The Overvoltage of Hydrogen in Liquid Ammonia

By *V. A. Pleskow*

One of the characteristic differences between liquid ammonia and water as a solvent is the exceptionally increased affinity of the former for the proton. Owing to this property liquid ammonia possesses a number of peculiarities, the most characteristic of which is the considerable shift of the normal hydrogen potential in liquid ammonia to the negative side; this shift attains 0.8 V[1]. There is no doubt, however, that the greater stability of the ammonium ion in comparison with H_3O^+ should effect not only the position of the thermodynamic equilibrium between the solution and the hydrogen electrode, but also the irreversible process of the discharging of the ions during electrolysis; it could be surmised that the overvoltage of hydrogen in liquid ammonia should be considerably higher than in aqueous solutions.

As has already been indicated in one of our earlier papers[2], one of the reasons for the stability of solutions of the alkali metals in liquid ammonia is, probably, just this high overvoltage of hydrogen, which hampers its evolution. Unfortunately, the number of papers dealing with a study of the overvoltage in non-aqueous solutions is very small, and of this number reliable results have been obtained only in a few investigations. To the latter group belong the investigations carried out by

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[1] V. Pleskow a. A. Monosson, J. Phys. Chem. (Russ.), 6, 1299 (1935).

[2] V. Pleskow a. A. Monosson, J. Phys. Chem. (Russ.), 6, 1286 (1935).

Lewina and Zilberfarb[3] and Novoselsky[4]. These writers point out that in ethyl alcohol the dependence of the overvoltage of hydrogen on mercury upon the current density is in agreement with the Volmer theory, and moreover that the absolute values of the overvoltage are smaller than those for the case of water. In liquid ammonia the overvoltage has not been studied at all, except for the very crude work of A. Grovening and H. Cady[5] who studied the overvoltage during the electrolysis of solutions of the salts of a number of metals.

Experimental part

The hydrogen overvoltage was measured in a 0.1 *N* solution of NH_4Cl (which is an analogue of HCl in aqueous solutions) at a low temperature.

As was pointed out by Lewina and Sarinsky[6], in order to obtain correct values for the overvoltage, especially at small current densities, the purity of the solutions and of the electrodes are of decisive importance. Owing to this the experiments described below were carried out with the greatest possible precautions not to introduce any impurities.

Solvent. Synthetic liquid ammonia, condensed into a tank containing metallic sodium, was additionally purified before admitting it into the apparatus by passing it through a tube filled with finely devided potassium. These tubes, which are a very effective means of purifying gaseous ammonia, (and also other gases in those cases when a small admixture of ammonia is not harmful), were prepared by distribu ting a concentrated solution of metallic potassium in liquid ammonia over the surface of the chips of glass which filled the tube. After the ammonia has evaporated, the metal which remains possesses a greatly developed surface and is extre-

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[3] S. Lewina a. M. Silberfarb, Acta Physicochimica URSS, **4**, 275 (1936).
[4] U. Novoselsky, Ber. Inst. physik. Chem. (Ukr. SSR), **8**, 225, **11**, 125 (1938).
[5] A. Grovening a. H. Cady, J. Phys. Chem., **30**, 1597 (1926).
[6] S. Lewina a. V. Sarinsky, J. Phys. Chem. (Russ.), **11**, 621 (1937).

mely active (in air it ignites immediately). Details of the preparation of such tubes are given in another paper[7]. The specific electrical conductivity of the liquid ammonia which was employed in the present investigation did not exceed 10^{-8} reciprocal ohms (at —50° C).

Ammonium chloride. This was a Kahlbaum reagent which was recrystallized twice and then sublimed in vacuum before using.

Stop-cocks and ground joints. The electrolyte in the apparatus did not come into contact with any of the greased stop-cocks or ground joints. The stop-cocks through which the gaseous ammonia and hydrogen passed were greased only along the adges (except for the stop-cocks at the end).

Before using, the vacuum grease which was employed was preliminarily extracted several times with liquid ammonia at room temperature.

Cryostat. To maintain a constant temperature, a liquid ammonia cryostat described by Monosson and Pleskow[8] was employed, the level of the liquid in which was automatically kept constant[7]. Temperature fluctuations did not exceed 0.2° C.

The apparatus. Measurements were carried out with a stationary electrode which had a comparatively large surface and was polarized by a continuously flowing current. The strength of the polarizing current, taken from a 240 V. storage battery, was measured with a needle galvanometer; the potential of the cathode was measured with the aid of a usual compensation bridge, a mirror galvanometer (sensitivity 10^{-10} A) serving as the zero instrument.

1. Mercury electrode

In view of the fact that the most accurate observations of the overvoltage of hydrogen in water were made with a mercury electrode, the initial experiments were carried out with this metal. An apparatus was constructed which permitted measurements to be carried out with an electrode having a surface of the order of 15 cm.^{2}; the metallic mercury was subjected to very careful cleaning and then was distilled twice in vacuum. It was found, however, that a relation

[7] V. Pleskow, J. Phys. Chem., **12**, 255 (1938).
[8] A. Monosson a. V. Pleskow, J. Phys. Chem. (Russ.), **3**, 221 (1932).

between the overvoltage and the current density could not be obtained owing to the fact that during electrolysis (at —38° C) an ammonium amalgam quantitatively forms on the cathode. This amalgam dissolves in the mercury and its formation is the main depolarizing process. As is known, a similar phenomenon also occurs to some extent in aqueous solutions (see, for example, the work of S. Naray-Szabo and L. Szlatinay[9]). In liquid ammonia evolution of hydrogen did not occur even at current densities of the order of 10^{-2} A/cm.^{2}. The potential of the cathode, after switching on the polarizing current, at first increased quickly to a value of about 0.2 V. and then slower, up to 0.8—0.9 V.; it did not become constant even after an interval of 8—10 hours. Upon breaking the circuit, the amalgam electrode which was formed on the cathode kept its high potential which only very slowly decreased with time. Owing to this an attempt was made to study the overvoltage on solid mercury, since in this case the formation of an ammonium amalgam would be possible only in the surface layer. Measurements carried out at —50° C actually showed a very considerable increase in the overvoltage. Upon switching on the polarizing current, a quick increase in the potential of the cathode to 1.5—1.7 V. occurred; and the larger the density of the polarizing current, the faster this change in potential took place. Upon switching off the current, the potential of the cathode began to fall slowly; and the smaller the quantity of electricity which had been preliminarily passed through the electrode, the faster this fall in potential occurred. At large current densities (10^{-2} A/cm.^{2}), a greyish film, visible to the naked eye, appeared on the surface of the electrode and evolution of hydrogen commenced.

Thus it can be concluded that, on solid mercury also, during electrolysis the formation of comparatively stable film of an ammonium amalgam takes place. This film slowly diffuses into the electrode and makes exact measurements of the hydrogen overvoltage impossible. It is beyond all doubt, however, that the magnitude of the latter is considerably higher (approximately by 0.8—0.9 V.) than it is in water.

[9] S. Naray-Szabo a. L. Szlatinay, Z. physik. Chem., A 173, 89 (1935).

2. Nickel elektrode

The measurements were carried out in the apparatus represented schematically in Fig. 1. The nickel cathode *K*, made of Kahlbaum nickel plate, was 25 × 35 mm. in size and was situated

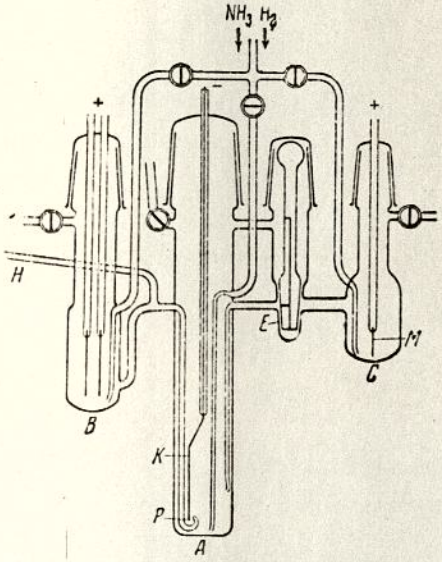

Fig. 1.

in the central vessel *A*. At a distance 0.5 mm. from the surface of the electrode, there was located the finely drawn out end of the tube *P* connected with the vessel *B* which contained the reference hydrogen electrode (details of the construction of the hydrogen electrode are given in a paper by Pleskow and Monosson[1]). Polarization of the electrode was accomplished with the aid of the platinum anode *M*, located in the vessel *C* which was separated from *A* by the ground joint *E*. Before an experiment the nickel electrode was cleaned with a hot solution of alkali, washed with water, and placed into the apparatus which was then immediately

evacuated thoroughly and filled with hydrogen. After this, the lower part of the tube *A* containing the electrode was placed into an electric furnace and heated to 400° C over a period of 2—3 hours in a continuous stream of hydrogen. Then the apparatus was cooled,

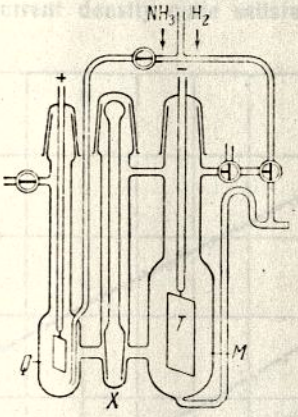

Fig. 2.

placed into the cryostat, and, through the connecting tube *H*, the parts *A* and *B* were filled with a 0.1 *N* solution of NH_4Cl in liquid ammonia. This solution was preliminarily prepared in vessel *M* (Fig. 2), located in a separate cryostat and, for the purpose of purification, was subjected to prolonged elecrolysis with a current of about 1 mA. A large nickel electrode *T* served as the cathode; the anodic compartment *Q* was isolated by a carefully made ground joint *X*. During the electrolysis the solution was continuously stirred by a current of hydrogen. The solution in the anodic compartment of the main apparatus (Fig. 1) was prepared separately by means of direct condensation of ammonia. After filling the apparatus with the electrolyte, hydrogen was bubbled through the latter continuously. Measurements were carried out at —50° C.

This study showed that, under the conditions described, the potential of the polarized nickel electrode could be measured (in

one experiment) with an accuracy of about 2 mV; deviations between different experiments were larger but did not exceed 5 mV. The results of the overvoltage measurements within the current density interval 10^{-7}—10^{-4} A/cm.^{2} are presented in Fig. 3 (upper curve). As can be seen from the drawing, the dependence of the overvoltage upon the current density quite satisfactorily obeys Tafel's

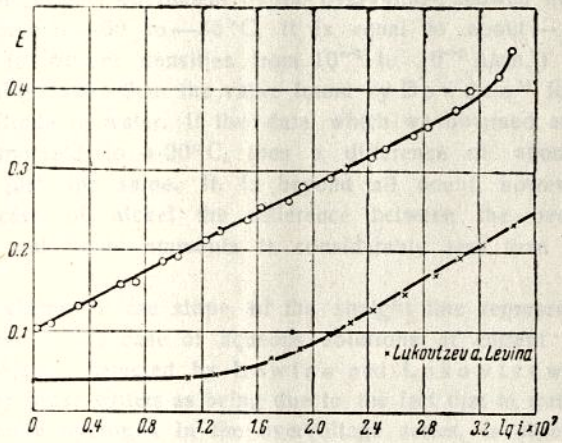

Fig. 3.

logarithmic equation; and furthermore the slope of the straight line (0.090) is very close to the one predicted by Volmer's theory $\left(\frac{2RT}{F} = 0.088 \text{ at } -50.0^\circ \text{C}\right)$. Only at the current density 10^{-4} A/cm.^{2} a slight upward bend of the curve was observed; it should be mentioned that this bend, in contrast to the linear part, was irreversible. This can in all probability be explained as being due to the poisoning of the electrode by the products of electrolysis (which enter from the anodic compartment at considerable currents).

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[10] P. Lukowtzew a. S. Lewina, Acta Physicochimica URSS, 11, 21 (1939).

The lower curve in Fig. 3 represents the results of measurements carried out by Lukowtzew and Lewina[10], who employed a 0.1 *N* solution of HCl in water (at 20°C). As can be seen from the drawing, the values of the overvoltage in liquid ammonia lie approximately 0.2 V. higher than they do in water. This increase can be partially attributed to the difference in the temperatures at which the measurements were carried out. However, measurements of the temperature coefficient of the overvoltage showed that, within the interval —60 to —35° C, it is equal to about — 1.5 mV. per 1° C (at current densities from 10^{-6} to 10^{-5} A/cm.^{2}) which is considerably lower than the value found by Bowden[11] for a mercury electrode in water. If the data which we obtained at —50 C° are extrapolated to +20° C, then a difference of about 0.1 V. remains just the same. It is beyond all doubt, however, that in the case of nickel the difference between the overvoltage in water and liquid ammonia is considerably less than it is for mercury.

The change of the slope of the straight line representing the overvoltage in the case of aqueous solutions at current densities of 10^{-5} A/cm.^{2}, detected by Lewina and Lukowtzew and explained by those writers as being due to the fact that in water nickel stands before hydrogen in the overvoltage series, is absent in the case of liquid ammonia. The normal potential of nickel in liquid ammonia is unknown.

However, one may assume that it is shifted considerably less in comparison with water than it is in the case of hydrogen; in all probability the magnitude of the shift does not exceed that which occcurs in the case of zinc or bivalent copper. Therefore, nickel should be placed after hydrogen in the electrochemical series for the case of liquid ammonia, and the absence of an inflexion on the curve is quite natural.

3. Lead electrode

Preliminary measurements of the overvoltage of hydrogen on lead showed that it is undoubtedly considerably higher than it is in

[11] F. Bowden, Proc. Roy. Soc., London, (A), **126**, 107 (1929).

water and approaches 1.1—1.2 V. at current densities from 10^{-4}—10^{-5} A/cm.^{2}.

However, owing to experimental difficulties, in the apparatus employed it was impossible to obtain an electrode with a sufficiently clean surface and therefore these data can only be considered as approximate.

Summarizing the results of the above experiments, it can be stated that, in all the cases examined, the overvoltage of hydrogen in liquid ammonia is higher than it is in water; the difference, however, varies for different metals. Unfortunately, the present position of the theory of electrode processes does not permit an exact relation between the overvoltage and the properties of the solvent to be given; the only thing that is certain is that the character of the electrode must play a considerable rôle here. Apparently the most pronounced effect of the solvent is observed in the case of metals which do not adsorb hydrogen (mercury).

However, the experimental material which is available at present is as yet not sufficiently complete to give a final solution of this problem.

I consider it to be my pleasant duty to express my deep gratitude to S. Lewina for the valuable advice which she has given in the course of this investigation.

Summary

The overvoltage of hydrogen on nickel was determined in a solution of NH_4Cl in liquid ammonia at —50.0° C and current densities ranging from 10^{-7} — 10^{-4} A/cm.^{2}.

The dependence of the overvoltage upon the current density obeys Tafel's equation; the value for the slope of the straight line is close to that calculated on the basis of Volmer's theory.

The absolute values of the overvoltage are higher than those in an aqueous solution of HCl by 0.2 V.

A still greater difference (0.8—0.9 V.) is observed in the case of a mercury electrode; exact determination of the overvoltage on liquid and solid mercury could not be carried out owing to the forma-

tion of an ammonium amalgam during electrolysis. The increase in the hydrogen overvoltage in liquid ammonia (established also in the case of the lead electrode) is connected with the greater affinity of the NH_3-molecule for the proton.

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Received
May 15, 1939.