ELECTRODE POTENTIALS IN LIQUID AMMONIA.

By F. M. G. JOHNSON, M.Sc., AND N. T. M. WILSMORE, M.Sc.

*(A Paper read before the Faraday Society on Tuesday, March 19, 1907,
Dr. T. M. LOWRY in the Chair.)*

The real nature of the forces which are usually referred to under the name "Chemical Affinity" is a problem which has exercised the minds of chemists from the beginnings of their science. The answer to the problem, however, is still to seek, although it may possibly be supplied, at any rate in part, by further developments of the electron theory. At the same time the solution of a lesser problem—that, namely, of the relative measurement of chemical affinity—would seem to have been rendered possible, to some extent, by the more recent study of the energy changes taking place in chemical reactions.

The most rational way in which to measure the chemical forces existing between two substances, under given conditions, is to determine the maximum amount of useful work which could be done by the interaction of unit quantities of the substances under those conditions. It was suggested by Helmholtz in 1847, and definitely asserted by Lord Kelvin, then W. Thomson, in 1851, that the heat change accompanying a chemical reaction could be taken as a direct measure of this maximum useful work. For a considerable time this view met with general acceptance; and, in a modified form, as Berthelot's "Principe du Travail Maximum," would appear to survive in some quarters to the present day; but it has been shown by Willard Gibbs,* and later by Helmholtz,† to be in general incorrect. The real connection between the two quantities was very clearly stated by Helmholtz, who showed that the maximum amount of useful work which the system can do, called by him the change in the "free energy" of the system, is equal to the algebraic sum of the changes in "total" and "bound" energies, according to the well-known equation—

$$W = U + h.$$

Here W stands for the change in the "free" energy; U is the change in the "total" energy, which may be measured by the heat change produced when the reaction takes place in a calorimeter, without doing external work; and h is the change in "bound" energy (happily rechristened by Haber ‡ "latent" energy), viz., the heat which is taken from or given to the surroundings. Helmholtz has shown, further, that this "bound" or "latent" energy is related to the free energy according to the equation—

$$h = T \frac{dW}{dT},$$

which indicates that h only necessarily vanishes, viz., Kelvin's Rule (or Berthelot's Principle) is only strictly true at absolute zero. The measurement of W , the change in the free energy, is consequently of great importance. On

* *Trans. Conn. Acad.*, 1878.† *Mittlgn. der Berl. Akad.*, 1882.

‡ "Thermodynamik tech. Gasreaktionen."

ELECTRODE POTENTIALS IN LIQUID AMMONIA 71

the sign of W depends whether a given reaction can take place of itself or not, since no reaction can go on of itself, that is to say, no system can of itself change its configuration, and at the same time do work, unless its free energy can at the same time diminish; and a system is in stable equilibrium under given external conditions when its free energy is at a minimum.

The quantity W can be very conveniently measured when the reaction can be made to take place in a galvanic cell, for not only is electrical energy easy to measure with accuracy, but the requirement of complete reversibility is often very nearly fulfilled. Further, if we consider the energy change with reference to gram equivalents of the reacting substances, the quantity of electricity concerned in the change becomes fixed, in accordance with Faraday's law, and the potential of the cell is then a direct measure of the possible change in free energy. That is, we can measure W practically under static conditions.

An interesting series of measurements of the change in free energy taking place in the formation of salts from their elements has been made recently by M. de K. Thompson* by the help of this method.

According to the theory of Nernst, the potential of a galvanic cell may be regarded as the algebraic sum of a series of single potentials, viz., those existing at the two electrodes, together with the contact potentials between the different solutions, and that between the metals themselves. The last of these is constant for a given temperature, and also additive; and it may therefore be included in the electrode potentials, while the contact potentials between the solutions may often be either eliminated or allowed for. They are in general comparatively small. Apart, then, from these contact potentials, we may take the nett potential of the cell to be the sum of the two electrode potentials, each of which may be represented by the well-known formula of Nernst—

$$e = \frac{RT}{\nu F} \log_e \frac{C}{c},$$

C being a constant (for the given temperature T) depending only on the nature of the electrode, c the concentration of the ion with respect to which the electrode is reversible, ν the valency of this ion, and F the Faraday constant.

Nernst has pointed out that if the single electrode potentials be measured under definite conditions as to temperature, ionic concentration, &c., they become characteristic constants for the various elements. For unit ionic concentration the above equation may be written—

$$e_0 = \frac{RT}{\nu F} \log_e C.$$

C must be assumed to have the dimensions of a concentration; but, since it is not directly measurable as such, it is convenient to consider e_0 as the natural constant of the element forming the electrode; and the name "electrolytic potential" and the symbol $E.P.$ or ep † have been proposed for it.

As no satisfactory "absolute" standard for single electrode potentials is available, various arbitrary standards have been suggested. Nernst ‡ has

* *Trans. Am. Electroch. Soc.* 9, 337 (1906). *Journ. Am. Chem. Soc.* 28, 731 (1906).

† *Z. physik. Ch.* 35, 291 (1900). Since this is a specific property, the name "electrolytic potentiality" would perhaps have been more appropriate and more in keeping with such terms as conductivity, resistivity, &c.

‡ *Z. Elektroch.* 7, 253 (1900).

72 ELECTRODE POTENTIALS IN LIQUID AMMONIA

proposed to take the *ep* of hydrogen at 18° C. as zero, and on this basis a series of electrolytic potentials has been calculated for aqueous solutions by one of us.*

Now, from what has been said, it would follow that these electrolytic potentials must be looked upon as affinity "constants" of the elements; and, since they show a distinctly additive character, it would seem, at first sight, as if one could speak of the "affinity" of an element as something depending on that element alone, irrespective of any other element with which it might combine. There are, however, numerous exceptions to the simple addition law which seriously limit this generalisation. For example, we have to consider whether the electrode is reversible with respect to simple or to complex ions,† whether the element is in an active or passive state, or whether it is one of those which can form either anions or cations; and, even if we limit the additive rule to cases where the element forms simple ions, it must be used with caution.

Nevertheless it seemed to us to be worth while to test this generalisation further by means of measurements of electrolytic potential carried out under conditions differing as widely as possible from those associated with aqueous solutions. As a first step towards this end we have measured the electrode potentials of a series of elements, using liquid ammonia as the solvent, this substance having a constitution and properties very different from those of water, and, at the same time, being one of the few non-aqueous solvents which dissolve a fair number of salts to form good conducting solutions. The low boiling-point, however, introduces a difficulty in comparing our results with those obtained in aqueous solutions. Direct determinations of electrode potentials at ordinary temperatures under pressure would have involved great experimental difficulties; and this is also the case with measurements of temperature coefficients, unless wide extrapolation be resorted to. We would also point out that the existing data respecting the conductivities of salts in liquid ammonia are as yet insufficient to allow of satisfactory calculation of the degree of dissociation of the electrolytes we have used. It has therefore not been possible to apply the corrections necessary to obtain the true electrolytic potentials from our measurements; and consequently the present communication has in a sense a preliminary character.

The ammonia used was procured in iron cylinders, from which it could be run into suitable vessels as required. It was found to be very nearly pure, and it left but a small residue on evaporation. In cases where any impurity appeared likely to affect the results the ammonia was re-distilled before use.

The choice of salts to be employed as electrolytes was limited by their solubilities. As shown by the numerous measurements made by Gore,‡ and subsequently by Franklin and Kraus,§ of the solubilities of a large number of salts, the nitrates were in many cases the only metallic salts sufficiently soluble to form solutions of the strengths required for this work.

As a standard electrode, metallic cadmium in a saturated solution of cadmium nitrate was chosen; and the E.M.F.'s of the various metals, in contact with solutions of their salts of various strengths, were, in the first place, measured against this.

At first no satisfactory numbers could be obtained. It was then found that the CO₂ present in the air was sufficient to cause precipitation of the

* *Z. physik. Ch.* **35**, 291 (1900).

† Haber, *Z. Elektroch.* **10**, 433 (1904).

‡ *Proc. Roy. Soc.* **20**, 441 (1872), **21**, 140 (1873).

§ *Am. Chem. Journ.* **20**, 820 (1898).

ELECTRODE POTENTIALS IN LIQUID AMMONIA 73

salts in solution, thus causing an alteration of the concentration of the electrolyte. This difficulty was got over by passing a slow stream of hydrogen, previously saturated with ammonia, through the solutions.

In many cases the potentiometer method of measurement was employed, using a Dolezalek electrometer as null instrument. In some instances, however, it was found to be more satisfactory to use a d'Arsonval galvanometer, calibrated as a voltmeter, particularly in the case of some metals which give an E.M.F. falling slowly with time, as noticed by Cady* in his measurements of concentration cells. All measurements were made at -33.5° , the boiling point of ammonia.

The arrangement of the apparatus was as follows (Fig. 1) :—

FIG. 1.

A is the metal, the potential of which is to be determined. B is the cadmium electrode. C and D are tubes containing the solutions of the respective metallic salts. The solution in C was kept at a constant volume of 3 c.c. The vacuum vessel E contained the "solvent," about 0.5 N solution of KNO_3 in NH_3 . This solution should have a lower boiling-point than that in C to minimise change of concentration in the latter. F are small plugs of cotton wool to prevent mixing of the solutions. The Dolezalek electrometer. This was sensitive to less than 0.0005 volt. We would mention here that we have found lithium chloride far superior to calcium chloride for rendering the quartz fibre conducting. Calcium chloride appears to be rapidly decomposed by the air of the laboratory, probably being converted into carbonate. K is a small accumulator. L is a carefully calibrated resistance-box whose maximum error was about 0.03 per cent. M is a Weston cell. This was checked against various other cells, made at different times, and also against a standard Weston cell, which had

* *Journ. of Phys. Chem.* 9, 477 (1905).

74 ELECTRODE POTENTIALS IN LIQUID AMMONIA

been tested at the National Physical Laboratory. The voltage of the Weston cells was very close to 1.019 volts (Clark at $15^{\circ} = 1.433$); and our results are therefore given in accordance with this number.

In order to eliminate contact potentials between the various solutions as far as possible, a 0.5 N solution of potassium nitrate was used as solvent in all cases. In making up the solutions the right amount of salt was weighed out each time.

Silver.—The nitrate and iodide were used as electrolytes. As electrodes the purest silver foil obtainable and silver electrolytically deposited on platinum from a cyanide solution were employed. Both gave practically the same results.

Mercury.—Since mercurous salts are apparently unstable in liquid NH_3 , splitting up into mercuric salts and mercury, a mercuric salt had to be used. As already shown by Franklin and Kraus, mercuric nitrate leaves a yellow residue when added to liquid NH_3 . Mercuric iodide, which dissolves easily to form a colourless solution, was therefore used as solute. It is probable that the electrode is reversible with respect to mercuric compounds, as is the case with the aqueous solutions of potassium mercuric iodide used in the Wright electrolytic meter.

Lead.—The commercially pure metal, a sample prepared by the method of Stas, and also lead deposited electrolytically, were used. The potentials were practically the same. The nitrate, which gave a colourless solution, was employed as electrolyte. The iodide was tried, but a clear solution could not be obtained.

Zinc.—Kahlbaum's best quality and electrolytic zinc from Brunner Mond and Co. were tried. Both samples gave practically the same E.M.F.'s. The electrolyte was zinc nitrate. A steady E.M.F. is more easily obtained with zinc than with most of the other metals. On standing in contact with NH_3 , however, the surface of the metal slowly blackens.

Cadmium.—The "Kahlbaum" brand was used. Its purity was sufficiently attested by its behaviour in Weston cells. As solute the nitrate was taken. Like zinc, cadmium gives a fairly steady E.M.F. It was chiefly for this reason that it was chosen for a standard electrode.

Magnesium.—The commercial metal was employed. It was not possible to obtain any satisfactory measurements with magnesium nitrate as solute, and the iodide was therefore used.* The latter was prepared by decomposing the required amount of cadmium iodide dissolved in NH_3 , with excess of magnesium powder. On long standing in the solution magnesium becomes covered with a black layer, probably of the same nature as that observed by Divers† in his researches on NH_3 and NH_4NO_3 . Owing to the slight solubility of MgI_2 , a 0.1 N solution could not be investigated.

Nickel.—Commercial nickel is always impure. Electrolytically deposited metal and a specially pure sample from the Mond Nickel Co. were employed. The E.M.F. falls slowly till a constant value is reached.

Copper.—Gore‡ states that copper dissolves in liquid NH_3 with formation of a blue colour. Seely,§ however, maintains that it is insoluble in *anhydrous* NH_3 , and this was found to be the case. Moreover, it was also found that copper is insoluble in NH_3 containing water if oxygen is excluded. This is in line with the behaviour of copper and other metals in contact with

* It may be recalled here that magnesium and some other metals show too low an E.M.F. when in contact with aqueous solutions of their nitrates.—Cf. *Z. Physik. Ch.* **35**, 310 (1900).

† *Proc. Roy. Soc.* **21**, 109; *Phil. Trans.* **163**, 359 (1873).

‡ *Proc. Roy. Soc.* **21**, 143 (1873).

§ *Chem. News*, **23**, 169.

ELECTRODE POTENTIALS IN LIQUID AMMONIA 75

ammoniacal aqueous solutions, as shown by Matignon and Desplantes.* It was therefore deemed permissible to measure the E.M.F. of copper in the same way as in the case of the other metals, air being excluded by a current of hydrogen. It will be noticed that the value found for the 1.0 N solution is numerically less than that of the 0.1 N. This is no doubt due to association of the solute in the more concentrated solution. Electrolytic copper was used for the electrodes.

Potassium, Sodium, and Calcium.—Electrodes of these metals were made by fastening a small piece of the metal to be examined to the end of a short platinum wire sealed into a glass tube. The metal slowly dissolves in the NH_3 , but a fairly constant E.M.F. is produced. If enough alkali salt is present the distinctive blue colour, usually noticed when an alkali metal dissolves in NH_3 , is not formed. The E.M.F. of potassium is not so steady as that of sodium. If sufficient alkali metal is dissolved in the NH_3 to produce a blue colour, and a platinum electrode is immersed in the solution, an E.M.F. is set up identical with that obtained from the coherent alkali metal. All this tends to confirm the suspicion that the blue colour is due to a colloidal solution or suspension of the alkali metal itself. The phenomenon would thus seem to be analogous with the formation of "metallic fogs" in fused salts.†

TABLE I.

Combination.		Number of Observations.	E.M.F.
Ag	AgNO_3 $n/10$ $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}(\text{saturated})$ Cd	7	-0.963 ± 0.005
Ag	AgNO_3 $n/100$ " "	4	-0.932 ± 0.001
Ag	AgI $n/10$ " "	6	-0.885 ± 0.012
Ag	AgI $n/100$ " "	4	-0.827 ± 0.019
Hg	HgI_2 $n/10$ " "	2	$-0.895 (\pm 0.000)$
Hg	HgI_2 $n/100$ " "	2	$-0.867 (\pm 0.002)$
Cu	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ $n/1$ " "	2	$-0.68 (\pm 0.00)$
Cu	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ $n/10$ " "	3	$-0.70 (\pm 0.00)$
Cu	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ $n/100$ " "	2	$-0.58 (\pm 0.00)$
Pb	$\text{Pb}(\text{NO}_3)_2$ $n/10$ " "	2	$-0.515 (\pm 0.000)$
Pb	$\text{Pb}(\text{NO}_3)_2$ $n/100$ " "	3	$-0.495 (\pm 0.001)$
Ni	$(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ $n/10$ " "	2	$-0.500 (\pm 0.000)$
Cd	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ $n/10$ " "	2	$+0.047 (\pm 0.000)$
Cd	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ $n/100$ " "	3	$+0.086 (\pm 0.001)$
Zn	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ $n/10$ " "	4	$+0.353 (\pm 0.001)$
Zn	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ $n/100$ " "	4	$+0.376 (\pm 0.001)$
NH_4	$ \text{NH}_4\text{NO}_3$ $n/10$ " "	3	$+0.91 (\pm 0.01)$
Mg	$ \text{MgI}_2$ $n/100$ " "	2	$+1.26 (\pm 0.00)$
Ca	$ \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ $n/10$ " "	4	$+1.48 \pm 0.04$
Na	$ \text{NaNO}_3$ $n/10$ " "	4	$+1.56 \pm 0.02$
Na	$ \text{NaCl}$ $n/10$ " "	1	$+1.58$
K	$ \text{KI}$ $n/10$ " "	3	$+1.59 (\pm 0.01)$

Ammonium.—This was studied in the form of ammonium amalgam produced by electrolysis. At first it was attempted to prepare the amalgam from a solution of ammonium nitrate in NH_3 . A small drop of mercury was used as cathode, a current of high density was passed for a few seconds, and the E.M.F. of the drop was at once measured. It was not possible, however, to obtain constant values in this way, although they resembled in magnitude

* *Comp. Rend.* 140, 13, 27 (1905).

† Cf. Lorenz, *Die Elektrolyse geschmolzener Salze*, 1905.

76 ELECTRODE POTENTIALS IN LIQUID AMMONIA

those got by the second method, which was as follows : An aqueous solution of ammonium chloride was electrolysed, using a mercury cathode as before, and keeping the temperature as low as possible. The amalgam formed was then frozen, washed with liquid NH_3 , and its E.M.F. against ammonium nitrate solution was determined.

In the tables the + sign before the E.M.F. indicates that in the given combination the positive current tends to flow from left to right, and the - sign of course the reverse. Further, in accordance with this, the + sign before a single electrode potential indicates that the electrolyte is positive to the metal. The concentrations are in gram equivalents per litre.

The E.M.F.'s of the combinations actually measured are given in Table I., the "solvent" being, as already stated, a 0.5 N solution of KNO_3 .

In order to compare these results with measurements made in aqueous solutions, it was necessary to have some direct determinations against one of the usual standard electrodes ; and to this end the following arrangement was tried (Fig. 2) :—

FIG. 2.

It was found that solutions made with strong aqueous ammonium S.G. 0.880) do not freeze at the boiling-point of liquid ammonia ; and that they could therefore conveniently be used to fill the siphon joining the liquid NH_3 solutions with the $n/10$ calomel electrode. The following combinations were thus measured :—

If we assume that the E.M.F. of the $n/10$ calomel electrode is -0.338 volt,* or, in other words, that the E.M.F. of the standard hydrogen electrode is 0.0 volt, we obtain the following results :—

* *Z. Physik. Ch.* 35, 330 (1900).

ELECTRODE POTENTIALS IN LIQUID AMMONIA 77

$\text{Cd} \mid \text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \text{ satd.} \mid \text{NH}_4\text{OH} \mid \text{KCl } n/10 = + 1.041 \text{ volts.}$

$\text{Zn} \mid \text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O } n/10 \mid \text{NH}_4\text{OH} \mid \text{KCl } n/10 = + 1.403 \text{ volts.}$

$\text{Hg} \mid \text{HgI}_2 \text{ } n/10 \mid \text{NH}_4\text{OH} \mid \text{KCl } n/10 = + 0.164 \text{ volt.}$

The symbol NH_4OH stands for the aqueous ammonia solution. It should be noted that in these combinations there are unknown, and possibly considerable, contact potentials between the different solutions, and that there is a very considerable temperature gradient in the aqueous ammonia. We are, however, as yet unfortunately not able to allow for these.

From the last two combinations and the values given in Table I. for the $\text{Zn} \mid \text{Cd}$ and $\text{Hg} \mid \text{Cd}$ cells ($n/10$) we obtain two more values for the combination— $\text{Cd} \mid \text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \text{ satd.} \mid \text{NH}_4\text{OH} \mid \text{KCl } n/10$, viz., 1.050 and 1.059 volts respectively. In taking the mean it is probably advisable to give double value to the directly determined value, 1.041. We then obtain as the average + 1.048 volts, which, as a rough approximation, may be taken as the E.M.F. of the half element, $\text{Cd} \mid \text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \text{ satd.}$; and this number has accordingly been used in calculating the following single potentials (Table II.). In this table the numbers in the column headed E.P. are the electrolytic potentials calculated for normal ionic concentrations in aqueous solutions.*

TABLE II.

Metal.	Electrolyte.	E.M.F. in Liquid NH_3 .	E.P. in Aqueous Solution.	Difference.	
				For $n/10$.	For $n/100$.
K	KI $n/10$...	+ 2.64	+ 3.20	— 0.56	
Na	NaCl $n/10$...	+ 2.63	+ 2.82	— 0.19	
"	$\text{NaNO}_3 \text{ } n/10$...	+ 2.61	+ 2.82	— 0.21	
Ca	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O } n/10$	+ 2.53	+ 2.56	— 0.03	
Mg	$\text{MgI}_2 \text{ } n/100$...	+ 2.31	+ 2.54		— 0.23
			+ 1.49		+ 0.82
NH_4	$\text{NH}_4\text{NO}_3 \text{ } n/10$...	+ 1.96			
Zn	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O } n/100$	+ 1.424	+ 0.770		+ 0.65
	$n/10$	+ 1.401	+ 0.770	+ 0.63	
Cd	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O } n/100$	+ 1.134	+ 0.420		0.71
"	$n/10$	+ 1.095	+ 0.420	0.68	
Ni	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O } n/10$	+ 0.548	+ 0.228	0.32	
Pb	$\text{Pb}(\text{NO}_3)_2 \text{ } n/100$...	+ 0.553	+ 0.148		0.41
"	$n/10$...	+ 0.533	+ 0.148	0.39	
Cu	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O } n/100$	+ 0.47	— 0.329		0.80
"	$n/10$	+ 0.35	— 0.329	0.68	
"	$n/1$	+ 0.37	— 0.329		
Hg	$\text{HgI}_2 \text{ } n/100$...	+ 0.181	— 0.750		0.93
"	$n/10$...	+ 0.153	— 0.750	0.90	
Ag	$\text{AgI } n/100$...	+ 0.221	— 0.771		0.99
"	$n/10$...	+ 0.163	— 0.771	0.93	
"	$\text{AgNO}_3 \text{ } n/100$...	+ 0.116	— 0.771		0.89
"	$n/10$...	+ 0.085	— 0.771	0.86	

A glance at the table shows that, apart from the fact that the order of the potential series is practically the same in ammonia and in water, the quantitative agreement is far from close. With regard to the first five metals, it should be noted, however, that the E.P.'s given for K, Na, and Ca, and the

* *Z. Physik. Ch.* 35, 318 (1900).

78 ELECTRODE POTENTIALS IN LIQUID AMMONIA

first number for Mg, were calculated from the heats of formation of their halogen compounds. The sign of the difference (E.M.F.—E.P.) would indicate that these metals do not form truly reversible electrodes with ammonia solutions, owing to their too vigorous reaction with the solvent. Also a comparison of the E.M.F.'s of the other metals with those of these four increases the probability of the true electrode potentials of the latter being much higher than as found by us. A parallel instance is that of magnesium in aqueous solution.

As for the rest of the table, it is noticeable that the potentials in ammonia are uniformly much higher algebraically than those in water. This may be partly due to the contact and thermal potentials referred to above; but these can hardly be responsible for more than a small part of the difference; and in any case their effect must have been practically constant under the conditions of experiment. It is possible that the ionic concentrations in liquid ammonia are very much smaller than in corresponding aqueous solutions; and it is perhaps worth noting that addition of ammonia to aqueous solutions themselves produces changes of E.M.F. of similar magnitude and direction to the differences here considered. Examples of this are shown by copper and silver electrodes.

In conclusion, we cannot claim to have advanced far towards the measurement of the relative affinity of the elements in liquid ammonia solutions. A great amount of work requires to be done before satisfactory values for the electrolytic potentials in these solutions can be arrived at.

UNIVERSITY COLLEGE, LONDON.