$$\log f_{\pm} = \frac{-A\sqrt{C_i}}{1 + B\mathring{a}\sqrt{C_i}} \qquad (3)$$

using an ion size parameter of 5.5 Å. This value was chosen somewhat arbitrarily as the mean distance from the center of the sodium ion to the center of the cavity in an ion-pair. The final result is not very sensitive to the value of $\mathring{a}$ used but the value of 5.5 Å. was used from the beginning and was *not* used as an adjustable parameter. It is felt that any reasonable value of $\mathring{a}$ is better than using only the limiting law.

The calculations were performed by first neglecting reaction 2, resulting in an approximate value of K_1 given by

$$K_1^{(a)} = \frac{\alpha^2 C f_{\pm}^2}{1 - \alpha} \qquad (4)$$

A series of $K_1^{(a)}$ values were obtained in this manner as a function of concentration. $K_1^{(a)}$ was then plotted *versus* concentration and a test value of the true constant $K_1^{(t)}$ was obtained by extrapolation. K_2 was obtained from $K_1^{(a)}$ and $K_1^{(t)}$ through the relationship

$$K_2 = \left[\frac{(K_1^{(t)} - K_1^{(a)})}{2(C\alpha f_{\pm})^2} \cdot \frac{K_1^{(t)}}{K_1^{(a)}}\right]^{1/2} \qquad (5)$$

For a series of values of $K_1^{(t)}$, K_2 was calculated as a function of concentration. Table VI gives the results obtained for three values of $K_1^{(t)}$. The most constant value of K_2, 18.5, was obtained for $K_1^{(t)} = 9.2 \times 10^{-3}$. These calculations show that the data obtained can be fit with the type of equilibria postulated by the "monomer–dimer" theory.[2] However, either a spherical monomer unit or an ion-pair between sodium ion and the electron in a cavity could be the important unit. Of course these data provide no information concerning the structure of the dimer. An uncharged dimer rather than an $e_2^=$ unit was considered in this treatment. A treatment based upon the assumption of dimerization to $e_2^=$ centers has not been made but would be more complex because of additional ion-pairing equilibria. The values of K_1 and K_2 are to be compared with 7.2×10^{-3} and 27 obtained by Evers and Frank from the total conductance up to concentrations of 0.04 molar. On the basis of both sets of calculations, the dimerization constant K_2 appears to be smaller than the corresponding constant for potassium calculated[2b] from the magnetic resonance data of Hutchison.[13] Unfortunately the paramagnetic resonance data for sodium are not as extensive nor as internally consistent as the potassium data. It would be of interest to extend the magnetic data for sodium and also to evaluate λ_+ for potassium from transference number measurements. On the basis of our results and the magnetic evidence, one would expect more dimerization for potassium than for sodium and therefore a larger value of K_2. Transference number data for potassium are currently being obtained in this Laboratory.

Acknowledgments.—The authors wish to thank the U. S. Atomic Energy Commission for the financial support which made this work possible. Thanks are also due to Mr. F. E. Hood, whose many glass fabrications, repairs and special techniques made this apparatus workable.

[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN[1b]]

The Activity Coefficient of Sodium in Liquid Ammonia

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RECEIVED FEBRUARY 26, 1960

Transference number data from moving-boundary measurements and data from the e.m.f. of cells with transference were used to calculate the activity of sodium in liquid ammonia as a function of concentration. Consideration of ion-pairing and dimerization equilibria allowed extrapolation of the data to infinite dilution and resulted in values of 9.6×10^{-3} and 23, respectively, for the equilibrium constants of the two reactions

$$Na^+{\cdot}e^- \rightleftharpoons Na^+ + e^- \qquad (1) \qquad\qquad 2Na^+{\cdot}e^- \rightleftharpoons Na_2{\cdot} \qquad (2)$$

The results were combined with published vapor pressure data for the high concentration region and with calorimetric data to give a partial molar entropy of 16.9 ± 1.8 cal. deg.$^{-1}$ mole^{-1} for the solvated electron in the hypothetical ideal one molal solution.

Introduction

The activity coefficients of alkali metals in liquid ammonia can be determined in the high concentration range from data on the vapor pressure of ammonia above such solutions. Since the precision in this method is poor at low concentrations, it is necessary to use pure sodium as the standard state or simply to compute relative activity coefficients.[2a] Such data are useful for comparing the behavior of different metals and for studying phase equilibria but do not help to determine the nature of the ionized species in dilute solutions. Calorimetric data are available[2b,3] for the heat of solution of the metal to form dilute solutions, so that ΔH^0 for the process

$$NH_{3(l)} + Na_{(s)} \longrightarrow Na_{(am)}^+ + e_{(am)}^- \qquad (3)$$

can be calculated. The data of Pleskov[4] on the e.m.f. of cells were used by Jolly[5] and by Coulter[2b] to calculate ionic enthalpies and entropies for the alkali ions and to estimate the heat of solvation of

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[1] (a) To whom correspondence should be addressed. (b) This work was supported in part by the U. S. Atomic Energy Commission under Contract AT(11-1)-312.

[2] (a) P. R. Marshall and H. Hunt, *J. Phys. Chem.*, **60**, 732 (1956). (b) L. V. Coulter, *ibid.*, **57**, 553 (1953).

[3] G. A. Candela, M.S. Thesis, Boston University, 1952.

[4] V. A. Pleskov and A. M. Monoszon, *Acta Physicochim. U.R.S.S.*, **2**, 615 (1935); V. A. Pleskov, *ibid.*, **6**, 1 (1937).

[5] W. L. Jolly, U. S. Atomic Energy Comm., *U.C.R.L.-2201*, pp. 23 (1953).

the electron. However, it was not possible to obtain ΔF^0 for the process given by (3). Because of the solubility of the metals in ammonia, one cannot set up suitable cells without transference using the metals as electrodes. The use of dropping amalgam bridge electrodes similar to those used in aqueous solutions[6] would be complicated by the partition equilibrium of the metal between the ammonia and the mercury phases.

Almost fifty years ago, Kraus,[7] in the course of his classic studies of metal–ammonia solutions, measured the e.m.f. of cells with transference employing dilute solutions of sodium in ammonia. The type of cell which he studied was

$$\mathrm{Pt}|\mathrm{Na}(C_1 \text{ in } \mathrm{NH_3})\vdots\mathrm{Na}(C_2 \text{ in } \mathrm{NH_3})|\mathrm{Pt} \qquad (4)$$

in which the platinum electrodes appeared to behave reversibly towards the solvated electron. These data were used by Kraus to demonstrate the high value of the anionic transference number and its change with concentration. To make this calculation, Kraus assumed the activity ratio to be equal to the concentration ratio. Klein[8] has made e.m.f. measurement on metal–methylamine solutions and Fristrom[9] has extended the e.m.f. data of Kraus to other metals in ammonia and to temperatures other than $-33.5°$.

In view of the modern interpretations of the structure of dilute solution, activity coefficients undoubtedly play an important role. The measurement of transference numbers reported in a companion paper[10] makes possible the calculation of activity coefficient ratios using the data of Kraus. The equilibria postulated by modern theory can be used to extrapolate the data to the infinite dilution reference state. Use of vapor pressure data at higher concentrations allows calculation of the activity coefficient over the entire range of concentration from infinitely dilute solution to the saturated solution. These calculations and the interpretation of the results are the subjects of this paper.

Calculations and Results

The calculation of molar activity coefficient ratios requires a knowledge of the cation transference number, T_+, as a function of concentration. This can be obtained by subtracting from unity the measured value of T_-. Since the transference data covered the range 0.02 to 0.14 molar while the e.m.f. data of Kraus were obtained from 0.002 to 0.82 molar, it was necessary to extrapolate the transference data in both directions. Because of the independent value available for the intercept at $C = 0$,[10] the extrapolation to low concentrations should be quite reliable. Direct extrapolation to concentrations above 0.14 molar is hazardous because of the expected drop of T_+ to very low values. The total conductance passes through a minimum and then rapidly rises to a high value. A rapid drop of T_+ is expected because of an increase in λ_- rather than a rapid decrease in the cation conductance. The sodium ion conductance should decrease slowly and uniformly with increasing concentration. Because of this, the cation transference number at concentrations above the experimental range was calculated by dividing the extrapolated value of λ_+ by the total conductance Λ obtained from the data of Kraus[11] and Fristrom.[9]

Electromotive Force Data.—The e.m.f. data of Kraus[7] were obtained for a number of pairs of solutions, while the calculation of relative activity coefficients requires e.m.f. data relative to a particular reference solution. Thus it was necessary to treat the data of Kraus in a different manner than is normally done. If $\Delta\epsilon$ represents the e.m.f. observed for a cell having metal concentrations C_1 and C_2 and if C_1 and C_2 are not widely different, one can make the approximation

$$\frac{\Delta\epsilon}{\Delta \log C} = \frac{\Delta\epsilon}{\log \dfrac{C_2}{C_1}} \approx \frac{d\epsilon}{d \log C} \qquad (5)$$

A graph of $\dfrac{\Delta\epsilon}{\Delta \log C}$ *versus* log C (average) was made, and graphical integration was used to obtain ϵ *versus* log C as shown in Fig. 1. The smoothed values of ϵ are given in Table I. A reference concentration corresponding to *log* $C_{\mathrm{ref}} = -2.20$ was chosen for calculation of activity coefficients. This concentration is high enough to be fairly insensitive to errors in the e.m.f. measurements at the lowest concentrations and yet low enough so that the laws of dilute solution behavior can be applied to the reference solution.

The calculation of $\dfrac{y_\pm}{y_{\pm\mathrm{ref}}}$ followed standard procedure[12] and made use of the equation

$$\log \frac{y_\pm}{y_{\pm\mathrm{ref}}} = \log \frac{C_{\mathrm{ref}}}{C} + \frac{F}{4.606\, RT}\left[\frac{\epsilon}{T_{+\mathrm{ref}}} + \int_0^\epsilon \delta d\epsilon\right] \qquad (6)$$

in which

$$\delta = \frac{1}{T_+} - \frac{1}{T_{+\mathrm{ref}}} \qquad (7)$$

and F is the Faraday.

The value of $\int \delta d\epsilon$ was obtained by graphical integration and the procedure was checked by graphical differentiation of the integral curve. The resulting values of $y_\pm/y_{\pm\mathrm{ref}}$ are given in Table I along with the values of T_+, ϵ and $\int \delta d\epsilon$ used. The symbol $y_\pm$ refers to the stoichiometric mean molar activity coefficient. In the discussion of the extrapolation procedure which follows, $f_\pm$ represents the mean molar activity coefficient *of the ions present* and is presumed to obey the Debye–Hückel equation in dilute solutions.

Direct extrapolation of $y_\pm/y_{\pm\mathrm{ref}}$ to infinite dilution using the Debye–Hückel equation gives an approximate value of $y_{\pm\mathrm{ref}}$, but the curvature is too great for a reliable extrapolation to be made, and to evaluate this parameter the equilibria involved must be considered. The equilibria considered

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[6] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 489.

[7] C. A. Kraus, This Journal, **36**, 864 (1914).

[8] H. M. Klein, Ph.D. Thesis, Pennsylvania University, 1957; *Dissertation Abstr.*, **17**, 990 (1957).

[9] R. M. Fristrom, Ph.D. Thesis, Stanford University, 1949; *D.D.*, **16**, 32 (1948–1949).

[10] J. L. Dye, R. F. Sankuer and G. E. Smith, This Journal, **82**, 4797 (1960).

[11] C. A. Kraus, *ibid.*, **43**, 749 (1921).

[12] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1955, p. 200.

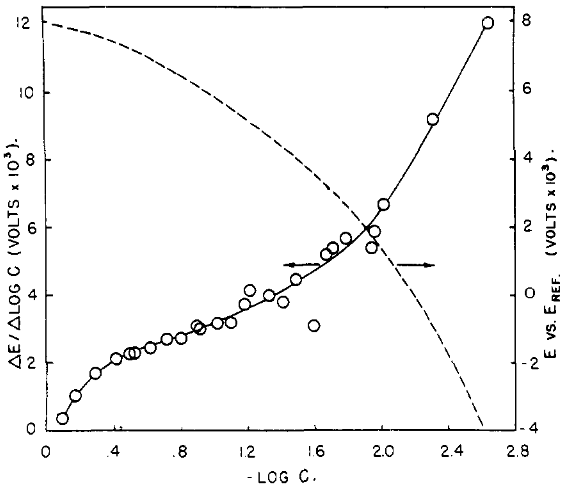

Fig. 1.—The e.m.f. data of Kraus[7] plotted in differential form and the resulting integral curve. Data are for sodium in ammonia at −33.5°.

were those postulated by Becker, Lindquist and Alder[13]

$$\mathrm{M^+{:}e^-} \overset{K_1}{\rightleftarrows} \mathrm{M^+ + e^-} \tag{1}$$

$$\mathrm{2M^+{\cdot}e^-} \overset{K_2}{\rightleftarrows} \mathrm{M_2} \tag{2}$$

It was assumed that the ionic species obeyed the Debye–Hückel equation[14]

$$\log f_\pm = \frac{-A\sqrt{C_i}}{1 + B\,\mathring{a}\sqrt{C_i}} \tag{8}$$

The numerical values of A and B used were 4.75 and 0.693, respectively, for ammonia at −33.5°. The parameter $\mathring{a}$ was arbitrarily chosen to be 5.5 Å. and was *not* adjusted for best fit. The constants K_1 and K_2 were "coupled"; that is, the data could be reproduced reasonably well over a range of values of K_1 provided that K_2 and $y_{\pm\mathrm{ref}}$ were suitably varied.

TABLE I

SMOOTHED DATA FOR ACTIVITY CALCULATIONS

$M \times 10^2$	T_+	ϵ (volt × 10^3)	$\int \delta d\epsilon$ (volt × 10^3)	$y_\pm/(y_\pm)_{\mathrm{ref}}$
0.178	0.133	−5.64	0.768	1.231
.398	.131	−1.69	.107	1.174
.631	.129	0.00	.000	1.000
1.00	.126	1.297	.115	0.8105
2.00	.118	2.987	.830	.5710
3.98	.104	4.328	2.350	.3839
7.94	.085	5.419	5.143	.2539
15.9	.062	6.309	10.12	.1705
31.6	.042	7.052	18.17	.1200
50.1	.028	7.450	26.47	.1002
79.4	.011	7.717	37.54	.0874

The value of $y_{\pm\mathrm{ref}}$ is sensitive to the value of K_1 used, and so an independent measure of $y_{\pm\mathrm{ref}}$ was used before fitting the two constants to the data. If α represents the fraction of the total sodium present as Na$^+$, then

$$\alpha = \frac{C_i}{C} \tag{9}$$

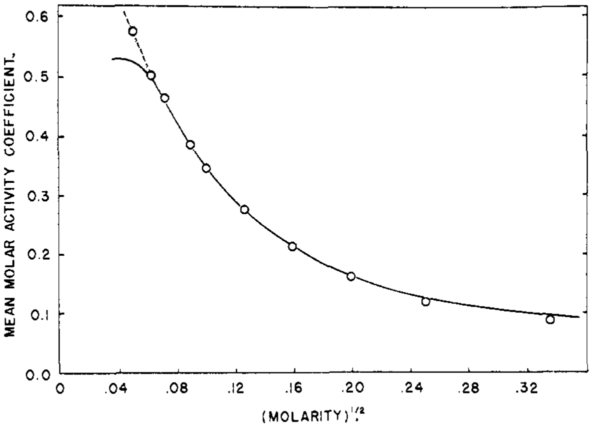

Fig. 2.—Mean molar activity coefficient of sodium in ammonia. Solid line calculated from e.m.f. and T-data; circles represent calculations from equilibrium constants.

and

$$y_\pm = \alpha f_\pm \tag{10}$$

with $f_\pm$ evaluated by (8). *For the reference concentration only,* α was estimated from conductivity data for Na$^+$ [10] to be 0.79. Since conductivity is very sensitive to the absolute value of α, while $\frac{y_\pm}{y_{\pm\mathrm{ref}}}$ is sensitive primarily to the ratio $\frac{\alpha}{\alpha_{\mathrm{ref}}}$, it was felt that this procedure would give a better value of $y_{\pm\mathrm{ref}}$ than the adjustment of K_1 and K_2 to give the best fit.

Having thus fixed $y_{\pm\mathrm{ref}}$, K_1 and K_2 were evaluated from the relative activity coefficients by a method of successive approximations. Equation 1 gives

$$K_1 = \frac{\alpha^2 C^2 f_\pm^{\,2}}{[\mathrm{M^+{\cdot}e^-}]} \tag{11}$$

To get an approximate value of K_1, the apparent constant $K_1^{(a)}$ was evaluated at each concentration as

$$K_1^{(a)} = \frac{\alpha^2 C f_\pm^{\,2}}{(1-\alpha)} \tag{12}$$

using the measured $y_\pm/y_{\pm\mathrm{ref}}$ and equation 10. Equation 8 was used to obtain $f_\pm$ and the entire procedure was repeated until consistent values of α and $f_\pm$ were obtained.

The parameter $K_1^{(a)}$ varied with concentration because of the presence of the second equilibrium. An extrapolation to infinite dilution gave an approximate value of $K_1^{(t)}$, the true equilibrium constant. K_2 was calculated from $K_1^{(t)}$ and $K_1^{(a)}$ using the relationship

$$K_2^{\,2} = \frac{(K_1^{(t)} - K_1^{(a)})K_1^{(t)}}{2(C\alpha f_\pm)^2 K_1^{(a)}} \tag{13}$$

After adjusting $K_1^{(t)}$ to give the most constant set of K_2 values, the two constants were combined with $f_\pm$ from equation 8, and $y_\pm$ was computed for comparison with the experimental values. The results are given in Table II and are shown graphically in Fig. 2. In this figure, the solid line represents the smoothed activity coefficient curve obtained from e.m.f. and transference number data, and the circles represent the calculated values using $K_1 = 9.6 \times 10^{-3}$, $K_2 = 23$. These compare very favorably with the values of 9.2×10^{-3} and 18.5

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[13] E. Becker, R. H. Lindquist and B. J. Alder, *J. Chem. Phys.*, **25**, 971 (1956).

[14] Ref. 6, p. 66.

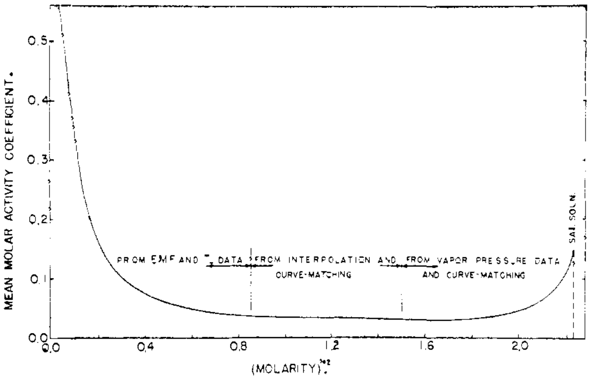

Fig. 3.—Mean molar activity coefficient of sodium in ammonia over the entire range of solubility.

obtained from the sodium ion conductance.[10] The deviation of the experimental curve from the calculated curve at low concentrations is probably due to an error in the e.m.f. measurements. The low concentration region of the e.m.f. curve (Fig. 1) is based upon only two points. Since a dilution method was used by Kraus, decomposition of the dilute solutions could easily account for the deviations.

TABLE II

COMPARISON OF OBSERVED AND CALCULATED ACTIVITY COEFFICIENTS FOR DILUTE SOLUTIONS

$M \times 10^2$	$y_\pm$ (l. mole^{-1}) Calcd.	Obsd.
0.251	0.576	0.527
.398	.504	.504
.502	.466	.464
.794	.388	.387
1.000	.350	.348
1.59	.277	.276
2.51	.213	.216
3.98	.161	.166
6.31	.119	.125
10.0	.087	.095

The vapor pressure data of Kraus, Carney and Johnson[15] were used to compute activity coefficients in the concentrated range based upon pure sodium metal as the standard state. The data of Marshall and Hunt,[2a] obtained at −45.4°, could not be used because of the presence of a two-phase region from mole fraction, $X_{\text{Na}} = 0.018$ to $X_{\text{Na}} = 0.067$ at this temperature.

Integration of the Gibbs–Duhem equation was performed graphically to obtain the activity of sodium in the concentrated region from the measured activity of ammonia. The method was checked by a second integration of the Gibbs–Duhem equation using the calculated sodium activity. The results agreed with the original values of the ammonia activity.

It was desirable to combine the dilute solution results and the results obtained from vapor pressures even though a considerable concentration gap remained between the two sets of measurements. Since two different standard states are involved, the relationship between activities is

$$(y_\pm C)^2 = k a_{\text{Na}} \qquad (14)$$

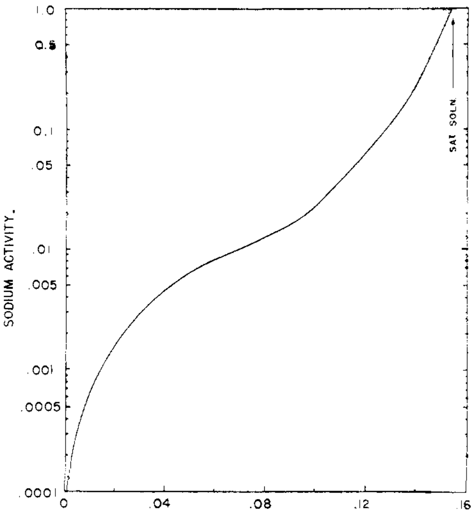

Fig. 4.—Activity of sodium (log scale) in ammonia *versus* mole fraction; standard state is pure solid sodium.

in which a_{Na} is the activity of the sodium based upon pure, solid sodium as the standard state and k is an unknown constant determined by the relative free energies of the two standard states. For the process

$$\text{Na}_{(s)} \longrightarrow \text{Na}^+_{(\text{am})} + \text{e}^-_{(\text{am})}$$

hypothetical, ideal one molar solution

$$\Delta F^0_\pm = -RT \ln k \qquad (15)$$

From (14) we can write

$$\log (y_\pm C)^2 = \log k + \log a_{\text{Na}} \qquad (16)$$

This suggested a method of evaluation of k.[16] Separate sheets of semi-log paper were used with $(y_\pm C)^2$ plotted *versus* C on one sheet and a_{Na} *versus* C on the other. The two sheets of graph paper were then moved vertically until the two sets of data could be connected by a smooth curve. The value of k was given by the ratio of the readings on the two semi-log axes for any concentration. The results are given in Table III and are shown graphically in Figs. 3 and 4. The value of k is 0.54.

TABLE III

ACTIVITY OF SODIUM IN AMMONIA OVER THE ENTIRE RANGE OF SOLUBILITY

X_{Na}	Molarity	a_{Na}[a]	$y_\pm$[b]
0.154	4.97	1.000	0.148
.143	4.65	0.294	.0860
.125	4.16	.0845	.0516
.100	3.43	.0234	.0328
.0833	2.93	.0139	.0296
.0625	2.27	.00872	.0304
.0476	1.77	.00596	.0322
.0278	1.07	.00262	.0354
.0196	0.762	.00153	.0379
.0164	.641	.00118	.0396
.0100	.399	.000642	.0468
.00505	.200	.000317	.0647

[a] Based upon pure sodium as the standard state. [b] Based upon the hypothetical, ideal, one molar standard state.

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(15) C. A. Kraus, E. S. Carney and W. C. Johnson, THIS JOURNAL, **49**, 2206 (1927).

(16) We are indebted to Professor R. H. Schwendeman for pointing out the feasibility of this method.

Discussion

The activity coefficient data in dilute solutions are certainly compatible with the ion-pairing and dimerization equilibria. The close agreement of the constants with those obtained from λ_+ data lends added support to the assumption that these two equilibria are involved. As with the conductance data the results reported here cannot distinguish between an ion-pair and a monomer unit.

Figure 3 shows that the mean molar activity coefficient is nearly constant over a very large concentration region. The extremes are only 25% apart, from 0.64 to 3.76 molar. Over this range, the mean ionic activity is nearly proportional to the total concentration, and the solution behaves as a nearly "ideal" binary electrolyte.

Figure 4 shows the variation of total activity (on a semi-log scale) with concentration. The inflection in the curve reflects the fact that in this concentration range at a temperature only 8.5 degrees below this, the system separates into two phases.

These results permit calculation of the standard free energy change for the solution process. For the process, $Na_{(s)} \rightarrow Na^+_{(am)} + e^-_{(am)}$, the values are:

(1) To form the hypothetical ideal solution, $C = 1$; $\Delta F_1^0 = +0.3$ kcal. mole^{-1}. (2) To form the hypothetical ideal solution, $m = 1$; $\Delta F_2^0 = -0.1$ kcal. mole^{-1}. (3) To form the hypothetical ideal solution, $X_{Na} = 1$; $\Delta F_3^0 = +3.8$ kcal. mole^{-1}.

These data can be combined with heat of solution data,[2b] which give $\Delta H^0 = +4.4$ kcal. mole^{-1}, to yield $\Delta S_1^0 = 17.1$ cal. deg.$^{-1}$ mole^{-1}; $\Delta S_2^0 = 18.7$ cal. deg.$^{-1}$ mole^{-1}; $\Delta S_3^0 = 2.5$ cal. deg.$^{-1}$ mole^{-1}. Using the value of 12.6 cal. deg.$^{-1}$ mole^{-1} for the partial molal entropy of sodium ion[2] and 10.8 cal. deg.$^{-1}$ mole^{-1} for the entropy of sodium at $-33.5°$ [17] gives $\bar{S}^0 = 16.9$ cal. deg.$^{-1}$ mole^{-1} (hypothetical ideal, $m = 1$) for the solvated electron.

Since extrapolation and interpolation were used extensively and also because smoothed curves were used for ϵ and T_+, we attempted to estimate the error in the final result. The estimate of the probable error in the smooth T_- curve is $\pm 0.6\%$.[10] Since T_- varies from 0.86 to 0.94 over the range studied, the probable error in T_+ is about $\pm 7\%$. The error in ϵ is not easy to estimate, but it is certainly less than the error in T_+ at high concentrations. The root mean square deviation of $\frac{\Delta \epsilon}{\Delta \log C}$ from a smooth curve is $\pm 4.6\%$ (probable error $= \pm 3\%$). Combination of all effects leads to an estimated probable error in $y_\pm / y_{\pm\,ref}$ ranging from 0.8% at 0.01 molar to 9.6% for a 0.63 molar solution. Because of extrapolation errors, this increases to about 16% at the point of tie-in with the vapor pressure data. Another uncertainty is introduced by choosing α_{ref} from conductance data, with the magnitude of this error unknown because of the dependence upon the conductance function chosen to represent the behavior of the ions. However, a rough estimate may be made based upon the experimental error. The estimated probable error in α_{ref} (6%) leads to an error of 4.2% in $y_{\pm ref}$. The combined effects give a probable error in $y_\pm$ varying from 4.3% at 0.01 molar to 10.5% at 0.63 molar. Consideration of all of these effects leads to an estimate of the probable error of ΔF^0 of ± 0.36 kcal. mole^{-1} which gives an uncertainty of ± 1.8 cal. deg.$^{-1}$ mole^{-1} for ΔS^0 assuming ΔH^0 to be accurate to ± 0.1 kcal mole^{-1}.

Acknowledgment.—The authors express appreciation to the U. S. Atomic Energy Commission for financial support of this research.

(17) F. Simon and W. Zeidler, *Z. physik. Chem.* (*Liepzig*), **123**, 383 (1926); National Bureau of Standards, *Circular 500*, "Selected Values of Chemical Thermodynamic Properties," 1952, p. 447.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, GEOLOGY AND PHYSIOLOGY AND THE INSTITUTE FOR THE STUDY OF METALS, UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS]

Apparatus and Methods for Low Temperature Heat Capacity Measurements. The Heat Capacity of Standard Benzoic Acid

BY ARTHUR G. COLE, JOHN O. HUTCHENS, R. A. ROBIE AND J. W. STOUT

RECEIVED OCTOBER 15, 1959

An apparatus and methods for the measurement of low temperature heat capacities of solids are described. The methods of correcting the data for heat interchange and for thermal gradients within the calorimetric system, as well as other necessary corrections, are discussed. The heat capacity of a Calorimetry Conference standard sample of benzoic acid has been measured in the temperature range between 10 and 300°K. and the results are compared with data from the National Bureau of Standards and from other laboratories.

For some ten years there has been in use in this Laboratory apparatus for measuring the heat capacity of solids in the temperature range between 10 and 320°K. Since the apparatus and particularly the method used for calculating the corrected heat capacities from the experimentally measured quantities differ in some respects from those described in the literature, they will be briefly described in the present paper. In order to check on the accuracy of our heat capacity measurements, we have measured the heat capacity of a standard sample of benzoic acid, and the results are presented in this paper.

Apparatus

Cryostat and Calorimeter.—The heat capacity apparatus is of the "isothermal" type consisting of a vacuum insulated calorimeter surrounded by a massive shield (called the "block") whose temperature remains nearly constant during a heat capacity measurement. The construction of this block and of the outer parts of the cryostat is similar