versely proportional to the density of conducting electrons. Using

$$R_H = -\frac{1}{ne}$$

where n is the number of conduction electrons per cc. and e is the electronic charge in coulombs, we find 5×10^{17} as a lower limit for the number of free electrons per cc. This figure is in substantial agreement with the number 10^{18} absorbing centers per cc. deduced from very crude measurements of the intensity of infrared absorption by powdered Cu_xWO_3.

In view of the crudity of our Hall voltage measurement, only qualitative significance can be given to the numerical comparison offered above. We are now in the process of refining our measurements to make the comparison more meaningful. In addition, we are extending our investigations to newly prepared $Pb_{0.4}WO_3$, which seems to be typically metallic, and to $Ag_{0.4}WO_3$, which is apparently semi-conducting.

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Free Energy Change and the Electron Electrode in Liquid Ammonia

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The standard free energy change for the reaction $Na_{(s)} \rightarrow Na^+_{(NH_3)} + e^-_{(NH_3)}$ has been determined experimentally by combining measurements on two types of galvanic cells: Na|NaI in liquid ethylamine|Na amalgam, for which the standard e.m.f. was found to be 0.828 ± 0.000 and 0.835 ± 0.001 volt at −50 and −70°, respectively, and Na amalgam|NaI in liquid ammonia||Na in liquid ammonia|inert metal, for which the standard e.m.f. was found to be −0.933 ± 0.020 volt at −50° and −0.947 ± 0.020 volt at −70°. These results have been used to obtain directly an experimental value for the solvation free energy of sodium ion in ammonia. Measurements are also reported for the distribution of sodium between mercury and liquid ammonia.

The existence of ion-like electrons in sodium-liquid ammonia solutions[2] suggests the possibility of constructing a galvanic cell which would give directly the free energy change for the reaction

$$Na_{(s)} \longrightarrow Na^+_{(NH_3)} + e^-_{(NH_3)}$$

The most obvious design—solid sodium as one electrode and an inert metal as the other, both immersed in the same solution of sodium in liquid ammonia—gives no useful information because the over-all cell reaction shown above comes to equilibrium as a dissolution equilibrium at the solid sodium–liquid ammonia interface. To bypass this difficulty, we have constructed two cells—in one of which the dissolution equilibrium was completely suppressed by amalgamation of the sodium and in the other of which the effect of such amalgamation on the voltage was determined. The two types of cells and their designations in this paper are

Cell I $Na_{(s)}|NaI\ in\ EtNH_2|Na_{(Hg)}$

Cell II $Na_{(Hg)}|NaI\ in\ NH_3||Na\ in\ NH_3|inert\ metal$

Before describing the structure and operation of these cells, we note two problems that arose in the course of this research. In order to choose an amalgam concentration that would be sufficient to repress the sodium dissolution equilibrium, it was necessary that we investigate the distribution of sodium between mercury and liquid ammonia. The second problem dealt with the choice of metal to use as an inert "electron electrode" in liquid ammonia. Kraus[3] in his work on transference numbers and Laitinen and Nyman[4] in their polarographic work with the "electron electrode" used platinum as the inert conductor. For ease in constructing the complicated closed systems of glass required to keep the sodium–ammonia solutions away from air, we used tungsten. However, since tungsten does not give reproducible results when used as an electrode in aqueous solutions, it was necessary that we show for ammonia solutions that platinum and tungsten electrodes give substantially equivalent results.

Experimental Procedure

Preparation of Materials.—All procedures were carried out in a high vacuum chain capable of producing pressures less than 1×10^{-6} mm. Degassing and baking out were carried out where needed. Ammonia, obtained from Matheson as anhydrous 99.9% pure, was triply distilled from its solutions with sodium before use. Sodium, obtained from Mallinckrodt, was purified by the method of Watt and Sowards.[5] Ethylamine, obtained from Eastman Kodak as a 33% solution in water, was first concentrated by distilling it off from a slurry of calcium oxide and then purified by redistilling it from its solution of lithium metal. Sodium iodide, Baker and Adamson reagent grade, was used directly without further purification except for drying. Mercury for the amalgams was scrubbed in a mercury oxifier, washed with nitric acid and triply distilled before use.

Distribution Experiments.—The distribution of sodium between mercury and liquid ammonia was determined in an all-glass system with a built-in pipet which served both to introduce gas for stirring the liquid ammonia solutions and to take samples of the solutions for analysis. In operation, a sodium–ammonia solution was formed in an outer jacket and a weighed amount of mercury dropped in through a ball-and-socket valve manipulated from the outside. Prepurified hydrogen bubbled through the pipet tip served to mix the solution. A pair of tungsten electrodes sealed through the outer jacket wall enabled concentration changes in the solution to be followed from measurements of the a.c. electrical resistance. After distribution equilibrium had been established, hydrogen pressure could be applied to force a sample of the ammonia solution into the pipet. Distribution experiments were also performed in which

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(1) On leave of absence at the Laboratoire de Chimie Minérale, University of Toulouse, Toulouse, France.

(2) See, for example, W. N. Lipscomb, *J. Chem. Phys.*, **21**, 52 (1953).

(3) C. A. Kraus, THIS JOURNAL, **36**, 864 (1914).

(4) H. Laitinen and C. Nyman, *ibid.*, **70**, 3002 (1948).

(5) G. W. Watt and D. M. Sowards, *ibid.*, **76**, 4742 (1954).

equilibrium was approached from the other side—that is, ammonia was added to a sodium amalgam.

After a sample of the ammonia phase had been taken, the apparatus was quenched in liquid nitrogen, the outside tube was detached, and the ammonia in the outside jacket and in the pipet separately evaporated off into measured volumes of standard sulfuric acid. Sodium in the pipet was determined by washing it out with ethanol and water and titrating the wash solution with standard acid. Total sodium in the jacket was determined similarly after washing out the sodium and the sodium amalgam, boiling with water until all reaction between amalgam and water had ceased, and titrating.

Cell I.—The "sodium-sodium amalgam" cell consisted essentially of an inverted "Y" tube with a tungsten electrode sealed into each arm of the "Y." The sodium electrode was formed by melting sodium around the tungsten in one arm; the sodium amalgam electrode, by breaking a sodium-containing ampule into a mercury pool in the other arm. Ethylamine could then be condensed into the cell on sodium iodide which had been added previously. For reproducible voltages, it was found necessary that the leads from the tungsten wires to the outside of the thermostat bath be insulated from the bath by lengths of glass tubing sealed to the cell. Furthermore, it was found that the observed cell voltage could vary as much as 10 to 20 millivolts from one run to the next unless the amalgam electrodes were annealed for at least an hour just below their eutectic temperature of −47°.

Cell II.—The "sodium amalgam-electron electrode" cell consisted essentially of an "H," with a tungsten electrode sealed in each leg of the "H" and a fritted glass disk in the cross-bar. The disk was originally of medium porosity but for our purposes it had been almost completely fused closed by careful heating around the edge. By trial and error it was possible to produce a disk which effectively prevented liquid transfer between the two compartments but still gave a reasonably low electrical resistance. For filling cell II, a weighed quantity of mercury, a weighed ampule of sodium, and a weighed quantity of sodium iodide were placed in one compartment and a weighed ampule of sodium in the other. Ammonia could then be distilled into the cell after evacuation and degassing of the fritted disk. Usually the voltage settled down in a matter of minutes but data were not considered reliable unless the voltage remained constant within two millivolts for at least an hour. In contrast to cells of type I, which essentially lasted indefinitely, the lifetime of cells of type II was only four or five hours, after which time the e.m.f. became somewhat erratic. This onset of erratic behavior was attributed to autocatalytic decomposition of the sodium-ammonia solution at the fritted disk. For analysis, ammonia was boiled off into measured volumes of standard sulfuric acid. With the pressures involved, only a negligible amount of ammonia could have been forced through the fritted disk.

Temperature Control and Measurement.—The distribution apparatus was thermostated by immersion in a large test-tube of boiling liquid ammonia, the temperature of which was −33.2 ± 0.2°. Cells I and II, which were run at both −50 and −70°, were immersed in a large Dewar flask filled with cold acetone. The bath was stirred mechanically, and the temperature was regulated manually by the addition of small pieces of Dry Ice. The temperature could be kept constant to ±0.2° by this method. More precise control was not necessary because it was observed that the thermal coefficients of the cells were low. Temperatures were measured by means of a copper-constantan thermocouple and a Leeds and Northrup Portable Precision Potentiometer. The junctions were immersed in tubes of paraffin oil with the reference junction kept at the ice point. The thermocouple was calibrated at the ice point, the freezing point of mercury and the CO_2 point.[6]

Test for Reversibility.—The thermodynamic reversibility of a galvanic cell can be determined by applying an external voltage to the cell just sufficient to balance its e.m.f. and then changing the external voltage infinitesimally so as to pass current in opposite directions through the cell.[7] If the electrode reactions are reversible, there should be no discontinuity in the voltage-current proportionality at the null point. In this research, we measured the voltages in the external circuit which were required to produce small galvanometer deflections on either side of the null point. Since the galvanometer was in series with the cell under investigation, its deflection was a measure of the current through the cell. For each of the cells studied, such a plot of external voltage *vs.* current produced a straight line.

Platinum-Tungsten Equivalence Test.—To test platinum and tungsten as equivalent electron electrodes, cell I was modified by the insertion of a piece of copper wire on the end of which was soldered a strip of platinum wire. With sodium-ammonia solution in the cell the voltage between the platinum and each of the tungsten electrodes was observed to be 0.00006 ± 0.00001 volt; it did not change from one tungsten electrode to the other. It may be that even this voltage was due not to any real difference between tungsten and platinum but rather to a small temperature gradient at the copper-to-platinum junction, which was only a few cm. below the level of the surrounding external thermostat bath.

Results

Distribution Experiments.—The distribution experiments were performed (1) by adding mercury to a solution of sodium in liquid ammonia and (2) by adding ammonia to a concentrated sodium amalgam. In every experiment of the first set, all of the sodium was extracted from the ammonia by the mercury. This by itself is not significant since geometrical considerations limited us to quantities of reagents such as to preclude formation of a sodium amalgam richer than 6.0 atomic % sodium. In the second set of experiments, four quite concentrated amalgams were equilibrated with liquid ammonia. The distribution results are shown in Table I. It is evident that the most dilute of these concentrated amalgams, even though it already contains 36.4 atomic % sodium, is still too dilute to allow any detectable sodium in the ammonia phase. Since in the following cells we did not exceed 2.5 atomic % sodium for the composition of the amalgam electrode, we can be reasonably sure that the dissolution equilibrium of sodium in ammonia has been completely repressed.

TABLE I

DISTRIBUTION OF SODIUM BETWEEN MERCURY AND LIQUID AMMONIA AT −33.2°

Amalgam	Equilibrium mole fraction of sodium Ammonia phase	 Mercury phase
1	Not measurable	0.364
2	2.10×10^{-4}	.503
3	6.15×10^{-3}	.582
4	1.12×10^{-2}	.603

Cell I.—Of the two "sodium-sodium amalgam" cells that were prepared, the first showed 0.8277 ± 0.0005 volt at −50° and 0.8331 ± 0.0003 volt at −70° and the second, 0.8284 ± 0.0002 volt at −50° and 0.8364 ± 0.0009 volt at −70°. As an average, we have taken the values

$$\text{at } -50^\circ \qquad E = 0.828 \pm 0.000 \text{ v.}$$

$$\text{at } -70^\circ \qquad E = 0.835 \pm 0.001 \text{ v.}$$

Cell II.—For the "sodium amalgam-electron electrode" cells, the observed voltages at −50° and at −70° are shown in Table II. The column headed "Sodium, *m*" indicates the concentration of sodium in the liquid ammonia adjacent to the "electron electrode" and the column headed

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[6] American Institute of Physics, "Temperature, Its Measurement and Control in Science and Industry," Reinhold Publ. Corp., New York, N. Y., 1941, p. 212.

[7] S. Glasstone, "Introduction to Electrochemistry," Van Nostrand Co., New York, N. Y., 1942, p. 184.

"NaI, *m*" indicates the concentration of sodium iodide in the liquid ammonia adjacent to the "sodium amalgam" electrode. The error limits quoted for E are the observed voltage fluctuations at a given temperature. In addition, there may be an uncertainty of 0.020 volt in each value of E because of possible strains in the sodium amalgam electrode—strains which could not in practice be annealed because of the limited lifetime of the cells.

TABLE II

OBSERVED E.M.F. OF "SODIUM AMALGAM–ELECTRON ELECTRODE" CELLS

Cell	Sodium, m	NaI, m	$-E$ at $-50°$	$-E$ at $-70°$
1	0.209	0.0445	0.6961 ± 0.0004	0.7250 ± 0.0005
2	.210	.172	.7210 ± .0003	.7608 ± .0008
3	.344	.0961	.7165 ± .0002	.7528 ± .0014
4	.377	.0902	.7132 ± .0005	.7411 ± .0012
5	.752	.0763	.6889 ± .0018	.7132 ± .0005

Discussion

For a cell of the type II, the over-all cell reaction can be written

$$\mathrm{Na}_{(\mathrm{Hg})} \longrightarrow \mathrm{Na}^+{}_{(\mathrm{NH}_3)} + \mathrm{e}^-{}_{(\mathrm{NH}_3)}$$

Because the cell contains a liquid junction, the observed voltage, E, includes a liquid junction potential, E_L. Using the Nernst relation, we may write

$$E = E° - \frac{RT}{F} \ln \frac{a_{\mathrm{Na}^+(\mathrm{NH}_3)}\, a_{\mathrm{e}^-(\mathrm{NH}_3)}}{a_{\mathrm{Na}(\mathrm{Hg})}} + E_L \qquad (1)$$

where $E°$ is the standard voltage, $a_{\mathrm{Na}^+(\mathrm{NH}_3)}$ and $a_{\mathrm{e}^-(\mathrm{NH}_3)}$ are the activities of sodium ion and of the electron in liquid ammonia, and $a_{\mathrm{Na}(\mathrm{Hg})}$ is the activity of the sodium in the amalgam. Actually, this last quantity is a constant. The sodium-mercury system[8] shows at 2.5 atomic % sodium an eutectic between pure mercury and the compound NaHg_4 and an eutectic temperature of about $-47°$. Thus, any sodium amalgam having less than 2.5 atomic % sodium, as in our work, when cooled either to -50 or $-70°$, separates into pure mercury and an eutectic mixture of mercury and NaHg_4. Since all the sodium is present only as the compound NaHg_4, we can consider $a_{\mathrm{Na}(\mathrm{Hg})}$ as a constant in eq. 1. If this constant is absorbed into $E°$, eq. 1 becomes

$$E = E°' - \frac{RT}{F} \ln a_{\mathrm{Na}^+} a_{\mathrm{e}^-} + E_L \qquad (2)$$

where $E°'$ indicates the standard e.m.f. referred to the new standard state and the NH_3 subscripts have been omitted for simplicity. Assuming that the activity of the sodium ion and of the electron in ammonia can be represented by the product of a molality m and an activity coefficient γ, we write

$$E = E°' - \frac{RT}{F} \ln m_{\mathrm{Na}^+} m_{\mathrm{e}^-} - \frac{RT}{F} \ln \gamma_{\mathrm{Na}^+} \gamma_{\mathrm{e}^-} + E_L \quad (3)$$

The first and third terms of the equation are known from these experiments; the fourth and fifth need to be estimated in order to find $E°'$.

For the fourth term, because of the scarcity of data on activity coefficients in liquid ammonia, we have had to assume that the single ionic activity coefficients needed are approximately the same (at corresponding concentrations) as those found by Sedlet and DeVries[9] for the mean ionic activity coefficients of sodium chloride in ammonia. Table III shows the numerical values assumed in the different cells and the magnitude of the activity coefficient term that would then appear in eq. 3. The error limits quoted correspond approximately to a 100% error in choice of activity coefficient.

TABLE III

ACTIVITY COEFFICIENTS ASSUMED FOR e^- AND Na^+

Cell	γ_{e^-}	γ_{Na^+}	$-(RT/F) \ln \gamma_{\mathrm{Na}^+}\gamma_{\mathrm{e}^-}$ At $-50°$	At $-70°$
1	0.1	0.3	0.067 ± 0.02	0.061 ± 0.02
2	.1	.1	.089 ± .02	.081 ± .02
3	.07	.2	.082 ± .02	.075 ± .02
4	.06	.2	.085 ± .02	.077 ± .02
5	.04	.2	.093 ± .02	.085 ± .02

The liquid junction potential has been estimated by using the Henderson equation.[10] For a boundary between two solutions of uni-univalent electrolytes, this equation takes the form

$$E_L = \frac{RT}{F} \frac{(U_1 - V_1) - (U_2 - V_2)}{(U_1 + V_1) - (U_2 + V_2)} \ln \frac{U_1 + V_1}{U_2 + V_2}$$

where U_1 is the product of the molality and the ionic mobility of the cation on one side of the boundary and U_2 is the product of the molality and ionic mobility of the cation on the other side of the boundary. V_1 and V_2 are the corresponding quantities for anions. According to Kraus and Bray[11] the ionic mobilities of sodium ions and iodide ions are 1.35×10^{-3} and 1.77×10^{-3} cm. per second, respectively, over a wide range of concentration. The ionic mobilities of electrons in liquid ammonia, as calculated from the transport numbers obtained by Kraus for sodium in liquid ammonia solutions, vary between 4.12×10^{-2} and 8.31×10^{-2} cm. per second over the range of concentrations we used. Columns two and three of Table IV give the results we have calculated for the liquid junction potentials of the various cells. The error limits indicated are those obtained by applying the Henderson equation to aqueous solutions.

The last two columns of Table IV give the results finally calculated from eq. 3 for $E°'$ of each cell. As most probable values for the "sodium amalgam–electron electrode" cell,

TABLE IV

ESTIMATED LIQUID JUNCTION POTENTIALS AND CALCULATED STANDARD E.M.F.'S

Cell	$E_L \pm 0.005$ at $-50°$	$E_L \pm 0.005$ at $-70°$	$-E^{0\prime} \pm 0.05$ at $-50°$	$-E^{0\prime} \pm 0.05$ at $-70°$
1	0.0771	0.0704	0.930	0.938
2	.0544	.0497	.928	.950
3	.0751	.0686	.939	.956
4	.0785	.0716	.942	.949
5	.1033	.0948	.940	.943

we take the following

at $-50°$ $E^{0\prime} = -0.933 \pm 0.02$ v.
at $-70°$ $E^{0\prime} = -0.947 \pm 0.02$ v.

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[8] H. E. Bent and A. F. Forziatti, THIS JOURNAL, **58**, 2220 (1936).

[9] J. Sedlet and T. DeVries, *ibid.*, **73**, 5808 (1951).

[10] S. Glasstone, ref. 7, p. 212.

[11] C. A. Kraus and W. C. Bray, THIS JOURNAL, **35**, 1315 (1913).

For cells of type I, the net reaction is

$$\mathrm{Na}_{(s)} \longrightarrow \mathrm{Na}_{(Hg)}$$

and the observed e.m.f. is given by

$$E = E^0 - \frac{RT}{F}\ln a_{\mathrm{Na}_{(Hg)}}$$

Again, since the concentration of sodium in the amalgam is kept below 2.5 atomic %, the sodium is in the electrode only as NaHg_4 and its activity is a constant. The observed voltage is invariant except with temperature, a prediction that agrees with our experiments, and, if the constant activity term is again absorbed into $E°$, the observed voltage is just the $E°'$ of the cell.

Combining the $E°'$ of the two cells, I and II, gives an $E°$ for the reaction

$$\mathrm{Na}_{(s)} \longrightarrow \mathrm{Na^+}_{(NH_3)} + \mathrm{e^-}_{(NH_3)}$$

(In so doing it might be noted that a true $E°$ referred to pure sodium as standard state is obtained and not an $E°'$. The term depending on the activity of sodium in the amalgam cancels out because it comes in negatively in the $E°'$ of cell I and positively in the $E°'$ of cell II.) The results are

at −50° $E° = -0.10 \pm 0.02$ v. $\Delta F° = 2.4$ kcal./mole

at −70° $E° = -0.11 \pm 0.02$ v. $\Delta F° = 2.6$ kcal./mole

Corresponding to these values of the standard free energy change is a standard entropy change of approximately 10 cal. per degree per mole.

These results are in remarkable agreement with those expected on the basis of the thermodynamic functions in liquid ammonia suggested by Jolly.[12] For 25° Jolly suggests

$$\mathrm{Na}_{(s)} \longrightarrow \mathrm{Na^+}_{(NH_3)} + \mathrm{e^-}_{(ext)} \qquad E° = 1.89 \text{ v.}$$

$$\mathrm{e^-}_{(NH_3)} \longrightarrow \mathrm{e^-}_{(ext)} \qquad E° = 1.93 \text{ v.}$$

Using standard heats of formation (−38.1 kcal./mole for sodium ion and 40.5 kcal./mole for the electron) to change these values from 25 to −50° and −70° we would have predicted the following

$$\mathrm{Na}_{(s)} \longrightarrow \mathrm{Na^+}_{(NH_3)} + \mathrm{e^-}_{(ext)} \qquad E°_{-50} = 1.82 \text{ v.}; \quad E°_{-70} = 1.80 \text{ v.}$$

$$\mathrm{e^-}_{(NH_3)} \longrightarrow \mathrm{e^-}_{(ext)} \qquad E°_{-50} = 1.88 \text{ v.}; \quad E°_{-70} = 1.87 \text{ v.}$$

$$\mathrm{Na}_{(s)} \longrightarrow \mathrm{Na^+}_{(NH_3)} + \mathrm{e^-}_{(NH_3)} \qquad E°_{-50} = -0.06 \text{ v.}; \quad E°_{-70} = -0.07 \text{ v.}$$

An experimentally determined value for the standard free energy change of

$$\mathrm{Na}_{(s)} \longrightarrow \mathrm{Na^+}_{(NH_3)} + \mathrm{e^-}_{(NH_3)}$$

makes possible an experimental evaluation of single ion solvation free energies. The over-all process above can be represented by the following cycle: (1) sublimation of solid sodium, (2) ionization of sodium gas, (3) ammoniation of sodium ions, (4) ammoniation of electrons. The free energy change of step (1) is well known and is equal to 18.7 kcal./mole at 25°. The free energy change of step (2) can be estimated from the first ionization potential of sodium as equal to 118.9 kcal./mole. For step 4 the free energy change can be rather reasonably estimated to be −11.9 kcal./mole. This value we have obtained by considering the reverse process, the desolvation of electrons from liquid ammonia. Its free energy change is 18.4 kcal., the energy required to expel electrons from liquid ammonia, less 6.5 kcal., the energy released when the cavities left behind collapse. The number 18.4 kcal. comes from 0.8 electron volt, the observed photoelectric work function of sodium-ammonia solutions reported by Ogg.[13] The number 6.5 kcal. is the calculated surface energy of a mole of cavities in liquid ammonia. For the surface tension, we have used 35.4 ergs per cm.^{2} from the work of Stairs and Sienko.[14] For the radius of the cavity, we have used 3.2 Å. as suggested by Lipscomb[2] on the basis of the density measurements of Kraus, Carney and Johnson.[15]

Using 2.5 kcal. for the free energy change of the over-all reaction, we calculate the free energy change of step 3 by difference to be −123.2 kcal./mole. There is probably a large uncertainty in this figure, perhaps as much as 10 kcal., because in several of the steps we have had to use data at different temperatures and to assume, in the absence of information on the entropy changes, that the free energy change is the same as the energy change. However, the result is of more than qualitative interest because it indicates that, at least in principle, it is possible experimentally to get a single ion solvation free energy, one which does not depend on any arbitrary apportionment of solvation effects between cations and anions.

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(12) W. L. Jolly, University of California Radiation Laboratory Report UCRL 2201, May, 1953.

(13) R. A. Ogg, Jr., *Phys. Rev.*, **69**, 668 (1946).

(14) R. A. Stairs and M. J. Sienko, THIS JOURNAL, **78**, 920 (1956).

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