Agreement was very satisfactory at *d* values of 1.50 or less.

TABLE II

X-RAY DATA. ALUMINUM(III) IODIDE

Sample I *d*	Sample I I/I_1 (est.)	Sample II *d*	Sample II I/I_1 (est.)	Literature[15] *d*	Literature[15] I/I_1
				3.70	0.05
3.35	1.0	3.43	1.0	3.50	1.00
2.96	0.5	2.98	0.4	3.08	0.50
				2.98	.05
2.10	.7	2.13	.8	2.14	.50
1.80	.9	1.82	.8	1.84	.38
1.77	.2	1.80	.2	1.80	.10
1.73	.2	1.74	.2	1.75	.13

The differences in the highest *d*-values for the two samples may be due to a very slight hydrolysis, which had occurred during the time the capillaries were being loaded. This hydrolysis was evidenced by the development of a very faint yellow tinge, instead of the original pure white powder. The material giving the lower *d*-values had the fainter color, and would be expected to be the purer. Since Hanawalt, Rinn and Frevel do not give their method of preparation of aluminum(III) iodide, nor the purity of the material used in their work, no conclusion from the comparison of results can be drawn.

CAMBRIDGE, MASSACHUSETTS RECEIVED MAY 31, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Electrode Potentials in Liquid Ammonia. I. Activities of Potassium and Sodium Chlorides

BY JACOB SEDLET[1] AND THOMAS DE VRIES

The activity coefficients of potassium and sodium chloride in liquid ammonia at −36° were determined from electromotive force measurements of cells of the type: K(Hg), KCl(m), $ZnCl_2 \cdot 6NH_3$(s), Zn(Hg) and Na(Hg), NaCl(m), $ZnCl_2 \cdot 6NH_3$(s), Zn(Hg). The closest distance of approach of the ions and the degree of hydration was estimated according to the method of Stokes and Robinson.

In the development of the chemistry and thermodynamics of liquid ammonia solutions the investigation of galvanic cells should prove as valuable as with aqueous systems. While several cells employing liquid ammonia as the solvent have been measured, liquid junction potentials were present in most cases, and no attempt was made to extrapolate the data to obtain the standard potentials. Several investigators[2] have studied cells of the type: M, MA, M'A', M', where M and M' are metals and MA and M'A' are soluble salts of the metals. In most cases a salt bridge was interposed between the two half cells.

Two cells free from liquid junction potentials have been measured at 25°. Elliott and Yost[3] measured the cell: Zn(Hg), $ZnCl_2 \cdot 6NH_3$(s), NH_4Cl(m), Tl(s), Tl(Hg), and Garner, Green and Yost[4] the cell: Zn(Hg), $ZnCl_2 \cdot 6NH_3$(s), NH_4Cl(m), $CdCl_2 \cdot 6NH_3$(s), Cd(Hg). These cells were found to behave reversibly.

In this work the zinc amalgam, zinc chloride electrode was combined with alkali metal amalgam electrodes to form the cells: K(0.2756% amalgam), KCl(m), $ZnCl_2 \cdot 6NH_3$(s), Zn (2 phase amalgam), and Na(0.2000% amalgam), NaCl(m), $ZnCl_2 \cdot 6NH_3$(s), Zn (2 phase amalgam). The composition of solid zinc chloride under the experimental conditions was determined by Biltz and Messerknecht.[5] In the present investigation a stationary pool of amalgam was used, and no reaction between the amalgam and the ammonia could be observed. The cells were measured at −36°, using amalgams of constant composition and varying the salt concentration from approximately 0.002 molal to saturation.

Since no data on the solubility of zinc chloride could be found in the literature, this quantity was determined at −36°. The dielectric constant of liquid ammonia at −36° was also measured since it was needed in the calculations.

Experimental

Materials.—Commercial anhydrous ammonia was dried over sodium and passed through a sintered glass plug to remove solid particles before being condensed in the apparatus.

Zinc amalgam was prepared by electrolyzing a zinc sulfate solution between a mercury cathode and platinum anode until a two-phase amalgam, containing about 2% zinc, was obtained. Potassium and sodium amalgams were prepared by similarly electrolyzing a solution of their carbonates until the desired concentration was obtained. The amalgams were stored over nitrogen.

All salts, except zinc chloride, were reagent grade and were further purified by recrystallization. Zinc chloride was prepared by electrolyzing a zinc sulfate solution with platinum electrodes and dissolving the metal in hydrochloric acid. The solution was evaporated to dryness and the salt dehydrated by heating in a vacuum prior to use.

Apparatus and Procedure.—The thermostat consisted of a one gallon dewar vessel filled with acetone and cooled by alcohol circulated by a centrifugal pump through Dry Ice and then through the bath. A bimetallic regulator controlled the operation of the pump as the bath temperature varied. Temperatures were measured with a five junction copper–constantan thermel calibrated at the sublimation point of carbon dioxide. All measurements were made at −36 ± 0.05°.

The electromotive force cell was of the conventional type with platinum wires sealed into the bottom of the H-cell which was closed at the top with ball and socket joints. A sintered glass plug in the cross arm prevented solid zinc chloride from coming over into the sodium amalgam compartment. The amalgams and zinc chloride were put into the cell with a stream of dry and oxygen-free nitrogen passing through the apparatus. Solutions of salts in liquid

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[1] Abstracted from the Ph.D. thesis of J. Sedlet, whose present address is Argonne National Laboratory, Chicago, Ill.

[2] F. M. G. Johnson and N. T. M. Wilsmore, *Trans. Faraday Soc.*, **3**, 77 (1907); G. I. Costeanu, *Compt. rend.*, **195**, 778 (1932); **197**, 1113 (1933); V. A. Pleskov and A. M. Monossohn, *Acta Physiochim.* (*U. R. S. S.*), **1**, 871 (1935); **2**, 615 (1935); **6**, 1 (1937); **13**, 659 (1940); **21**, 235 (1946).

[3] N. Elliott and D. M. Yost, THIS JOURNAL, **56**, 1057 (1934).

[4] C. S. Garner, E. W. Green and D. M. Yost, *ibid.*, **57**, 2055 (1935).

[5] W. Biltz and C. Messerknecht, *Z. anorg. Chem.*, **129**, 161 (1923).

ammonia were prepared in a separate side arm fitted with a magnetically operated stirrer. The solutions were forced over into the H-cell by a slight excess of ammonia gas under pressure.

The potentials reached a constant value in from two to five hours, depending on the concentration, and were observed for about four hours after becoming constant. The readings varied from ±0.1 mv. for the most concentrated solutions to ±0.3 mv. for the most dilute.

Samples of the alkali amalgams were analyzed each time they were used. The concentration of the potassium amalgam remained constant, but not the sodium amalgam. Hence cells were also measured in which the sodium chloride concentration was kept constant, and the composition of the amalgam varied. From these results the potentials of the cells in which the sodium chloride concentration varied were corrected to a sodium concentration of 0.2000 per cent. The concentration of the potassium amalgam was 0.2756 per cent.

The solubility of zinc chloride in liquid ammonia at −36° was determined to be $(1.70 \pm 0.05) \times 10^{-4}$ molal. The apparatus consisted of a closed glass vessel fitted with a magnetically operated glass stirrer so that about 50 ml. of liquid ammonia could be saturated with zinc chloride. After stirring for five hours, the solution was forced over through a sintered glass plug into a graduated vessel. After the ammonia was evaporated, the salt remaining was dissolved in dilute hydrochloric acid and analyzed for zinc with a polarograph.

The dielectric constant was measured with a General Radio Company Type 916-A Radio Frequency Bridge at a frequency of 4.110 Mc./sec. The liquid ammonia had a specific conductance of 10^{-6} mho. Three determinations of the dielectric constant gave values of 23.6, 23.8 and 23.8. These values plot favorably with data given by other workers at various temperatures.

Calculations and Results

To obtain the standard potentials of the cells, the electromotive force data (Tables I and II) were extrapolated according to the method of Hitchcock.[6] For the cell with sodium chloride as electrolyte, the reaction for the passage of one faraday of current is: $Na(Hg) + 1/2ZnCl_2 \cdot 6NH_3(s) = NaCl(m) + 1/2Zn(Hg) + 3NH_3$. The e.m.f. of the cell is given by

$$E = E^{\circ\prime} - \frac{2RT}{F} \ln m - \frac{2RT}{F} \ln \gamma - \frac{3RT}{F} \ln a_{NH_3} \quad (1)$$

Since the concentration of amalgam was maintained constant, the alkali metal activity is not included in equation (1) and the standard potential designated as $E^{\circ\prime}$. The molal activity coefficient γ of a uni-univalent electrolyte is given by the Debye–Hückel theory.

$$\log \gamma = -\frac{1.824 \times 10^{-6}}{(DT)^{3/2}} \sqrt{C} + BC - \log (1 + 0.034\, m) \quad (2)$$

In this equation D is the dielectric constant and the concentration is given in moles per liter. Equation (1) can be rewritten with the aid of equation (2) to give an expression suitable for extrapolation: $E + 0.09409\, m - 0.3372\sqrt{m} - 0.09409 \log (1 + 0.034\, m) = E^{\circ\prime\prime} = E^{\circ\prime} - B'm$. Two approximations were made in obtaining the latter equation. The concentration of electrolyte in volume units was approximated from the molality by the relation $c = dm$, with $d = 0.6851$ g./ml., the density of ammonia. The activity of ammonia in these solutions is not known, and was assumed to be unity. These approximations will not affect the extrapolation since they become valid in dilute solutions.

TABLE I

DATA FOR CELL: K(0.2756% amalgam), KCl(m), $ZnCl_2 \cdot 6NH_3(s)$, Zn(2 phase amalgam)

m	E	$E^{0\prime\prime}$	γ	γ'
0.001492	0.3834	0.1045	0.740	0.740
.001923	.3750	.1047	.705	.705
.003204	.3575	.1037	.650	.650
.004696	.3457	.1035	.591	.591
.01398	.3147	.1003	.425	.425
.01426	.3137	.0997	.426	.427
.02151	.3042	.0978	.356	.357
.02266	.3027	.0972	.351	.352

By extrapolation, $E^{0\prime} = 0.1052$

TABLE II

DATA FOR CELL: Na(0.2000% amalgam), NaCl(m), $ZnCl_2 \cdot 6NH_3(s)$, Zn(2 phase amalgam)

m	E	$E^{0\prime\prime}$	γ	γ'
0.002148	0.4835	0.2198	0.700	0.700
.002763	.4762	.2196	.666	.666
.004968	.4559	.2186	.591	.591
.008551	.4421	.2179	.500	.500
.01518	.4262	.2150	.416	.417
.01719	.4235	.2142	.398	.399
.03014	.4106	.2098	.313	.314
.03528	.4073	.2083	.288	.289
.04427	.4014	.2053	.257	.258
.07497	.3952	.1974	.185	.186
.09220	.3892	.1909	.169	.170
.1058	.3865	.1868	.156	.157
.1399	.3820	.1762	.135	.136
.2666	.3752	.1482	.0826	.0834
.2779	.3739	.1447	.0822	.0831
.4316	.3702	.1157	.0569	.0578
.5283	.3672	.0958	.0520	.0531

By extrapolation, $E^{0\prime} = 0.2208$

According to the above equation, a plot of the left member, designated as $E^{\circ\prime\prime}$, against m should be a straight line with the ordinate equal to $E^{\circ\prime}$ at $m = 0$. For the more concentrated solutions this curve showed some curvature, but approached linearity in dilute solutions such that reasonable extrapolations were possible for both cells.

The activity coefficients of potassium and sodium chloride were calculated by means of equation (1). The coefficients which were calculated assuming the activity of the ammonia to be unity are given in the columns headed γ in Tables I and II. To obtain the true activity coefficients it is necessary to know the activity of ammonia. A reasonable approximation for this quantity may be obtained by using the mole fraction of ammonia, assuming the solute to be 50% dissociated. The coefficients so calculated are given in the column headed γ'. An examination of the data showed that the coefficients approach those predicted by the Debye–Hückel limiting law in dilute solutions. The deviations, however, increased more rapidly with increasing concentration in ammonia than in water at equal concentrations.

Stokes and Robinson[7] proposed a modification of the Debye–Hückel equation, introducing a term to correct for the solvation of the ions and a

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[6] D. I. Hitchcock, THIS JOURNAL, **50**, 2076 (1928).

[7] R. H. Stokes and R. A. Robinson, *ibid.*, **70**, 1870 (1948).

term to convert from rational to molal activity coefficients. They were able to reproduce, quantitatively, the experimental activity coefficients in aqueous solution of a large number of electrolytes up to four and five molal. It is of interest to determine if the equation is valid for liquid ammonia solutions and, if so, to compare solvation in water and ammonia. The parameters were varied to obtain the best fit to the data for sodium chloride. The results are given in Table III. Good agreement was obtained for $a = 3.53 \pm 0.02$ Å., and $n = 2.5 \pm 0.2$ with an average difference between the calculated and observed coefficients of 4 in the third significant figure. Stokes and Robinson found for sodium chloride in water solution that $a = 3.97$ Å. and $n = 3.5$. This difference between the two solvents is reasonable in view of their dielectric constants.

TABLE III

COMPARISON OF EXPERIMENTAL ACTIVITY COEFFICIENTS OF SODIUM CHLORIDE WITH THOSE CALCULATED BY EQUATION OF STOKES AND ROBINSON

Parameters: $a = 3.53$; $n = 2.5$

m	$\gamma_{\text{exptl.}}$	$\gamma_{\text{calcd.}}$
0.001	(0.780)	0.778
.002	.705	.706
.003	.655	.658
.005	.589	.588
.01	.480	.484
.02	.372	.377
.05	.242	.245
.10	.160	.164
.20	.104	.103
.30	.0767	.0775
.40	.0614	.0629
.50	.0540	.0535

The hydration parameter could not be determined for potassium chloride since the terms in the equation containing n are negligible at the highest concentration used. The parameter, a, was determined by fitting the data to the Debye–Hückel equation for uni-univalent electrolytes, $\log \gamma = -A\sqrt{m}/(1 + aB\sqrt{m})$, where A and B are constants equal to 3.5835 and 0.3922, respectively. A value for a of 3.3 ± 0.1 Å. reproduces the data to ± 0.003 in γ. A value of 3.63 was found by Stokes and Robinson for potassium chloride.

LAFAYETTE, IND. RECEIVED JUNE 18, 1951

[CONTRIBUTION NO. 804 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Thermal Properties of the Alkali Metals. I. The Heats of Reaction of Sodium and Potassium with Water at 25°[1,2]

BY EUGENE E. KETCHEN AND W. E. WALLACE

The heats of reaction of potassium and sodium with an infinite quantity of water at 25° were measured and found to be $-47{,}190 \pm 80$ and $-44{,}350 \pm 70$ calories/gram atom, respectively. These results are in reasonably good agreement with other recent determinations except for Roth and Kaule's work on the sodium–water reaction.

Introduction

While determining the heats of formation of sodium–potassium alloys reported in the following paper, it became necessary to have reliable values for the heats of reaction of the two pure metals with water. Since several earlier determinations of these heat effects led to somewhat divergent results,[3,4] particularly for potassium, it seemed desirable to carry out a redetermination of these important thermochemical quantities in the hope that more reliable values might emerge. The measured heat effects are of interest not only for their use in obtaining heats of alloying but also because much of the thermochemical information pertaining to sodium and potassium compounds depends on the determinations of the heat produced when the metals react with water.

Experimental Methods

Calorimeter.—The calorimeter employed in this study was the instrument constructed for studying the heats associated with the formation of ionic solid solutions.[5] Constructional details and operating characteristics have been reported in connection with that work. The only modification needed in the present study was the replacement of the crushing devices used to introduce the salts into the calorimeter by a special chamber for carrying out the metal–water reaction.

The reaction chamber consisted essentially of a monel rod drilled out to receive the reactants and nickel plated on the interior to improve its corrosion resistance to the alkaline solution produced. Its operation will be made clear in the discussion which follows.

In a typical experiment approximately 0.002 to 0.006 gram atom of alkali metal contained in a crushable glass bulb was allowed to react with about 20 g. of water. From 90 to 270 calories of heat were developed, being communicated for the most part to water (about 1 kg.) surrounding the reaction chamber.

There are several sources of difficulty customarily associated with experiments of this type. These have presumably been eliminated in the reaction chamber used. Much of the trouble stems from the violence with which the reaction takes place. In such reactions the reactants are frequently blown apart before the process has gone to completion. To minimize this possibility a series of baffles was provided. Evidently these baffles were very effective in confining the reactants for the relatively short reaction time for if any alkali metal had been thrown up and lodged above the water level, reaction would have been continued with water vapor and this mishap would have been recognized by the thermal response of the calorimeter toward the conclusion of an experiment. With the chamber employed no such behavior was ever observed. In preliminary experiments using a chamber of a somewhat different design a slow

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[1] From a thesis submitted to the University of Pittsburgh by Eugene E. Ketchen in partial fulfillment of the requirements for the Doctor of Philosophy degree, August, 1950.

[2] This work was assisted by the Office of Naval Research and the Atomic Energy Commission.

[3] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

[4] W. A. Roth and H. L. Kaule, *Z. anorg. Chem.*, **253**, 352 (1947).

[5] M. A. Fineman and W. E. Wallace, THIS JOURNAL, **70**, 4165 (1948).