2. The conductance of hydrobromic acid has been measured over the same temperature range; limiting values for its equivalent conductance at five temperatures have been given.

3. The results of earlier investigations have been recalculated and shown to yield values of K_1 in substantial agreement with those newly determined.

4. The temperature variation of the K_1 for bromine becomes anomalous in the neighborhood of 0°; but the departure of $d(\log K_1)/d(1/T)$ from constancy is much less than that observed by Jakowkin in the case of chlorine.

5. The existence of pentabromide ion is highly probable; the values of $(Br^-)(Br_2)^2/(Br_5^-)$ are calculated to be 0.025 at 0° and 0.050 at 25°, in agreement with the results of earlier investigations.

BERKELEY, CALIF. RECEIVED APRIL 9, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Activity of Sodium in Concentrated Liquid Amalgams

BY E. S. GILFILLAN, JR., AND H. E. BENT

The purpose of this investigation of concentrated sodium amalgams is two-fold. In the first place it is desired to compare the activity of sodium in eighty-five atom per cent. amalgam, which is liquid at room temperature, with that of the pure metal. The use of this material in cleaving organic compounds is now so common as to make it desirable to discover the activity of this amalgam as compared with the pure metal and dilute amalgams. The second purpose of this investigation is to correlate the deviations from Raoult's law with those previously observed in experiments on dilute sodium amalgams. Sodium amalgams offer an extreme case of deviation from Raoult's law and hence are of particular interest from the standpoint of the theory of solutions.

Experimental Method

Most of the experimental detail has been described elsewhere.[1] The sodium was Kahlbaum material which had been filtered through a glass capillary in a vacuum to remove surface impurities. Unpublished work in this Laboratory by one of us with A. F. Forziati indicates that distillation of the sodium does not affect the e. m. f. of the cell. The amalgams were made up to approximately the correct composition and sealed in glass capsules. These were placed in the apparatus, the system evacuated and the tips of the capsules broken by means of magnetically controlled hammers. The composition of the liquid phase was determined by means of the data of Vanstone.[2] His excellent phase diagram permits one to read at each temperature the composition of the liquid phase with a probable error of something like 0.1% on the sodium side of the eutectic and perhaps 0.2 to 0.3% on the more dilute side of the eutectic. Sodium iodide in ethylamine served as the electrolyte. When first prepared the cell did not give constant values for the e. m. f. After agitating the electrolyte for some time the values became more reproducible. Some difficulty was experienced with amalgam "C" which at first gave rather erratic results. This was attributed to lack of homogeneity, for after repeated fusions and solidifications it gave good results. Difficulty was also experienced after a few days when two of the electrodes suddenly developed very high internal resistance. The platinum wire sealed into the cell was very fine (40 gage) and may have been broken by the expansion and contraction of the solid amalgams. After time had been allowed for equalization of concentration in the electrolyte the reproducibility was very good, the root-mean-square of the cross-checks being 0.03 mv.

Experimental Results

The observed e. m. f. data are given in Table I and represented graphically in Fig. 1. To relate these data to Raoult's law it is necessary to calculate the activity of solid sodium at the temperatures employed in our experiments referred to the supercooled liquid as the standard state. This may be accomplished if one knows the melting point, the heat of fusion and ΔC_p. Griffiths[3] has found the melting point to be 97.6° and the

---

[1] Bent and Gilfillan, THIS JOURNAL, **55**, 3989 (1933).

[2] Vanstone, *Trans. Faraday Soc.*, **7**, 42 (1911).

[3] Griffiths, *Proc. Roy. Soc.* (London), **89**, 561 (1914).

TABLE I

THE E. M. F.'S FROM SODIUM TO LIQUID SODIUM AMALGAMS

t	A			B			C	D		
21	...			−0.09			...	0.01		
22	...			...			0.14	.05		
23	...			.21			.38	.31		
24	...			.47			.50	.51		
25	0.01	0.01	0.01	.52	0.68		.77	.71	0.75	0.75
28	.02			.92			...	1.43		
30	...			1.14			...	1.88	1.92	
31	.01			1.26			...	2.14		
32	.01	−.02		1.33			...	2.40		
33	.02			1.47			...	2.63		
34	.02	.02		1.53	1.50		...	2.86	2.92	2.85
35	−.01	.01		1.54	1.60	1.54	1.68	3.22	3.17	3.19
36	...			1.63	1.63		1.74	3.45	3.49	3.48
37	...			1.72			1.83	3.72		
38	−.01			1.83	1.77		1.92	3.97	3.97	3.96
39	...			1.89			1.99	4.24		
41	...			2.02	2.05	2.15	2.15	4.75	4.73	4.82
43	...			2.18			2.31	5.37		
45	.03			...			...	5.94	5.96	5.96

The e. m. f.'s recorded are from solid sodium to the amalgams indicated at the top of the columns, at the centigrade temperature given at the left. The unit is the millivolt. Where more than one e. m. f. is given for a given amalgam, at a given temperature, the measurements were made on different days.

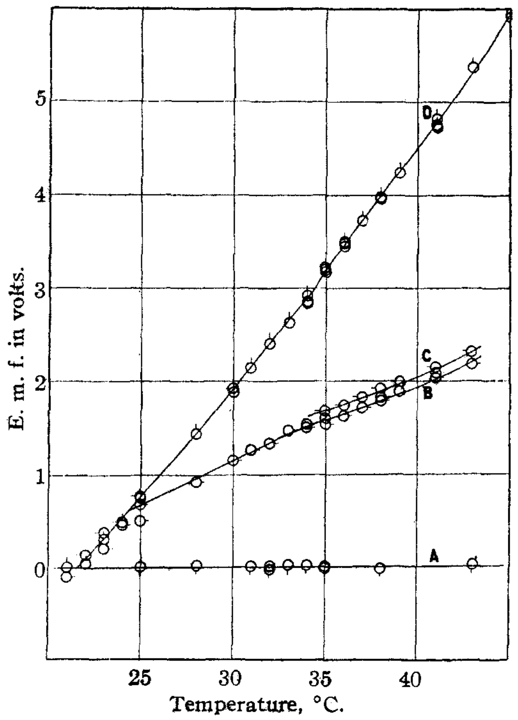

Fig. 1.—The e. m. f. of amalgams A, B, C and D, respectively, against solid sodium. Amalgams A and D are two phase at all temperatures. Amalgam B is two phase at the lower temperatures.

heat of fusion to be 633 calories per mole. Experimental data do not permit a very precise determination of C_p. This is not serious, however, over the small temperature range involved. Taking the "smoothed" values for the heat capacity of solid sodium from the "International Critical Tables" and the values of Dixon and Rodebush[4] for liquid sodium one obtains the equation for the process of fusion

$$\Delta C_p = -0.00873(T - 414)$$

Combining this with the heat of fusion gives

$$\Delta H = -107.0 + 3.614T - 0.004365T^2$$

Substitution in the expression

$$\frac{d \ln a}{dT} = -\frac{\Delta H}{RT^2}$$

gives

$$\log a = -4.3835 + (23.39/T) + 1.8194 \log T - 0.0009543T$$

for the activity of solid sodium, taking the supercooled liquid as the standard state. We have assumed that if there are two allotropic modifications of sodium, as suggested by Cohen and de Bruin,[5] that on the surface of the metal, in contact with an electrolyte reversible to sodium ion, only the stable form would be present.

With the aid of the above equation Table II has been calculated. The first three lines giving the mole fraction of sodium were obtained directly from the paper by Vanstone. The value for amalgam B was obtained from the temperature at which it became two phase. The intercept of the curves for amalgams B and D in Fig. 1 gives this temperature.

TABLE II

THE DEVIATION OF CONCENTRATED SODIUM AMALGAMS FROM RAOULT'S LAW

Temperature.......	25°	30°	35°	40°	45°
1 N_2 for Amalgam A	0.857	0.866	0.875	0.884	0.889
2 N_2 for Amalgam B	.849	.849	.849	.849	.849
3 N_2 for Amalgam D	.848	.843	.836	.828	.823
4 $-\log a_2$ for Amalgam A	.0875	.0805	.0736	.0668	.0629
5 E solid Na to Amalgam B	.00067	.00115	.00158	.00197	.00219
6 $-\Delta \log a_2$ from A to B	.0113	.0191	.0259	.0317	.0349
7 $-\Delta \log a_2$ liquid Na to B	.0988	.0996	.0995	.0985	.0978
8 E solid Na to Amalgam D	.00077	.00192	.00318	.00452	.00532
9 $-\Delta \log a_2$ from A to D	.0130	.0319	.0520	.0728	.0848
10 $-\Delta \log a_2$ from liquid to D	.1005	.1124	.1256	.1396	.1477
11 $-\log a_2/N_2$ Amalgam A	.0205	.0180	.0156	.0133	.0118
12 $-\log a_2/N_2$ Amalgam B	.0277	.0285	.0284	.0274	.0267
13 $-\log a_2/N_2$ Amalgam D	.0289	.0382	.0478	.0576	.0631

The values in line (4) were obtained by means of the above equation for the activity of solid sodium.

---

(4) Dixon and Rodebush, THIS JOURNAL, **49**, 1162 (1927).

(5) Cohen and de Bruin, *Z. physik. Chem.*, **89**, 751 (1915).

This procedure is justified because within the experimental error the activity of sodium in amalgams on the sodium side of the eutectic is the same as that for the pure metal.

The values of the e. m. f. in lines 5 and 8 were read from the curves in Fig. 1. These e. m. f. data multiplied by the faraday equivalent and divided by 2.303 RT give the differences between the activities of sodium in the various amalgams and amalgam A, as shown in lines 6 and 8. Since amalgam A gives zero potential against pure sodium the values in lines 6 and 8 may be added to the values in line 4 to give, in lines 7 and 10, the activity of sodium referred to supercooled liquid as the standard state.

Finally, the last three lines in the table give the log of the ratio of the activity to the mole fraction, a quantity which would be zero if Raoult's law were obeyed.

One may calculate from the experimental data the partial molal heat of solution of sodium in amalgam B and the partial molal entropy of solution. The calculation is of interest not so much on account of the precision of the results but as a check on the reliability of the experimental data. Thus from the equation

$$\overline{H}_2 = 23{,}065[-E + T(\mathrm{d}E/\mathrm{d}T)]$$

one obtains values for $\overline{H}_2$ which range from 657 calories at 25° to 482 calories at 43°. Subtracting from these values the heat of fusion of sodium at the corresponding temperature gives $\overline{H}_2$ referred to liquid sodium as the initial state. The relation

$$\Delta S = (\Delta H - \Delta F)/T$$

gives the change in entropy for the process of dissolving liquid sodium in amalgam B as 0.71 to 0.15 e. u. This value, if Raoult's law were obeyed as far as entropy is concerned, would be $-R \ln N_2$, which is 0.325. As would be expected from the e. m. f. data the sodium is behaving very nearly in accord with Raoult's law. This variation in ΔS from 0.71 to 0.15 is a good indication of the reliability of the e. m. f. data, as an error of 0.00005 volt at 25° and a similar error at 43° would entirely account for this variation in ΔS.

Discussion of Results

The first comparison to be made is with the thermal data of Vanstone. From his phase diagram the temperature of the first eutectic is found to be 21.4°. From these e. m. f. data this point is the intersection of the temperature e. m. f. curves for amalgams A and D and is found to be 21.6°. The difference, 0.2°, is well within the experimental error of the e. m. f. data. Vanstone's curve indicates a transition between two forms of Na_3Hg at 34.4°. The corresponding break in the temperature–e. m. f. curve of amalgam D is not great but appears to be at 34.4 ± 1.0°. Vanstone's data are not conclusive as to the nature of the solid phase which separates on the sodium side of the eutectic. The value of the e. m. f. for amalgam A of 0 ± 0.00002 volt indicates that the solid phase is sodium with not more than 0.08 atom per cent. of impurity.

These data indicate that concentrated sodium amalgam if in equilibrium with the solid metal will behave in organic reactions exactly as solid sodium except with regard to the rate of the reaction. The use of a liquid allows the continual formation of fresh surface and should therefore lead to more complete reactions, where there is the possibility of a precipitate. On the other hand, the presence of the mercury might slow down the reaction slightly where only soluble products were formed.

The next question to be considered is the relation of these data to those obtained from dilute amalgams.[6] Hildebrand[7] has emphasized the convenience of expressing deviations from Raoult's law for both solvent and solute by a single constant β, which of course is a function of the temperature and is characteristic of each system. The applicability of this simple equation ($\log a_1/N_1 = {}^1/_2\,\beta N_2^2$) has already been considered in the case of dilute sodium amalgams.[8] It has been shown that at 608 and 648°K. the vapor pressure data could be represented by such an equation with a fidelity of about one per cent. The experimental accuracy was somewhat better than this. The most concentrated amalgam investigated was 39 atom per cent. sodium.

The application of this simple equation to e. m. f. data on dilute liquid sodium amalgams was not nearly so successful. From Richards and Conant's data ${}^1/_2\beta$ is found to be -12.89 from the intercept and -10 from the slope of the curve.

---

[6] Unfortunately a plot of deviations from Raoult's law including all of these researches does not add much to the discussion. If one plots the logarithm of the activity divided by the mole fraction against the mole fraction squared, one end of the plot becomes unduly compressed. Furthermore, the activity of the mercury in concentrated amalgams, as is shown in the following section, is to be obtained only by an interpolation which involves great uncertainty.

[7] Hildebrand, "Solubility," The Chemical Catalog Co., New York, 1924, p. 47.

[8] Bent and Hildebrand, THIS JOURNAL, **49**, 3011 (1927).

Taking the most concentrated amalgam in Table II (considering the sodium as the solute in spite of the fact that it is present in the largest concentration) $\log a_2/N_2$ is found to be -0.0205. Hence $-{}^1/_2\beta$ is unity.

An alternative method of treating deviations from Raoult's law is to assume that partially dissociated compounds are present in solution. The phase diagram indicates that there are many such compounds between sodium and mercury. The behavior of dilute sodium amalgams has been accounted for in large measure by this assumption. No great success is achieved in accounting for these data on concentrated sodium amalgams by means of the assumption of compound formation. The best agreement with the experimental data which could be obtained by assuming only one compound, namely, Na_3Hg with a dissociation constant of five, is not good. Doubtless a better agreement could be obtained by assuming other known compounds to be important. However, the range of concentration studied did not seem to warrant the introduction of more arbitrary constants.

The very small partial molal free energy of sodium in concentrated sodium amalgam is interesting in connection with the following statement by Gerke,[9] "Hitherto, the concept of partial molal free energy has not been used to split up the free energy of formation of a compound from its constituent elements into two parts. . . ." Gerke then goes on to point out that in dilute amalgams the partial molal free energy of mercury is nearly zero while that of sodium is large. We disagree with Gerke, however, who concludes that this is significant in indicating that in the formation of the compound with mercury the sodium contributes practically all of the free energy change. The partial molal free energies are a function of the concentration of the solution and in the case of the concentrated amalgams reported in this paper the partial molal free energy of the sodium is small while that of mercury is large. It is, therefore, apparently not possible to choose a unique process for the formation of a compound which will result in partial molal free energies of any particular theoretical significance.

The Vapor Pressure of Mercury

Since no equation can be given for the deviations from Raoult's law over the whole range of concentration, it is not possible to give an accurate value for the vapor pressure of mercury from sodium amalgams rich in sodium. We may, however, obtain some idea of the order of magnitude of this quantity. One could express the activity of sodium by an equation of the type $\log a_2/N_2 = a + bN_1 + cN_1^2$, etc., if sufficient data were available. The nature of the phase diagram prevents one working with liquid amalgams at room temperature over any considerable range of concentration. We can approximate the limits for such an equation by considering the values which have been obtained experimentally for the two ends of the curve. The interpolation applies to a supercooled liquid amalgam in the range of concentration which is ordinarily solid. We have already shown that one cannot reconcile the data at the two extremes of concentration by means of the single coefficient of N_1^2. We may assume, however, that the actual curve lies between the limiting curves obtained by the equation $\log a_2/N_2 = 1/nkN_1^n$ when n is given, successively, values necessary to fit the two ends of the curve. This procedure seems reasonable as it is simply equivalent to assuming in the power series that the actual equation will lie between the two curves which would be obtained if on the one hand only the lowest power was used and on the other hand only the highest power. The values so obtained for n from dilute amalgams is 1.53 and for the concentrated amalgams is 3. If we substitute this expression for $\log a_2/N_2$ in the equation ($\log a_1/N_1 = -\int N_2/N_1 \, d \log a_2/N_2$), we obtain the expression

$$\log \frac{a_1}{N_1} = -k\frac{N_1^{n-1}}{n-1} - \frac{N_1^n}{n} + \frac{k}{n(n-1)}$$

The Henry's law constant is then obtained by allowing N_1 to equal zero, which gives $\log a_1/N_1$ equal to $k/n(n-1)$. The equation

$$\log \frac{a_2}{N_2} = \frac{1}{n} kN_1^n = \frac{k}{n}(1 - nN_2 \ldots)$$

gives the value of k/n equal to -12.89 referred to solid sodium as the standard state, or -13 referred to supercooled liquid. Hence

$$\log \frac{a_1}{N_1} = \frac{k}{n(n-1)} = \frac{-13}{n-1}$$

and $\log a_1/N_1$ lies between -24.5 and -6.5. These are undoubtedly extreme values. An average value of n is 2.25, which gives -11 for $\log a_1/N_1$. Thus the vapor pressure of mercury from concentrated liquid sodium amalgam ($N_2 = 0.85$)

---

[9] Gerke, THIS JOURNAL, **45**, 2508 (1923).

would be of the order of magnitude of 10^{-15} mm. The largest value which one could obtain from the above limits would be 10^{-10} mm. This is of the order of magnitude of the vapor pressure of sodium. Hence one can conclude that in all probability the vapor pressure of mercury is less from this amalgam than that of sodium.

Conclusions

1. The activity of sodium in concentrated liquid sodium amalgam is approximately the same as that of the solid metal.

2. Sodium amalgams cannot be well represented by the equation log $a_2/N_2 = {}^1/_2\ \beta N_1^2$, which has been used successfully in treating so many solutions.

3. The vapor pressure of mercury from concentrated liquid sodium amalgam is probably much less than 10^{-10} mm.

CAMBRIDGE, MASSACHUSETTS RECEIVED APRIL 11, 1934

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF ADRIAN COLLEGE]

The System Zinc Oxalate, Potassium Oxalate, Water. II. At 35°

BY V. METLER

It has been shown[1] that the complex compound $K_2Zn(C_2O_4)_2 \cdot 7H_2O$ exists in stable equilibrium with solutions of potassium oxalate saturated with zinc oxalate at 25°. The hydrate was observed to be unstable, becoming anhydrous when exposed to the air. Scholder and Linstrom[2] prepared the anhydrous compound.

In the present investigation the solubility of zinc oxalate and potassium oxalato-zincate in solutions of various concentrations of potassium oxalate has been determined at 35°, and the existence of the hydrated complex compound $K_2Zn_2(C_2O_4)_3 \cdot xH_2O$ is demonstrated.

Other complex compounds of the type $K_2M_2''(C_2O_4)_3$ have been prepared by Scholder and coworkers.[3]

Experimental

Materials used in this work were from the same lot or of the same general purity as those described in Part I.

A small thermostat regulated at 35 ± 0.02° was used, with a device for rotating small saturation bottles. The glass stoppers of the bottles were covered with wax while in the thermostat.

The same methods of analysis were used as before.

Preparation of the Complex Salts.—A description of the method of preparing the potassium oxalato-zincate already has been given.[1] Well-formed crystals of the anhydrous salt $K_2Zn(C_2O_4)_2$ form from the heptahydrate, or from the compound $K_2Zn_2(C_2O_4)_3$ described below, when they are shaken at 35° with a saturated solution of potassium and zinc oxalates. This preparation is preferable to that formed when the heptahydrate is dehydrated in air since the latter tends to form colloidal solutions.

Solubility Determinations

Stable Systems.—Solutions of various concentrations of potassium oxalate were saturated with zinc oxalate (solutions 12–29), or the hydrated complex salt, $K_2Zn(C_2O_4)_2 \cdot 7H_2O$ (solutions 1–11). After allowing time for saturation, samples of the solution were withdrawn and analyzed. The wet solid phase was dissolved and analyzed as described in Part I.

The analytical results are summarized in Table I and presented graphically in Fig. 1.

Triple points A and B are the average of two separate saturations in which both solid components were shown to be present by analysis of the wet solid phases.

It may be seen that zinc oxalate is the stable solid phase in equilibrium with solutions up to 25.28% $K_2C_2O_4$ (and saturated with zinc oxalate). From this concentration to saturation with both potassium oxalate and the oxalato-zincate the solutions are in equilibrium with anhydrous $K_2Zn(C_2O_4)_2$. Algebraic extrapolation on the assumption of this latter formula is in agreement with the graph.

The portion of the curve representing solutions in equilibrium with $ZnC_2O_4 \cdot 2H_2O$ coincides with the corresponding portion of the curve determined at 25°.

Metastable System.—In the preparation of the heptahydrate, thin, hexagonal crystals of another complex compound form. Its composition when dried in air is $K_2Zn_2(C_2O_4)_3 \cdot 5H_2O$.[4]

Solutions of potassium oxalate were saturated with this compound at 35°. Several solutions with their corresponding solid phases are indicated by squares in Fig. 1. All tie-lines cross the $K_2Zn_2(C_2O_4)_3$–H_2O axis. Since the tie-lines lie very nearly parallel to this axis, the water content of the metastable complex is indefinite. By algebraic extrapolation the formula of the complex salt appears to be $K_2Zn_2(C_2O_4)_3 \cdot 12H_2O$.

Solutions in contact with both zinc oxalate and the trioxalato salt when sampled at intervals of twelve to twenty-four hours showed a very slow increase in oxalate

---

[1] Metler and Vosburgh, THIS JOURNAL, **55**, 2625 (1933).

[2] Scholder and Linstrom, *Ber.*, **63**, 2831 (1930).

[3] Scholder, Gadenne and Niemann, *ibid.*, **60**, 1496 (1927).

[4] *Anal.* Calcd. for $K_2Zn_2(C_2O_4)_3 \cdot 5H_2O$: Zn, 23.22; C_2O_4, 46.89. Found: Zn, 23.38; C_2O_4, 46.70.