range, do not agree with those made by Richards and Forbes over the smaller range $(\mathrm{Zn}) = 0.9$ to 0.05; such disagreement does exist if the most dilute amalgam considered in each set is taken as reference electrode; as Crenshaw[2b] has pointed out, a comparison on this basis is not trustworthy if (as is likely to be the case) the result for either dilute amalgam is in error.

Pearce and Eversole consider that their recent measurements confirm those of Richards and Forbes, but disagree with those of Crenshaw.

Crenshaw[2b] has recently been able to bring all three sets of results into agreement by the following procedure: $[-E/0.00009922T - \log 1/(N + 1)]$ is calculated for each value of the mole fraction of zinc in each set of data. To the values of this activity function thus obtained from the data of Pearce and Eversole, 2.0085 is added; a correction of 2.6775 is similarly applied to the values derived from the data of Richards and Forbes. The corrected values corresponding to all three sets of results are then plotted against $1/(N + 1)$, the mole fraction of zinc; at the higher mole fractions, a straight line is obtained which, by a somewhat uncertain extrapolation, is extended to infinite dilution. This method of comparing the results necessarily lacks directness and simplicity; although it is perhaps preferable to employing an uncertain dilute reference electrode, it seems definitely less convincing than the straightforward method employed in the text (*cf.* Fig. 1).

(8) π_{id}, the ideal electromotive force for the cells of Richards and Forbes, and E_{id} differ because they involve different concentration units, and slightly different values for the fundamental constants.

E_{act} and ΔE at 23.09° for the *n*th amalgam of Richards and Forbes were calculated as follows. Since

$$\pi_{\mathrm{id}} = 29.361 \log [\Sigma(\mathrm{Zn})_3^{\nu}/\Sigma(\mathrm{Zn})_n^{\nu}]$$

and the logarithms of the concentration quotients for all their amalgams are given by these authors, π_{id} was easily obtained. Also,

$$\pi_{\mathrm{id}} - D\pi = \pi_{\mathrm{act}} = E_{\mathrm{act}} = E_{\mathrm{id}} - \Delta E$$

so that E_{act} and ΔE are readily calculable by use of the $D\pi$ values, which are also listed in Reference 1.

(9) Crenshaw's detailed experimental results show how rapidly his dilute amalgams were losing zinc; while the electromotive forces of the more concentrated amalgams remained unchanged for weeks, a cell containing a dilute amalgam and the two-phase reference amalgam usually maintained a constant electromotive force for a matter of minutes only; after that the electromotive force increased, indicating loss of zinc from the dilute amalgam.

calculating ΔE. Figure 1 demonstrates convincingly and for the first time that all the final results of the three accurate investigations are in good agreement. Crenshaw[2b] has already reached a similar conclusion, but in a less straightforward manner, by extrapolating an activity function to infinite dilution.[7] Hildebrand has stated[5a] (p. 506) that his equation will not fit Crenshaw's results; since these agree with the others, we must conclude that assuming the existence of Reaction 2 does not suffice to explain the deviations of the electromotive measurements from ideality if the zinc amalgams are in fact ideal solutions. Since Fig. 1 shows them to be ideal solutions within the relatively large concentration range where $\Delta E = 0$ (the range, that is, within which the electromotive forces—losses of zinc neglected—conform to the limiting horizontal line), we assume provisionally that they remain ideal over the entire range of composition; and that the equilibria, Reactions 2 and 3, are wholly responsible for the apparent deviations from ideality encountered at the higher concentrations.

Interpretation of the Experimental Data

Our polymerization hypothesis, which assumes the simultaneous existence of Zn_2 and Zn_3 in rapid equilibrium with monatomic zinc will receive quantitative support if we can show that reasonably constant values of K_2 and K_3 can be calculated from the experimental data. The complex Eq. 4 obviously cannot furnish the point of departure for a simple method of performing these calculations. A simple method, employing Crenshaw's concentration units, has been devised, however, and will now be outlined.

If the zinc amalgams are ideal solutions, Eq. 1 may be written

$$E_{\text{id}} = E_{\text{act}} = 0.09922T \log [(\text{Zn})_1/(\text{Zn})_2] \qquad (5)$$

the concentration of total zinc, $\Sigma(\text{Zn})$, in Eq. 1 being replaced by the concentration of monatomic zinc. Figure 1 shows that $(\text{Zn}) = \Sigma(\text{Zn})$ for the more dilute amalgams; if any such dilute amalgam is chosen as common reference electrode, the evaluation of (Zn) for each of the more concentrated amalgams presents no difficulty. These evaluations were accordingly carried out for each set of measurements, and the corresponding values for the "equilibrium quotient," K'', defined by

$$(\text{Zn})^2/[\Sigma(\text{Zn}) - (\text{Zn})] = K'' \qquad (6)$$

were calculated. K'' would obviously be identical with K_2, the equilibrium constant of Reaction 2, if only this reaction were of importance; under these conditions it should therefore be reasonably constant. Instead, these K'' values showed a pronounced trend in the direction pointing to the existence of a higher polymer, say Zn_3.

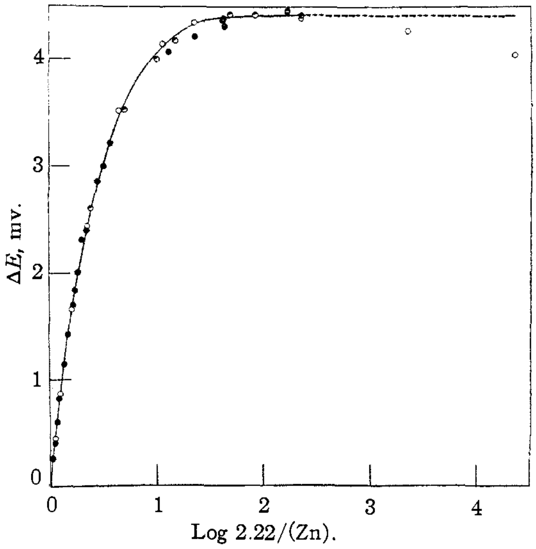

Fig. 1.—Deviations of the electromotive force for zinc amalgams near room temperature. The reference amalgam, for which $\Delta E = 0$, contains 2.220 g. Zn/100 g. Hg. ○, Crenshaw; ●, Pearce and Eversole; ◐, Richards and Forbes.

If Zn_2 and Zn_3 are the only polymers co-existing, then $\Sigma(\text{Zn}) = (\text{Zn}) + (\text{Zn}_2) + (\text{Zn}_3)$, and therefore by Eq. 6

$$K'' = (\text{Zn})^2/[(\text{Zn}_2) + (\text{Zn}_3)] = (\text{Zn})^2/[(\text{Zn})^2/K_2 + (\text{Zn})^3/K_3] \qquad (7)$$

the expression on the right being obtained by introducing the equilibrium constants of Reactions 2 and 3. The K'' values for any pair of amalgams, a and b, fix a pair of equilibrium constant values (one for K_2 and one for K_3) because

$$(1/K'')_a = 1/K_2 + (\text{Zn})_a/K_3 \text{ and } (1/K'')_b = 1/K_2 + (\text{Zn})_b/K_3 \qquad (8)$$

$$\text{whence, } K_3 = \Delta(\text{Zn})/[\Delta(1/K'')] \qquad (9)$$

Calculations of K_3 were carried out by reckoning both increments for each of the more dilute amalgams from the most concentrated amalgam in the series; this procedure corresponds to the "long interval" method of evaluating specific rates and also to the experimental method of measuring each of the more dilute amalgams against the most concentrated. Since Fig. 1 shows the data from the three sets of accurate measurements to

TABLE I

K_2 AND K_3 FROM THE RESULTS OF PEARCE AND EVERSOLE AT 25°

No.	1	2	3	4	5	6	7
Σ(Zn)	2.2200	2.0874	1.9968	1.9037	1.8136	1.6353	1.4818
E_{act}	65.160	64.630	64.204	63.789	63.391	62.377	61.393
(Zn)	1.5733	1.5097	1.4604	1.4140	1.3709	1.2668	1.1734
K''	3.827	3.945	3.976	4.084	4.245	4.355	4.464
K_3	....	8.16	11.53	9.72	7.88	9.68	10.72
Σ(Zn) (calcd.)	2.2200[c]	2.0913	1.9945	1.9057	1.8253	1.6388	1.4803

No.	8	9	10	11	12	13
Σ(Zn)	1.3556	1.3052	1.2009	1.1105	1.0096	0.7912
E_{act}	60.528	60.180	59.280	58.467	57.448	54.768
(Zn)	1.0970	1.0676	0.9954	0.9344	0.8631	0.7006
K''	4.653	4.797	4.822	4.958	5.085	5.414
K_3	10.27	9.58	10.72	10.72	11.00	11.39
Σ(Zn) (calcd.)	1.3563	1.3100	1.1992	1.1088	1.0068	0.7877

No.	14	15	16	17	18	19
Σ(Zn)	0.6978	0.6037	0.17633	0.098837	0.051742	0.009858
E_{act}	53.392	51.656	36.700	29.421	21.195	Ref. elec.
(Zn)	0.6294	0.5498	0.17163	0.097383	0.051329	(0.009858)[a]
K''	5.790	5.618	6.267	6.522	6.379	....
K_3	10.65	12.29	13.79[b]	13.66[b]	14.56[b]	....
Σ(Zn) (calcd.)	0.6970	0.5990	0.17535	0.09851	0.05163	0.009869

Final values: $K_2 = 9.09$; $K_3 = 10.4$ (the arithmetic mean of the first fourteen values is 10.3).

[a] Assumed value. [b] Value omitted in taking average. [c] Value determining finally selected K_2.

be in good agreement, it follows that our hypothesis cannot conflict with any of these data if it agrees well with the data from the set of measurements best adapted to testing it, namely, those of Pearce and Eversole. Accordingly, the results of the other calculations will not be given; those corresponding to the data of Pearce and Eversole are summarized in Table I.

The K'' values in Table I clearly show a trend so marked and so consistent that it can scarcely be attributed to experimental errors; this trend, which indicates qualitatively the presence of a polymer higher than Zn_2, might have been predicted from the failure of Eq. 4 in conforming to Crenshaw's results.[10] There is no *trend* in the K_3 values, and the following analysis will show that their constancy is sufficiently good to establish our polymerization hypothesis as highly plausible. We observe first that, in accord with Eqs. 8, a K_3 result higher than the average means that the K_2 value paired with it will be correspondingly lower; the deviations from constancy for these two quantities are thus simply related. Next we notice that slight uncertainties in composition, which appear to be the most serious sources of error in these investigations, will have the greatest effect on K'' (and hence on K_2 and K_3) at the highest concentrations, where the increments in Eq. 9 are very small, and at the lowest, where the differences Σ(Zn)–(Zn) are not much larger than the uncertainties themselves. (To illustrate: if (Zn) for Nos. 2, 10 and 18 were assumed to be only 0.1% higher than in Table I, K_3 would be changed, respectively, to 6.9, 10.4 and 12.3.) The most convincing way to test our polymerization hypothesis is by using the finally selected K_2 and K_3 values to calculate Σ(Zn) for comparison with the amount of zinc used in making each amalgam; these calculations have been performed, with—as Table I shows— excellent results; only in three cases (Nos. 5, 15 and 16) is there an appreciable discrepancy (slightly larger than 0.5%) between the calculated and the experimental values.

Figure 1 indicates that this discrepancy in the last two cases is due to loss of zinc, so that the calculated Σ(Zn) values may well furnish a more reliable estimate of the actual composition of these amalgams than do the amounts of zinc used in preparing them. Since no "smoothing out" of the results has been done, the close agreement of

(10) To show that assuming the existence of Reaction 2 alone fails to explain the experimental results, we need only attempt to calculate Σ(Zn) for, say, No. 1 on this basis. If only Reaction 2 were of importance, K'' would equal $(Zn)^2/(Zn)_2$; employing $K'' = 4.7$, the arithmetical mean of the first 15 Table I values, we obtain $(Zn_2) = 0.5266$; whence $\Sigma(Zn) = 2.0999$, a value that is unacceptable because it is 6% too low.

the two $\Sigma(\text{Zn})$ columns is gratifying—not often is it possible to find solutions that can be regarded as ideal over the entire range of composition and described so accurately by the assumption of two simple equilibria. The constitution of the liquid zinc amalgams at room temperature thus seems to be reasonably well established; our polymerization hypothesis, when applied to the results of Pearce and Eversole, gives for the composition of the saturated amalgam at 25°: $(\text{Zn}) = 1.5733$, $(\text{Zn}_2) = 0.2723$ and $(\text{Zn}_3) = 0.3744$.

An examination of the calculations based on the other accurate experimental results does not significantly alter these conclusions. For Crenshaw's data, three series of such calculations—employing as reference electrode the amalgam for which $\Sigma(\text{Zn})$ was, respectively, 0.1, 0.01 and 0.001—have been carried out; the results of all three sets are substantially in accord. The resulting individual K_3 values do not vary significantly more than those in Table I, but the average thereof is some 10 or 15% *lower* than the value selected from Table I; K_2 is correspondingly higher. The K_3 values from the results of Richards and Forbes are more erratic, and show a trend such that K_3 decreases with $\Sigma(\text{Zn})$. The average of these would be appreciably *higher* than 10.4, the Table I result; but the concentration range of Richards and Forbes' measurements is restricted, so that this average cannot be given serious weight. Since Pearce and Eversole have by far the greatest number of results extant for the concentration range where K_2 and K_3 can be most accurately determined, we shall adopt the values selected from Table I as final.

Summary and Conclusion

The electromotive force data for zinc amalgams have been re-examined, and it has been shown for the first time that all the final experimental results of the three accurate investigations made near room temperature agree excellently for the more concentrated amalgams and well for the dilute, whose investigation is complicated by their tendency to lose zinc. The deviations of these electromotive forces have been explained on a polymerization hypothesis that assumes the simultaneous existence of Zn_2 and Zn_3 in rapid equilibrium with monatomic zinc. A simple method for calculating the dissociation constants for these polymers has been devised and successfully applied to the electromotive force data; the constants thus obtained are satisfactory, so that the polymerization hypothesis and consequently the constitution of the liquid zinc amalgam at room temperature seem reasonably well established. If the validity of the polymerization hypothesis is granted, then it follows that the zinc amalgams at 25° behave as ideal solutions over the entire range of composition and that the fundamental laws underlying the Nernst equation govern them to within the precision of the measurements. The existing experimental work for other temperatures has permitted only these qualitative conclusions: the heats of dissociation of both polymers are small, that of Zn_3 being the greater.

Since the polymers have heats of dissociation not greatly exceeding RT, they cannot be very stable compounds. We must remember, therefore, that the evidence we have adduced for their existence, although as convincing as evidence of its kind can be, is after all indirect in nature; for we have shown only that zinc amalgams at 25° deviate from the laws of ideal solutions *almost exactly as though* Zn_2 and Zn_3 existed in rapid equilibrium with monatomic zinc. Here, as in the cases of many other solutions, it is difficult to decide whether such deviations, by whatever thermodynamic method they are established, should be attributed to compound formation or to a less definite interaction among the molecules composing the solution; a final decision becomes possible only when more direct experimental methods have "proved" the presence or absence of the compounds in question. Where aqueous solutions are concerned, their Raman spectra are often of service; but corresponding evidence for amalgams does not yet seem to be available.[11] Until it does appear, our indirect evidence would seem sufficiently strong to warrant regarding our polymerization hypothesis as provisionally established: for (1), this hypothesis involves only two equilibria (a much larger number would militate against it); (2), the corresponding equilibrium constants are accurately established (say, to within 5 or 10%); (3), no other set of two equilibria can be formulated that will fit the experimental data so well; and (4), any satisfactory alternative explanation of the deviations in question will have to yield ΔE values practically in-

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[11] In connection with our polymerization hypothesis, it is interesting to observe that many metallic vapors, probably including those of zinc, show band spectra indicating the presence of dimers. See Shawhan, *Phys. Rev.*, **48**, 343 (1935), and Robertson, *Nature*, **136**, 308 (1935), where other references are given.

distinguishable from those given by our polymerization hypothesis; whether any explanation based on intermolecular forces, but not assuming compound formation, will do this becomes doubtful when we remember (see Fig. 1) that ΔE becomes constant long before "infinite dilution" is reached.

It is not claimed, finally, that a *concentration* treatment of amalgams is generally preferable to a treatment in terms of *activities*. The latter quantities are always valuable since they stand, by definition, in simple relation to the free energies of the amalgams, and thus bridge the gap between the thermodynamic functions for an amalgam and its stoichiometric composition. But when amalgams become experimentally indistinguishable from ideal solutions in the manner of Fig. 1, then it seems desirable to try a concentration treatment also, in order to determine whether the deviations from ideality at the higher concentration cannot be quantitatively accounted for by assuming polymerization of the solute; for we may discover in this way what molecular species actually exist in these amalgams.

SCHENECTADY, N. Y. RECEIVED OCTOBER 1, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Energies and Entropies of Activation of the Reaction between Bromoacetate and Thiosulfate Ions[1]

BY VICTOR K. LA MER AND MILDRED E. KAMNER

In the theory of chemical kinetics there are two important quantities which determine the specific rate constant k, namely, the energy of activation E_{act}, defined through the differential form of the well-known Arrhenius equation

$$d \log k/dT = E_{act}/2.3RT^2 \qquad (1)$$

and the action constant $B = \log \alpha$ in the integrated form, namely

$$k = \alpha e^{-E_{act}/RT} \qquad (2)$$

$$\log k = B - E_{act}/2.3RT \qquad (3)$$

E_{act} represents the average energy of those molecules which react minus the average energy of all the molecules in the system, all quantities being defined per mole. La Mer[2] has shown as a consequence of this definition of E_{act}, due to Tolman, that

$$B = \log \alpha = \frac{1}{2.3R}\int_0^T \left(\frac{\partial E_{act}}{\partial T}\right)\frac{dT}{T} + \text{constant} \qquad (4)$$

determines the frequency with which the activated molecules react. In the special case where E_{act} remains independent of T at all temperatures, the integration constant in (4) equals log Z^0. In the case of unimolecular reactions Z^0 is the frequency of breaking the reactive bond in the activated molecule, whereas in a true bimolecular reaction Z^0 equals the collision frequency at unit concentrations. The dimension of B is time^{-1}.

The first term of B represents the increase in entropy due to the temperature dependence of E_{act} for the process, inactive molecules ⟶ active molecules, and hence has been called[2] the entropy of activation. Further experimental evidence for the temperature dependence of B and E_{act} for a zero type reaction will appear in another paper.[3]

The present paper will deal primarily with the temperature dependence of the kinetic salt effect in a reaction between ions of the same sign to ascertain in how far interionic attraction influences E_{act} and B. The bromoacetate-thiosulfate ion reaction $BrCH_2COO^- + S_2O_3^= \longrightarrow S_2O_3CH_2COO^= + Br^-$ was selected for the experimental study since it is almost unique among ionic reactions for the absence of side reactions and the high precision with which the velocity constant can be determined.[4]

Accordingly, the experiments were designed to test the behavior of E and B for (a) change of temperature at constant concentration of reactants; (b) change of ionic strength (Brönsted–Debye effect) for the same temperature interval; (c) the effect of substituting high valence cations like La^{+++} for the lower valence ions Ba^{++} and Na^+ at the same ionic strength, and (d) the influence of dielectric constant produced by the addition of non-electrolytes.[5]

The Limiting Law for E_{act} and B.—Equation

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[1] A preliminary report of these data was given in THIS JOURNAL, 55, 1739 (1933). A more complete report was read at the St. Petersburg, Florida, meeting of the Society in March, 1934.

[2] La Mer, *J. Chem. Phys.*, 1, 289 (1933); THIS JOURNAL, 55, 1739 (1933).

[3] V. K. La Mer and M. L. Miller, *ibid.*, 57, 2674 (1935).

[4] La Mer and Fessenden, *ibid.*, 54, 2351 (1932).

[5] La Mer and Kamner, *ibid.*, 57, 2669 (1935).