have presented evidence of ionic bonding for sulfate and secondary phosphate ions in the second sphere. Results of their work were not conclusive with other electrolytes.

It might be noted that a possible explanation based upon displacement of part or all of the coordinating groups of the original complex by electrolyte ions was ruled out for a number of reasons. First, ammonia is known to form a very stable covalent bond to cobalt (III), whereas sulfato complexes are in general much less stable. Second, from the point of view of super-complexing, which is electrostatic in character, the divalent ions such as the sulfato ion would be expected to show the clustering behavior more readily than univalent ions such as chloride, nitrate, or perchlorate, a prediction which is in accord with the experimental result. Third, the color stability of the solutions provides a reason for discounting a theory based upon displacement of the ammonia molecules in the original complex, inasmuch as displacement of coördinating groups might reasonably be expected to cause a change of color; actually no such color change occurs. Fourth, the size and charge of the ion that would result from such a displacement should lead to less hydrated ions; for example, if a sulfate ion replaced two ammonia molecules, the resulting ion would be a univalent cation which would be less highly hydrated than the original trivalent ion and, hence, would be expected to diffuse more rapidly; if two sulfate ions replaced four ammonia molecules, a univalent negative ion would result, again with a higher diffusion rate, which would orient differently with respect to the dropping mercury electrode and might be expected to be more easily reduced if indeed any change would result; the experimental result is in the opposite direction.

Summary

1. Capillary active substances such as gelatin and octyl alcohol were found to shift the half-wave potentials for the first reduction step of the hexamminecobaltic ion to more negative potentials.

2. The optimum drop rate for most favorable conformity with the Ilkovic equation was established.

3. Supporting electrolytes of good coördinating ability were found to shift the half-wave potential for the first reduction step of the hexamminecobaltic ion to more negative potentials and to decrease the diffusion rate of the cobaltic complex. A "super-complex" of anions of the indifferent electrolyte clustered about the central complex by electrostatic and ion-dipole attraction is postulated.

URBANA, ILLINOIS RECEIVED APRIL 12, 1948

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Polarography in Liquid Ammonia. II. The Electron Electrode[1]

BY H. A. LAITINEN AND C. J. NYMAN[1a]

The electrode reactions which might occur at a cathode on electrolysis of anhydrous liquid ammonia solutions have been summarized by Makishima.[2] For a platinum electrode, metal deposition, reduction in valence state of the metal ion, hydrogen discharge, and electron dissolution are possible processes. The dissolution of electrons was observed by several investigators when a salt solution, whose ions were non-reducible, was electrolyzed with a platinum cathode. On electrolysis of solutions of tetramethylammonium chloride and hydroxide and tetraethylammonium chloride between platinum electrodes at -34°, Palmaer[3] obtained in each case a blue solution, which he attributed to the electron or to the "free alkylammonium radical." Similar observations were made by Kraus[4] and by Schlubach.[5] Forbes and Norton[6] have prepared solutions of tetramethyl-, tetraethyl-, tetrapropyl-, tetrabutyl-, trimethylbutyl-, triethylbutyl-, tripropylbutyl-, tributylmethyl-, tributylethyl- and diethyldibutylammonium ions and electrons by electrolysis of the iodides of these ions between platinum electrodes. Cady[7] and Kraus[8] found on electrolysis of sodium solutions between platinum electrodes that the transfer of electrons from the electrode to the solution was the only cathodic process which occurred and that the opposite transfer was the only anodic process which occurred.

All the processes listed for a platinum cathode can also occur at a dropping mercury cathode. In addition, there is the possibility of amalgamation of the cation of the salt solution, as is known to be the case with the alkali metal ions.[1] For electrons to enter solution from the surface of a dropping mercury cathode, the potential of electron dissolution must be more positive than the amalgamation potential of the cation of the salt solution.

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[1] Presented before the Division of Physical and Inorganic Chemistry at the Chicago Meeting of the American Chemical Society, April, 1948. For paper I, see THIS JOURNAL, **70**, 2241 (1948).

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[2] S. Makishima, *J. Faculty Eng. Tokyo Imp. Univ.*, **21**, 115 (1938).

[3] W. Palmaer, *Z. Elektrochem.*, **8**, 729 (1902).

[4] C. A. Kraus, THIS JOURNAL, **35**, 1732 (1913).

[5] H. H. Schlubach, *Ber.*, **53**, 1689 (1920).

[6] G. S. Forbes and C. E. Norton, THIS JOURNAL, **48**, 2278 (1926).

[7] H. P. Cady, *J. Phys. Chem.*, **1**, 707 (1897).

[8] C. A. Kraus, THIS JOURNAL, **30**, 1323 (1908); **36**, 864 (1914).

When a transfer of electrons from the electrode to the solution, or the reverse process, takes place, the electrode can be considered to be an electron electrode. It was found possible to study these processes polarographically with both platinum and dropping mercury electrodes.

Experimental

The electrolysis cells and apparatus for preparing the anhydrous liquid ammonia solutions, as well as the thermostat, have been described previously.[1] Unless otherwise specified, the cell with the internal reference electrode was used.

The dropping mercury electrode had the following characteristics in a saturated solution (0.0057 M) of tetrabutylammonium iodide in liquid ammonia at −36°. At a pressure of 20 cm. of mercury, the drop time t was 5.1 sec. (open circuit), and the mass of mercury flowing through the capillary was 1.184 mg./sec.

The platinum electrode was of a type described by Laitinen and Kolthoff,[9] and consisted of a platinum disc sealed to the end of a glass tube in such a manner that the disc was vertical when the electrode was in place. The area of the electrode was about 3.1 sq. mm.

The reference electrode used in this investigation was a mercury pool in 0.005 M iodide solution.

A Sargent Model XX polarograph was used. The calibration of this instrument was checked by inserting a known resistance in place of the electrolysis cell and measuring accurately the applied potential. With these data the current flowing through the circuit was calculated and compared with that indicated by the recorder. All applied potential values were checked by means of a student type potentiometer.

The ammonia, obtained from the Matheson Company, was dried by condensation on sodium before being distilled into the electrolysis cell.

The alkali metal salts were C. P. materials of commerce and were dried at 110° before use.

The tetraalkylammonium iodides were prepared in an organic preparations course at the University of Illinois. The tetramethyl- and tetraethylammonium iodides were recrystallized from 95% ethanol, the tetrapropylammonium iodide from 50% ethanol-50% ethyl acetate solution, and the tetrabutylammonium iodide from absolute ethyl acetate. Residual current curves of 0.005 M solutions of these salts in liquid ammonia showed no waves at potentials which corresponded to alkali metal reduction, and the salts were therefore considered free of such impurities.

Sodium amide was prepared by the reaction of sodium with liquid ammonia in the presence of a trace of ferric nitrate hexahydrate as described by Greenlee and Henne.[10]

Theoretical

A polarogram made with a dropping mercury electrode on a 0.001 molar solution of sodium iodide in a saturated solution of tetrabutylammonium iodide is shown in Fig. 1. It is proposed that the increase in current at potentials more negative than 2.3 volts was due to the dissolution of electrons. Assuming, for the present, that this was the process which occurred, an equation for the current–voltage curve obtained can be derived.

The potential of an electrode behaving as an electron electrode should be given by a Nernst expression of the type

$$E_e = E^0_e - \frac{RT}{F} \ln C_e \qquad (1)$$

where E_e is the potential of the electrode; E^0_e is the standard potential of the electron electrode; and C_e is the concentration of the electron at the surface of the electrode in moles per liter. Assuming that the Ilkovic equation describes the behavior of an electron with regard to its diffusion from a dropping mercury electrode, then

$$C_e = i/6.05 \times 10^5 D^{1/2} m^{2/3} t^{1/6} \qquad (2)$$

where i is the current which flows (microamperes); D is the diffusion coefficient of the electron; m is the mass of mercury flowing through the capillary (mg./sec.); and t is the drop time of the capillary in seconds. On substitution of C_e from equation 2 into equation 1, the expression

$$E_e = E^0 - \frac{RT}{F} \ln i/6.05 \times 10^5 D^{1/2} m^{2/3} t^{1/6} \qquad (3)$$

is obtained. Equation 3 can be simplified by writing

$$E_e = A - \frac{RT}{F} \ln i \qquad (4)$$

where

$$A = E^0_e + \frac{RT}{F} \ln 6.05 \times 10^5 D^{1/2} m^{2/3} t^{1/6} \qquad (5)$$

Equations 3 and 4 give the potential of a dropping mercury electrode when a current of i microamperes flows due to the dissolution of electrons. The constant A represents the potential of the electrode when a current of one microampere is flowing. A depends on E^0_e and on the characteristics of the electrode in a manner given by equation 5. If the process is reversible, a plot of E *versus* log i should have a slope of −0.047 at −36°. The value of A can be determined most accurately from a plot of this type.

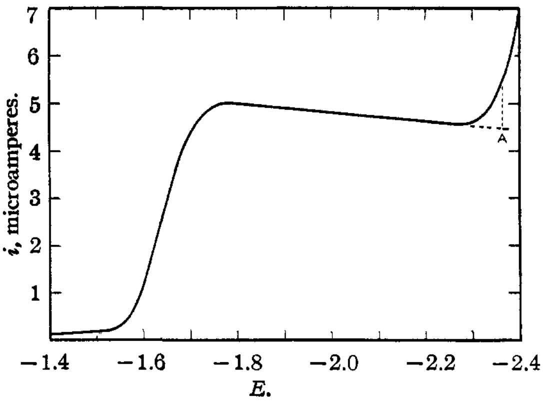

Fig. 1.—Polarogram of 0.001 M NaI in saturated $(C_4H_9)_4$-NI, dropping mercury electrode.

An expression similar to equation 4 would also describe the current–voltage curve obtained when using a platinum electrode. The constant A would change for different electrodes, because the diffusion of electrons would vary with the area and

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[9] H. A. Laitinen and I. M. Kolthoff, THIS JOURNAL, **61**, 3344 (1939).

[10] K. W. Greenlee and A. L. Henne, "Inorganic Syntheses," **2**, 128 (1946).

shape of the electrode and with the orientation of the electrode surface.

Data and Discussion

On electrolysis of solutions of uni-univalent salts with a dropping mercury electrode, the three possible cathodic reactions which must be considered are hydrogen discharge, amalgamation of the cation, and electron dissolution. Since it has been previously reported that the alkali metal ions can be reduced polarographically in liquid ammonia, salts of these ions cannot be used as electrolytes in a study of mercury as an electron electrode. Tetrabutylammonium iodide was chosen as the one to be studied in this connection because it gives a very negative break in water solution, and it was hoped that it would prove to be nonreducible in liquid ammonia even at the most negative potentials. From the polarogram in Fig. 1 it is seen that the value of A is 0.72 volt more negative than the sodium half-wave potential. In the discussion which follows, it will be shown that this break is caused by the transition of electrons from the electrode to the solution and not by one of the other two processes.

If the increase in current at potentials more negative than 2.3 volts was caused by hydrogen discharge, then the value of A should be a function of ammonium ion concentration. Pleskov and Monosson[11] found the dissociation constant of liquid ammonia to be 1.9×10^{-33} at $-50°$. Assuming it to be the same at $-36°$, the ammonium ion and amide ion concentrations are equal to 4.4×10^{-17} mole per liter in a neutral solution. If the amide ion concentration were increased to 10^{-4} mole per liter, the ammonium ion concentration would be decreased to 1.9×10^{-29} mole per liter. From the Nernst equation, this would cause hydrogen discharge to be more difficult and the constant A to be 0.58 volt more negative than in a neutral solution. A polarogram was run on a solution which contained 10^{-4} mole of sodium amide per liter and which was saturated with tetrabutylammonium iodide. In this solution the value of A was found to be 0.70 volt more negative than the sodium half-wave potential. Since there was no shift in the value of A with a decrease in ammonium ion concentration, the process observed could not have been hydrogen discharge.

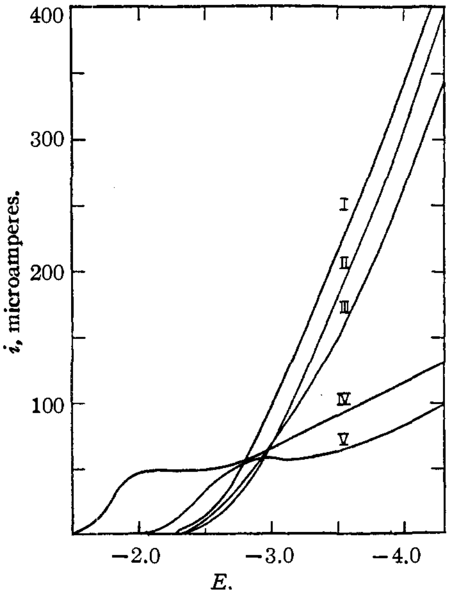

Fig. 2.—Polarograms with dropping mercury electrode: curve I, 5×10^{-3} M $(C_2H_5)_4NI$; curve II, satd. $(C_4H_9)_4NI$; curve III, 5×10^{-3} M $(C_3H_7)_4NI$; curve IV, 5×10^{-3} M NaI; curve V, satd. $(CH_3)_4NI$.

If the increase in current was due to reduction of the cation to form an amalgam, a limiting current should have been observed, such as the one obtained on the polarographic reduction of 0.005 molar sodium iodide solution (Curve IV, Fig. 2). On the other hand, if no amalgamation occurred, the only other cathodic process which could have occurred was the dissolution of electrons. A polarogram for a saturated solution (0.0057 M) of tetrabutylammonium iodide (Curve II, Fig. 2) showed no limiting current even at potentials as negative as 4 volts. This was a good indication that the process was not amalgamation of the tetrabutylammonium ion.

If the process was that of electron dissolution, then the cation of the salt solution should have no effect on the potential of electron dissolution, and, therefore, the tetrabutylammonium ion may be replaced by any ion which is not reduced at these potentials. In this connection, a series of experiments was carried out using tetramethyl-, tetraethyl-, tetrapropyl- and tetrabutylammonium iodides. A polarogram (Curve V, Fig. 2) of a saturated solution (0.0042 M) of tetramethylammonium iodide showed a limiting current similar to that shown by sodium ion. This was not unexpected since McCoy[12,13] and co-workers had previously prepared tetramethylammonium amalgam at $-34°$ by electrolysis of the chloride salt in absolute methanol. They were unable to prepare tetraethylammonium amalgam under similar conditions. A polarogram (Curve I, Fig. 2) of a solution of tetraethylammonium ion showed no limiting current, but the constant A was more positive than for the tetrabutylammonium iodide solution. This can be seen more conveniently from Fig. 3, which is plotted on a larger scale. The tetraethylammonium iodide curve was very erratic and not nearly so well defined as the tetrabutylammonium iodide curve. It appears possible that both electron dissolution and amalgamation of the cation might have occurred with the tetraethylammonium iodide solution. The current–voltage curve (Curve III, Fig. 2) for the tetrapropyl-

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(11) V. A. Pleskov and A. M. Monosson, *Acta Physicochim. U. R. S. S.*, **1**, 713 (1935).

(12) H. N. McCoy and W. C. Moore, THIS JOURNAL, **33**, 273 (1911).

(13) H. N. McCoy and F. L. West, *J. Phys. Chem.*, **16**, 261 (1912).

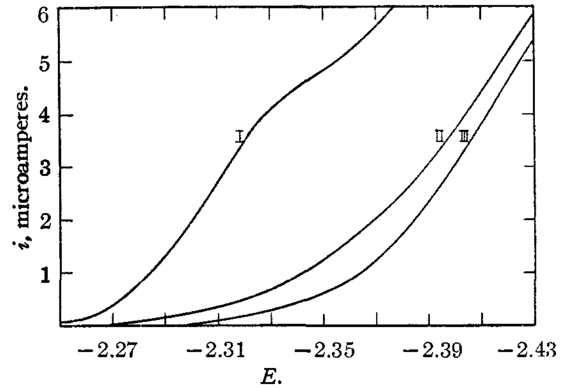

Fig. 3.—Polarograms with dropping mercury electrode: curve I, 5×10^{-3} *M* $(C_2H_5)_4NI$; curve II, 5×10^{-3} *M* $(C_3H_7)_4NI$; curve III, satd. $(C_4H_9)_4NI$.

ammonium iodide was almost identical in every respect with the current–voltage curve of tetrabutylammonium iodide. This curve is also shown in Fig. 3. The values of *A* obtained from these curves by plots of *E versus* log *i* are recorded in Table I along with the slopes of such plots. The fact that these quantities are almost identical for tetrapropyl- and tetrabutylammonium iodide solutions and the fact that no limiting current was obtained indicated that the same process, electron dissolution, took place in both solutions.

It might be expected that the current–voltage curves for sodium ion and tetramethylammonium ion would show a sharp increase in current at −2.36 volts if that is the potential at which electron dissolution occurs. One reason that a sharp rise is not encountered is the fact that the concentration of positive ions at the surface of the electrode is vanishingly small, because they are being amalgamated as fast as they reach the electrode surface. If the cations are being amalgamated, then the solution surrounding the electrode would have a very high resistance as compared to the bulk of the solution, and the flow of current would be impeded. From the slopes of the current–voltage curves at the more negative potentials, the maximum resistances of the solutions at the electrode surface can be calculated. The maximum resistances of the solutions of 0.005 *M* tetraethyl-, 0.005 *M* tetrapropyl- and saturated tetrabutylammonium iodide solutions were about 5,000 ohms, and the resistances of saturated tetramethyl ammonium iodide and 0.005 *M* sodium iodide solutions were about 20,000 ohms. A gradual rise in current is observed at very negative potentials for the latter two salts on electrolysis, and this must correspond to some cathodic process which in all probability is electron dissolution.

It has already been mentioned that liquid ammonia solutions of cations and electrons can be prepared electrolytically using a platinum cathode, if the cations are stable in the presence of the solvated electron. As in the case of the dropping mercury electrode, changing the type of cation of the salt solution should have no effect on the potential of electron dissolution. Polarograms of solutions of lithium, sodium, tetramethylammonium and tetrabutylammonium iodides using a platinum electrode are shown in Fig. 4, and the similarity of the curves bears out the fact that the process is the same in each case. The values of *A* were nearly constant, but the slopes of the *E versus* log *i* plots differed from the theoretical value by a considerable margin. These quantities are also recorded in Table I. The difference between the observed slopes and the theoretical ones may be due to poor diffusion conditions in the solutions near the electrode surface or possibly to a potential drop caused by the resistance of the solution. In any event, diffusion to a stationary electrode is not so well defined as to a dropping mercury electrode.

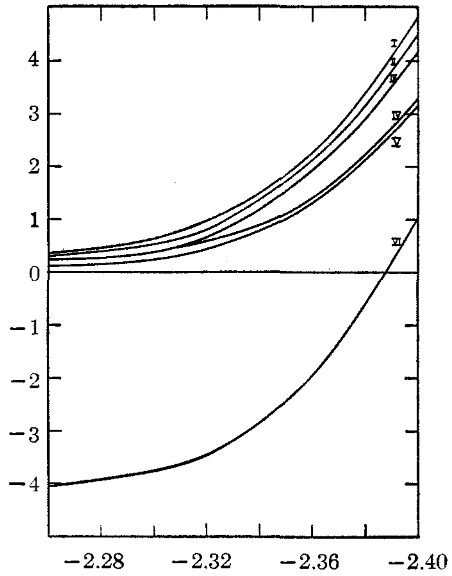

Fig. 4.—Polarograms with stationary electrodes: curve I, satd. $(C_4H_9)_4NI$ with mercury surface; curve II, 5×10^{-3} *M* NaI, Pt surface; curve III, satd. $(C_4H_9)_4NI$, Pt, surface; curve IV, 5×10^{-3} *M* LiI, Pt surface; curve V, satd. $(CH_3)_4NI$, Pt surface; curve VI, 6×10^{-3} *M* Na, Pt surface.

TABLE I

Electrode	Salt	Concn., m./l.	*A*, v.	Slope *E* *vs.* log *i*
Drop Hg	$(C_2H_5)_4NI$	0.005	−2.26	.....
Drop Hg	$(C_3H_7)_4NI$	.005	−2.34	−0.064
Drop Hg	$(C_4H_9)_4NI$	.0057	−2.36	− .063
Pt	LiI	.005	−2.35	− .104
Pt	NaI	.005	−2.34	− .120
Pt	$(CH_3)_4NI$	.0042	−2.35	− .105
Pt	$(C_4H_9)_4NI$	.0057	−2.34	− .098
Stationary Hg	$(C_4H_9)_4NI$	.0057	−2.34	− .093
Pt	Na metal	.006	−2.35	− .073

To determine whether the electrode material affected the potential of electron dissolution, a polarogram was run on a tetrabutylammonium iodide solution using a stationary mercury electrode. The platinum electrode used in the experiments described previously was plated with copper and then with mercury until a smooth film of mercury covered the electrode surface. If the same process occurred at the mercury surface as at the platinum surface on electrolysis of a tetrabutylammonium iodide solution, then the values of *A* and the slopes of the *E versus* log *i* plots should be comparable, because the shape and area of the electrodes were approximately the same. This was observed experimentally and, therefore, the process was the same. These experiments also indicate that there is no detectable overvoltage to the dissolution of electrons either from a platinum or mercury surface. Curve I in Fig. 4 is the polarogram of a tetrabutylammonium iodide solution using the stationary mercury electrode, and the data obtained from it are recorded in Table I.

The platinum electrode used above was plated with copper and, as in the case of the stationary mercury electrode, it should have the same area and shape as the platinum electrode. It was found on electrolysis of a saturated solution of tetrabutylammonium iodide using the copper electrode that *A* was more positive than for a platinum electrode, and that it varied between -1.5 and -1.8 volts. Reproducible values could not be obtained. Apparently, hydrogen discharge occurred at the copper surface more readily than the dissolution of electrons. This would indicate that freshly plated copper has a low hydrogen overvoltage in liquid ammonia, while bright platinum and mercury have high hydrogen overvoltages. Pleskov[14] has reported that mercury has a higher hydrogen overvoltage in liquid ammonia than in water.

Platinum black electrodes have been reported by Pleskov and Monosson[15] to function as reversible hydrogen electrodes in liquid ammonia. This indicates that such electrodes have little or no hydrogen overvoltage. When a platinum black electrode was used as the cathode for obtaining a current–voltage curve of a solution of tetrabutylammonium iodide, a large current was observed as soon as a negative potential was applied. At a constant potential, 0.1 volt more negative than the reference electrode, the current flowing slowly decreased. This would be the state of affairs if the process were hydrogen discharge from an unbuffered solution. That hydrogen discharge is not the process which takes place at the surface of a bright platinum electrode is indicated by the fact that solutions of electrons can be prepared by electrolysis using platinum cathodes and that metal solutions are stable in the presence of bright platinum electrodes.

In addition to having a cathodic process with the formation of an electron solution, there should be a corresponding anodic process with the transfer of electrons from the solution to the electrode. The anodic transfer can take place at any potential more positive than that of electron dissolution. On electrolysis of a solution of sodium metal, an anodic current was observed at the platinum electrode, and the polarogram obtained is shown by Curve VI in Fig. 4. An H-type cell, with a sintered glass disc to separate the anode and cathode compartments, was used for this experiment. One compartment contained the sodium solution and the platinum electrode, and the other contained the mercury reference electrode in a saturated solution of tetrabutylammonium iodide. A trace of mercuric iodide was added to the tetrabutylammonium iodide solution to depolarize the reference electrode. The potential at which the anodic current has decreased by one microampere in this experiment should be the same as the potential at which the cathodic current has increased by one microampere on electrolysis of a salt solution. The value of *A* observed for the sodium solution was very close to that observed for salt solutions as can be seen from Table I. The fact that the curve goes smoothly through the zero current line indicates that there is no overvoltage for either the dissolution process or the reverse process.

An unsuccessful attempt was made to obtain an anodic curve using the dropping mercury electrode in a sodium solution. The failure to obtain a polarogram was attributed to the fact that sodium solutions are not stable in the presence of mercury because of sodium amalgam formation.

A solution of tetrabutylammonium ions and electrons was prepared by electrolyzing solutions of tetrabutylammonium iodide in an H-type cell between mercury pool electrodes. Anodic current–voltage curves were obtained for solutions prepared in this manner, but the results were not reproducible. An anodic current was observed at potentials as negative as -2.3 volts.

Makishima[2] calculated the standard potential of the electron electrode to be 2.45 volts more negative than the standard potential of a lead electrode or 2.04 volts more negative than the standard potential of the hydrogen electrode at $-34°$. Forbes and Norton[6] have measured the oxidation potentials of the solutions of tetraalkylammonium ions and electrons mentioned earlier as well as the oxidation potentials of solutions of lithium, sodium and potassium. The concentrations of cations and electrons in these solutions were of the order of 0.005 *M*, and the oxidation potentials of all were found to be 2.590 ± 0.015 volts more negative than the potential of a silver electrode in a saturated solution of silver nitrate at $-78°$. There was no general trend in the variation of potential with concentration of electron, and it may be possible that their analytical method for determining the concentration of electron was not accurate enough to establish such a trend.

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(14) V. A. Pleskov, *Acta Physicochim., U. R. S. S.*, **11**, 305 (1939).

(15) V. A. Pleskov and A. M. Monosson, *ibid, U. R. S. S.*, **1**, 871 (1935).

By a consideration of the current–voltage curve for a solution of sodium metal, the standard potential of the electron electrode can be evaluated. The potential at which the current–voltage curve crossed the zero current axis is a function of the surface concentration of electron, and since at this potential no current is flowing, the concentration at the surface of the electrode should be equal to the concentration in the bulk of the solution. The current–voltage curve crossed the zero current axis at −2.388 volts, and the concentration of electron at the electrode surface was 0.006 mole per liter. On substitution of these data into equation 1, the standard potential of the electron electrode was estimated to be 2.49 volts more negative than the mercury reference electrode. It is possible to relate this potential to the standard potential of the hydrogen electrode in liquid ammonia. The difference between the potential of the mercury reference electrode and the potential of a lead electrode in an 0.1 N lead nitrate solution was previously reported[1] as 0.318 volt at −36°. Pleskov and Monosson[15] have reported the difference of potential between a lead electrode in 0.1 N lead nitrate solution and a hydrogen electrode in 0.1 N ammonium nitrate to be 0.352 volt at −50°. The partial pressure of hydrogen in the system was 450 mm. Neglecting the temperature coefficient of the above cell and the activity coefficient of the ammonium ion, the difference of potential between a lead electrode in 0.1 N lead nitrate solution and the standard potential of the hydrogen electrode was calculated to 0.310 volt. Combining these cells, the standard potential of the electron electrode is 1.86 volts more negative than the standard potential of the hydrogen electrode.

Equation 5 can be used to calculate the standard potential of the electron electrode, since the remaining terms can be evaluated. The diffusion coefficient can be calculated from the equivalent conductance of the electron at infinite dilution, and the other terms are experimental quantities. Kraus found that the limiting conductance of the electron at infinite dilution was 910 ohm^{-1}-cm.^{2}-equiv.$^{-1}$. Using the equation

$$D = RT\lambda^0/zF^2 \qquad (6)$$

derived by Nernst,[16,17] the diffusion coefficient D of the electron can be calculated. R is 8.317 volt-coulombs, T is the absolute temperature, λ^0 is the equivalent conductance of the electron at infinite dilution, z is the charge of the electron, and F is 96,500 coulombs. At −36°, D is 1.93 × 10^{-4} sq. cm./sec. The drop time of the electrode was 1 sec., and m was 1.184 mg./sec. For polarograms of saturated solutions of tetrabutylammonium iodide, the average value of the constant A was −2.36 volts with reference to the potential of a mercury pool in a saturated solution of tetrabutylammonium iodide. Substituting these data into equation 5, the standard potential of the electron electrode was estimated to be 2.55 volts more negative than the mercury reference electrode and 1.92 volts more negative than the standard potential of the hydrogen electrode at −36°.

These two values for the standard potential of the electron electrode are in fair agreement with the theoretical values calculated by Makishima.

The potential at which the dissolution of electrons occurs has an important theoretical and practical significance. It represents the limit to the negative potentials which can be applied to an electrode for polarographic measurements in liquid ammonia.

It is possible to relate the standard potential of the electron electrode to the solubility of metals in the following way. When a metal dissolves in liquid ammonia to form solutions of cations and electrons, according to the reaction

$$\mathrm{M} \longrightarrow \mathrm{M}^{n+} + n\mathrm{e}^-$$

an anodic and cathodic process are taking place simultaneously. In the dissolution of metal ions, the potential of the metal is given by the expression

$$E_1 = E^0_{\mathrm{M}} + \frac{RT}{nF}\ln C_{\mathrm{M}^{n+}} \qquad (7)$$

For the dissolution of electrons, the potential of the metal is given by the expression

$$E_2 = E^0_{\mathrm{e}} - \frac{RT}{nF}\ln (C_{\mathrm{e}^-})^n \qquad (8)$$

Since both processes are taking place at the same electrode, the potential E_1 must be equal to E_2 at all times, and therefore

$$E^0_{\mathrm{M}} - E^0_{\mathrm{e}} = -\frac{RT}{nF}\ln C_{\mathrm{M}^{n+}}(C_{\mathrm{e}^-})^n \qquad (9)$$

The logarithmic term $C_{\mathrm{M}^{n+}}(C_{\mathrm{e}^-})^n$ is equivalent to the solubility product of the metal, and the solubility of the metal is given by $C_{\mathrm{M}^{n+}}$. These relationships have been pointed out previously by Makishima[2] and were used by him in evaluating the standard potential of the electron electrode. Equation 9 implies that univalent metals whose standard electrode potentials are more negative than that of the electron electrode will be more soluble than one mole per liter. Conversely, univalent metals whose standard potentials are more positive than the standard potential of the electron electrode have a maximum solubility less than one mole per liter. Equation 9 has been found to be valid, at least qualitatively, for those alkali metals and alkaline earth metals whose solubilities and standard electrode potentials are known. Theoretically all metals would be soluble to an extent governed by equation 9. The most positive metals would have an infinitesimally low solubility.

Summary

1. Platinum and mercury electrodes were found to function as electron electrodes in liquid ammonia solutions when the cation of the in-

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(16) W. Nernst, *Z. physik. Chem.*, **2**, 613 (1888).

(17) J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **61**, 825 (1939).

different electrolyte was non-reducible. An equation was derived for the polarograms obtained and for estimation of the standard potential of the electron electrode from polarograms of salt solutions.

2. Two different types of measurements gave values of −1.86 and −1.92 volts for the standard potential of the electron electrode *versus* the standard potential of the hydrogen electrode at −36°. These values are roughly in agreement with a theoretical value of −2.04 volts calculated by Makishima.

3. A relationship between the solubility of metals in liquid ammonia and the standard potential of the electron electrode was presented.

URBANA, ILL. RECEIVED APRIL 15, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MCMASTER UNIVERSITY]

Natural Variations in the Isotopic Content of Boron and its Chemical Atomic Weight

BY H. G. THODE, J. MACNAMARA, F. P. LOSSING AND C. B. COLLINS

Introduction

Several years ago it was suggested by W. J. Whitehouse and B. Pontecorvo that small variations in the isotopic abundances of boron might explain discrepancies in neutron capture crossection measurements made by different investigators using boron as a standard. As a result of this suggestion, seven or eight boron mineral samples were collected from various parts of the world with the object of determining the variation, if any, in the abundances of the boron isotopes with a mass spectrometer. However, interest in the neutron capture crossection aspect of the problem decreased and the problem was dropped for a while because of other work. The problem was again taken up during the past year because of general interest in the abundances of the boron isotopes. Inghram[1] made a careful study of the isotopic content of boron, but unfortunately did not publish information on the sources of his samples. Other investigators have demonstrated variations in the isotopic content of carbon,[2] and oxygen[3] in nature, and it would not be surprising to find some variations in the isotopic content of boron.

Urey and Greiff[4] first showed from thermodynamic considerations that the isotopes of the light elements did differ slightly in chemical properties. These differences in chemical properties result in some fractionation of the isotopes in natural processes. Isotopic exchange constants involving the isotopes of carbon, nitrogen, oxygen and sulfur have been calculated by the methods of statistical mechanics and checked by experiments.

Recently Urey[5] made a further study of the thermodynamic properties of isotopic substances and reviewed the theoretical and experimental results obtained to date. The boron exchanges which have been investigated from a theoretical point of view are limited to the boron halides. Exchange processes involving these particular compounds cannot readily be realized experimentally at normal temperatures. Of particular interest is the predicted difference in vapor pressures of isotopic boron chlorides. These differences predicted in the thermodynamic properties of isotopic boron compounds suggest that some isotopic exchange process might occur in nature which would result in a slight fractionation of the isotopes.

A change in the ratio of the boron isotopes can, of course, be effected by neutron irradiation. However, neutron intensities in the earth's surface due to cosmic ray and other sources would seem at the present time to be too low, especially in geological deposits below the surface, to account for possible variations in the isotopic ratios. To date, nine samples of boric acid, eight of known origin, prepared from boron minerals obtained from widely separated geological deposits, have been investigated. These samples were converted to boron trifluoride gas and the ratio B^{11}/B^{10} determined with a mass spectrometer. The results obtained for the nine samples are reported in this paper.

Experimental

Preparation of Samples.—The boron trifluoride samples used in the mass spectrometer investigations were prepared by a method described previously.[6] Stoichiometric quantities of potassium fluoborate, anhydrous boric oxide and concentrated sulfuric acid are mixed together in a flask and the mixture is heated strongly *in vacuo*. The boron trifluoride produced is bubbled through concentrated sulfuric acid saturated with boric oxide to remove hydrogen fluoride and moisture. The boron trifluoride is condensed by means of liquid air and is further purified by distilling from one ampoule to another, discarding the first and last portions. Care was taken at this point to avoid possible fractionation of the isotopes.

The anhydrous boric oxide used is prepared by dehydrating boric acid in a vacuum oven for two hours at 200° and the potassium fluoborate is prepared by treating boric acid with hydrogen fluoride to produce fluoboric acid which is converted to form the potassium salt by titration with 5 *N* potassium hydroxide. The boron samples came in the form of boric acid. All of these but one were prepared from borates by the usual treatment with sulfuric acid. The potassium salts are crystallized out first at elevated temperatures, after which the temperature is reduced to bring out the borax. (The borax is then treated with sulfuric acid to produce boric acid.) The boron sample obtained from Tuscany in Italy is ob-

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[1] Inghram, *Phys. Rev.*, **70**, 653 (1946).

[2] Nier and Gulbransen, THIS JOURNAL, **61**, 697 (1939).

[3] Murphy and Nier, *Phys. Rev.*, **59**, 771 (1941).

[4] Urey and Greiff, THIS JOURNAL, **57**, 321 (1935).

[5] Urey, *J. Chem. Soc.*, Part 2, 562 (1947).

[6] "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1939, p. 21.