

U. D. C. 541.13 EXPERIMENTAL

HYDROGEN OVERPOTENTIAL ON MERCURY AT LOW CURRENT DENSITIES. I. ACIDIFIED POTASSIUM IODIDE SOLUTIONS

L. I. Krishtalik

I have previously shown¹ that barrierless discharge (i.e. a process for which the activation energy is equal to the heat of reaction) becomes theoretically possible at low cathodic potentials for metals with the highest hydrogen overpotentials.

Hydrogen overpotential at very low current densities has also been studied by other workers on mercury²⁻⁴, and by Kolotyarkin and Frumkin⁵ on lead sponge. The conditions of measurement used in some of those investigations^{2,5} were such that, in all probability, barrierless discharge was not achieved.

Mituya observed a sharp bend in the curve at current densities of $10^{-9.5}$ – $10^{-10.5}$ A cm⁻², i.e. approximately in the region predicted by theory¹. The slope of the curve below the break was ~40 mV, i.e. lower than the theoretical slope by a factor of about 1.5. However, Mituya's values for the overpotential and the capacitance are in serious disagreement with the best published data for comparable current densities — probably because his platinum anode was too close to the cathode⁶⁻⁸.

The choice of experimental materials and procedure in the present work was guided by the following considerations. In 1 N acid, the calculated current density for transition from normal to barrierless discharge is¹ of the order of 10^{-10} A cm⁻². The hydrogen overpotential is known^{9,10} to be considerably lower, with the usual slow discharge, in acid solutions of salts having strongly adsorbed anions and in concentrated solutions of acids. For barrierless discharge, on the other hand, the hydrogen overpotential should not be significantly affected by the composition of the solution¹. Therefore, the onset of barrierless discharge can be expected at higher current densities in solutions of these types, and these are more convenient from the experimental point of view.

One unsatisfactory feature of the procedure used by Bowden and Grew² is that neither the cathode nor the solution could be changed during the experiment to check the reproducibility of the results. I have therefore chosen a method similar to that described by Iofa et al.⁹, in which the final purification of the solution is by electrolysis with an auxiliary mercury cathode.

According to the elementary theory of electrolytic purification¹¹, the time needed to purify a solution by a given amount is proportional to the thickness of the diffusion layer and to the ratio of the electrolyte volume to the area of the cathode, i.e. to the effective thickness of the layer of electrolyte. An approximate calculation shows that the rate of purification can be increased by 1–2 powers of ten by vigorous stirring and by carrying out the electrolysis in a thin layer of solution.

Purification of Reagents

The mercury was treated with alkali and with nitric acid (with air bubbling through for a day). It was then distilled twice *in vacuo* in an apparatus of the type described by Chmutov¹².

Hydrochloric acid of "chemically pure" and "analytically pure" grades was redistilled four times, the middle fraction being collected in approximately 70% yield. Potassium iodide of "chemically pure" grade was recrystallised twice, twice distilled water being used for the second crystallisation. Water was redistilled three times — the third time with additions of KOH and KMnO₄. The tetrabutylammonium chloride† had been purified by lengthy washing with cryoscopic benzene, double recrystallisation from rectified acetone, and drying under vacuum at 40°.

Hydrogen was prepared by electrolysis of a solution of "chemically pure" KOH (purified from carbonate by adding barium hydroxide). It was passed, in turn, through fused CaCl₂, a furnace containing platinised silica gel, an alkaline plumbite solution, CaCl₂, an activated charcoal trap cooled in liquid nitrogen, and acid of approximately the same concentration as used in the experiment.

Cell Construction and Procedure

The construction of the electrolysis cell is shown schematically in Fig. 1. The cell is generally similar to that described by Iofa et al.⁹: the main points of difference, introduced in the hope of improving the purification of the solution, are as follows.

The apparatus was made entirely of quartz‡. To enable the solution to be used in a shallow layer, the tips of the

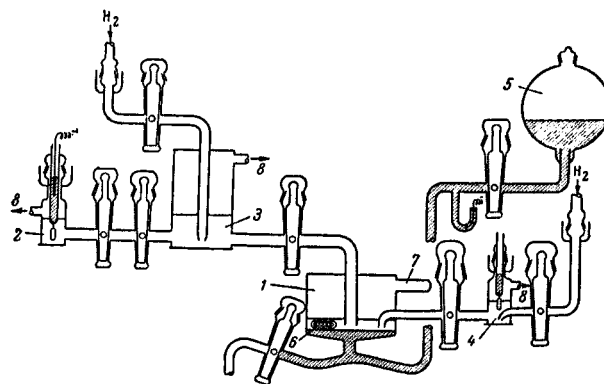


Fig. 1. Electrolysis cell:

- 1) cathode compartment; 2) anode compartment; 3) ballast vessel;
- 4) hydrogen reference electrode compartment; 5) mercury reservoir (connected to the cell through a mercury-filled joint);
- 6) floating magnetic stirrer; 7) side-arm for magnetic float;
- 8) gas outlet (through a mercury-filled tap and a mercury seal).

† Kindly supplied by Yu. M. Kessler.

‡ Only the mercury reservoir was made of Pyrex glass.

siphons connecting the cathode compartment to the anode compartment and to the reference electrode were set at the same level.

The solution was stirred by means of a magnetic stirrer sealed in a quartz capsule, floating on the mercury surface. Operation of the stirrer (at 4 c/s) produced waves of ~ 1 mm amplitude on the mercury surface. The stirrer was operated only during purification of the solution: during the measurements it was transferred to a side-arm in the upper part of the cathode compartment.

The anode was a silver wire in 1 N HCl.

The apparatus was kept in an air thermostat at $25.0^\circ \pm 0.2^\circ$. Before each experiment, the cell and all associated items and glassware were kept in an alkaline permanganate solution for 2 days (the solution was renewed during the treatment). This was followed by two portions of twice distilled hydrochloric acid, and lastly by four-times distilled acid. After assembly, the apparatus was purged with hydrogen: the intermediate and the cathodic section were evacuated to a residual pressure of ~ 50 mmHg, and refilled with hydrogen, 20–40 times, and the entire apparatus was then swept with hydrogen for ~ 16 h (hydrogen flow ~ 0.5 litre h^{-1}). The solution was then added to the central compartment, and hydrogen was passed for 6–16 h. When the sweeping out was completed, the solution was transferred by pressure into the appropriate compartments of the cell, the magnetic stirrer was energised, and electrolytic pretreatment was begun at a current density of $\sim 10^{-4}$ A cm^{-2} . During this preliminary electrolysis (16–24 h) the cathode was renewed 3 times; each time, a small volume of solution was also rejected, so that the tubes were washed with mercury and with the solution 4 times. Before the first change of cathode the layer of solution was 6–10 mm deep; by the end of the treatment it had dropped to 3–7 mm. The steady potential usually increased a little after the first change of cathode, but further changes of cathode usually had no effect on the potential.

After each experiment the concentration of acid in the catholyte and in the hydrogen electrode compartment was measured, and a correction for the change in equilibrium potential was applied. The correction was usually less than 4–5 mV.

The potential was measured on an LP-5 electronic potentiometer or on an MV-11 electronic voltmeter (marketed by the East German firm of Klamman and Granert); the current was measured on an M-193 (precision class 1.0) or an M-194 (precision class 0.5) multirange instrument.

Polarisation curves were plotted after 1.5–2 h polarisation at 10^{-4} A cm^{-2} . The curves were determined from high to low current densities, and then from low to high. Each value of the potential remained stable for at least 10–15 min; at the lowest current densities the constancy of the potential was checked for even longer times.

In KI solutions at $i \approx 10^{-5}$ – 10^{-4} A cm^{-2} the potential settles slowly. This causes hysteresis, the effect being more marked the faster the curve is explored. At lower current densities, when η is close to 60 mV, the potential reaches a steady value quickly, and the forward and reverse plots agree to within 2–4 mV. It is interesting to note that the potential settles quickly even when $i > 10^{-5}$ A $\times \text{cm}^{-2}$ if a tetrabutylammonium salt is added to the acidified KI solution. There have been previous reports^{9,10} of hysteresis in the steeply rising region of the curve for

acidified KI solutions: the hysteresis is ascribed to slow establishment of the adsorption equilibrium. However, Tsa Ch'uang-hsin and Iofa¹⁴ have not observed hysteresis on mercury in 2 N KI, and are inclined to believe that the hysteresis is due to iodine or mercury ions present as impurities. It is possible that certain impurities influence the rate at which the adsorption equilibrium is established when the amount of iodide adsorbed varies very rapidly with potential. In any case, hysteresis is absent in the region of low current densities, which is the most interesting to us, and the reproducibility of the results is good.

DISCUSSION

Fig. 2 shows some typical polarisation curves. Their most characteristic feature is the large decrease in slope at low current densities — from upwards of 100 mV to a value close to 60 mV.

A curve of this type cannot be ascribed to experimental error. In view of the careful purification, the reproducibility of the results, and the constancy of the potential when the cathode is changed, it is most unlikely that the break in the curve is due to impurities.

The decrease in slope of the polarisation curve at low current densities could be due to spontaneous dissolution of the cathode. Under these conditions, however, the slope changes continuously, and the linearity of the plot is lost: this is not so in the present work. At most of the points, the potential corresponds to such low equilibrium concentrations of HgI_2^- that the limiting spontaneous dissolution current must be negligibly small compared with the hydrogen-evolution current.

The following experiment, which was repeated several times, demonstrates the absence of misleading effects

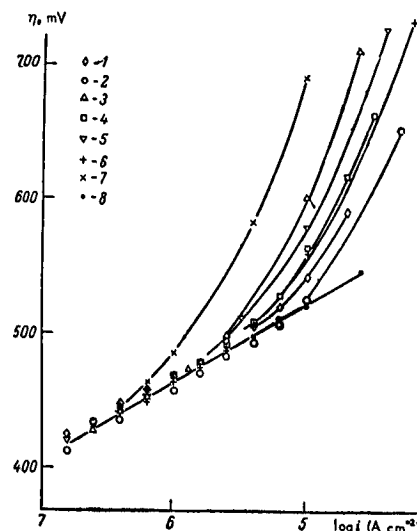


Fig. 2. Typical polarisation curves in acidified solutions of the following composition:

- 1) 6.8 N KI + 0.5 N HCl; 2) 6.8 N KI + 0.35 N HCl;
- 3) 4.7 N KI + 0.4 N HCl; 4) 4.3 N KI + 0.9 N HCl;
- 5) 3.9 N KI + 0.7 N HCl; 6) 3.2 N KI + 1.2 N HCl;
- 7) 0.8 N KI + 0.8 N HCl; 8) 3.0 N KI + 0.9 N HCl + 0.0013 N $(\text{C}_4\text{H}_9)_4\text{NCl}$.

from impurities or from spontaneous dissolution of the cathode. When a steady potential had been obtained (in the region of $b \approx 60$ mV), vigorous stirring of the solution was begun. This lowered the potential by 20–40 mV by improving the supply of depolariser; the potential then rose (reduction of traces of impurity) and became steady at 4–8 mV below the initial value. This small drop is consistent with the increase in surface area of the cathode due to stirring. It occurs also at high current densities, and disappears as soon as stirring is stopped. Thus, the potentials measured at lower current densities are practically unaffected by vigorous stirring, i.e. by conditions which favour the supply of impurities and which accelerate spontaneous dissolution. The conclusion is that the type of polarisation curve observed in this work is real, and not the result of experimental error.

Thomas¹⁵ suggests that a slope of approximately 60 mV may arise from a variety of mechanisms, in particular from slow recombination coupled with a logarithmic hydrogen adsorption isotherm. However, a logarithmic isotherm is not applicable at the low coverages which are known to exist on mercury¹⁶, and this explanation of the 60 mV slope cannot be upheld.

The hypothesis¹⁷ of a slow first-order chemical reaction (slow surface diffusion) is also unlikely for mercury, since it is usually associated with the presence of different types of adsorption site on a metal surface.

Another possible explanation of the break in the polarisation curve involves a rearrangement of the double layer in the vicinity of the zero-charge point¹⁷. However, Conway¹⁸ considers this treatment improbable.

In the present experiments the break occurs fairly close to the zero-charge point for KI solutions, but, as will be shown in a later paper, in concentrated acids the break occurs at ~ 0.4 V from the zero-charge point: clearly, there is no direct link between the two parameters.

Thus, none of the mechanisms usually considered can account for a slope of about 60 mV at a mercury cathode.

I have previously shown that a new type of electrode reaction — barrierless discharge — is to be expected at low cathodic potentials for metals with high hydrogen overpotential. In this process the activation energy is equal to the heat of the reaction, $\alpha = 1$, and $b = 59$ mV.

With barrierless discharge the overpotential should be independent of the pH and of the ψ_1 potential. This is because when $\alpha = 1$ the effect of the bulk concentration of H_3O^+ ions and of the ψ_1 potential on the surface concentration is exactly compensated by the effect of these variables on the potential difference across the double layer¹.

My experimental results are in complete agreement with this conclusion.

A special feature of the behaviour observed in acid solutions of KI is the steep rise of the polarisation curve at potentials more negative than the zero-charge point: this is associated with desorption of iodide ions^{9,10,13,14}. These phenomena have been observed also in the present experiments (Fig. 2). However, at potentials more positive than the zero-charge point the slope of the η -log i curve is close to the normal value, dropping sharply to ~ 60 mV when the potential is further decreased. Perhaps the most important observation is that the overpotential is a very sensitive function of the composition of the solution in the region where b is high, whereas all the curves

coalesce (within the limits of experimental error) when $b \approx 60$ mV. In the region of high b the separation between the individual curves can be 200 mV or more, whereas at low b all the curves fall within a band of 15–18 mV, the average departure from the mean being 4.5 mV (computed from 18 independent experiments, see Table). It should be noted that the deviations of the individual curves from the mean are not systematic, and bear no relation to the composition of the solution.

This behaviour is exactly what would be expected for a transition from normal to barrierless discharge of the H_3O^+ ion. The slope of the curve (average value 58.3 mV) is practically the same as the theoretical value of 59.1 mV.

The hydrogen overpotential in acidified KI solutions can be altered not only by changing the acidity or the anion concentration, but also by introducing the adsorbable tetra-butylammonium cation. In the region of normal discharge, addition of this ion accelerates the process by virtue of the mutually enhancing adsorption¹⁵ of the $(C_4H_9)_4N^+$ and I^- ions. In the region of barrierless discharge, as theory predicts, its addition had practically no effect on the overpotential (see Fig. 2 and Table).

The phenomena of barrierless discharge is, essentially, a manifestation of the vanishingly small activation energy for the reverse process (ionisation of hydrogen) at sufficiently positive potentials. The existence of non-activated ionisation justifies the belief that the discharge process can also become non-activated at sufficiently negative potentials. It seems likely that all discharge processes can occur in three forms, increase in overpotential causing transition from one form to the next — barrierless, normal, and non-activated. The conditions leading to each of these types of behaviour depend on the particular characteristics of the reaction.

The writer does not believe that the evolution of hydrogen on mercury is the only example of a barrierless process. Many workers have observed, under a variety of

TABLE. Basic parameters of the polarisation curves in the low-slope region.

Solution, KI + HCl, N	η at 10^{-6} A cm ⁻² , mV	Slope b , mV	Range of log i for which $b \approx 0.06$ V
6.8+0.6	459	55	6.4–5.2
6.8+0.55	461	60	6.6–5.4
6.8+0.55	461	55	6.8–5.4
6.8+0.55	461	55	6.8–5.6
6.8+0.5	458	59	6.8–5.4
6.8+0.4	467	63	6.4–5.6
6.8+0.35	463	60	6.6–5.8
6.0+0.4	473 *	60	6.6–6.2
4.7+0.4	466	62	6.6–5.8
4.7+0.9	468	56	6.6–5.6
4.0+1.0	460	55	6.8–5.8
3.9+0.7	468	60	6.8–5.8
3.4+1.0	458	59	7.2–5.8
3.2+1.2	465	60	6.4–5.6
3.0+0.4	475 *	62	6.6–6.2
0.8+0.8	(469) **	(~60)	6.6–6.4
6.8+0.4+1.10 ⁻³ ***	475	52	6.6–4.8
3.0+0.9+1.3.10 ⁻³ ***	469	54	6.8–4.8
3.4+0.8+1.10 ⁻⁴ ***	460	62	6.4–6.0

* Extrapolated from current density of $10^{-6.2}$ A cm⁻².

** Estimated approximately owing to narrow range with $b \approx 60$ mV.

*** The last figure gives the normality of $(C_4H_9)_4NCl$.

conditions, polarisation curves with a slope of approximately 60 mV in the evolution of hydrogen on silver^{17,18-23}, gold²⁴, tungsten¹⁷, molybdenum²⁴, platinum¹⁷, and rhodium²⁵ cathodes. These studies are not detailed enough to justify firm conclusions, but it seems probable that barrierless discharge or barrierless electrochemical desorption occurs in some of them. We have also observed a slope of approximately 60 mV in our work²⁶ on the evolution of chlorine on graphite, the experimental results being in good agreement with the rules of barrierless discharge. A search for new instances of barrierless processes is planned.

SUMMARY

An improved method of measuring overpotential at low current densities has been developed. The hydrogen overpotential has been measured in acidified KI solutions down to current densities of about 10^{-7} A cm⁻². All the solutions examined showed a linear variation of overpotential with logarithm of current density, having a slope of $b = 60$ mV at low current densities. At higher current densities $b \geq 100$ mV. In weakly acid KI solutions the overpotential in the region of $b \approx 60$ mV is practically independent of the composition of the solution and of the structure of the double layer, whereas these factors have a very significant effect in these same solutions when $b \geq 100$ mV. The observed relations are satisfactorily explained by the previously postulated¹ barrierless discharge of H_3O^+ ions.

20. A.A. Antoniou and F.E. Wetmore, *Canad. J. Chem.*, **37**, 222 (1959).
21. B.E. Conway, *Proc. Roy. Soc.*, **256A**, 128 (1960).
22. I.M. Tordesillas, L.P. Bicelli, and B. Rivolta, *Ann. Chim. (Italy)*, **49**, 1585 (1959).
23. Ya. M. Kolotyrkin and L.A. Medvedeva, *Dokl. Akad. Nauk SSSR*, **140**, 168 (1961).
24. N. Pentland, J.O'M. Bockris, and E. Sheldon, *J. Electrochem. Soc.*, **104**, 182 (1957).
25. J.P. Hoare and S. Schuldiner, *J. Chem. Phys.*, **25**, 786 (1956).
26. L.I. Krishtalik and Z.A. Rotenberg, *Zhur. Fiz. Khim.*, **39**, 907 (1965) [*Russ. J. Phys. Chem.*, (in the press)].

Moscow

Received 14th October 1963

U. D. C. 532.7:541.11

ENTROPY IN ETHANOLIC SOLUTION OF UNIVALENT CATIONS HAVING AN INERT-GAS ELECTRONIC CONFIGURATION

E. K. Zolotarev

The energies of solvation of Li^+ , Na^+ , and K^+ in ethanol calculated by Izmailov¹ from electrochemical data and the heats of solvation determined by Mishchenko² enable the entropies of these ions in ethanolic solution to be calculated.

The entropy of an ion in solution can be computed by means of the equation

$$S_{soln}^i = \Delta S_{olv}^i + S_g^i - R \ln 24.45, \quad (1)$$

where ΔS_{olv}^i and S_g^i are the entropies of solvation of the ion and the ionic gas respectively, and $R \ln 24.45$ is a correction for the compression of the ionic gas on dissolution³.

The values calculated by Izmailov¹ for the entropies of solvation of the ions Li^+ , Na^+ , and K^+ are respectively -50.0, -35.3, and -24.3 e.u. The entropy of the gaseous ions can be taken from Ref. 4.

Calculation of the entropies of Li^+ , Na^+ , and K^+ in ethanol by means of Eqn. (1) yields the following results

$$S_{C_2H_5OH}^{Li^+} = -25 \text{ e.u.}; \quad S_{C_2H_5OH}^{Na^+} = -6 \text{ e.u.}; \quad S_{C_2H_5OH}^{K^+} = 6 \text{ e.u.}$$

These values can be checked indirectly by two independent methods.

1. Karapet'yants' comparative method for calculating physicochemical properties⁵ suggests the linear relationship

$$S_{C_2H_5OH}^i = AS_{H_2O}^i + B. \quad (2)$$

A similar relation for the heats of formation in water and in a metal has already been confirmed by experimental data⁶. Fig. 1 shows that Eqn. (2) is satisfactorily obeyed.

2. It can be shown on the basis of Kapustinskii's work⁷ that the entropy of similarly charged solvated ions is linked with the radius of the solvate (Stokes radius) by the relation

$$S^i = \frac{a}{r_s} + b. \quad (3)$$

1. L.I. Krishtalik, *Zhur. Fiz. Khim.*, **34**, 117 (1960) [*Russ. J. Phys. Chem.*, **53** (1960)].
2. F.P. Bowden and K.E.W. Grew, *Discuss. Faraday Soc.*, **1**, 86 (1947).
3. J. Horiuti and A. Mituya, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **2**, 79 (1951).
4. A. Mituya, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **4**, 228 (1957).
5. Ya. M. Kolotyrkin and A. N. Frumkin, *Zhur. Fiz. Khim.*, **15**, 346 (1941).
6. A. N. Frumkin, *Zhur. Fiz. Khim.*, **34**, 931 (1960) [*Russ. J. Phys. Chem.*, **441** (1960)].
7. A. Mituya, and T. Obayashi, *Zhur. Fiz. Khim.*, **34**, 679 (1960) [*Russ. J. Phys. Chem.*, **322** (1960)].
8. A. I. Tsinman, *Zhur. Fiz. Khim.*, **36**, 1388 (1962) [*Russ. J. Phys. Chem.*, **744** (1962)].
9. Z. A. Iofa, B. N. Kabanov, E. M. Kuchinskii, and F. Chistyakov, *Zhur. Fiz. Khim.*, **13**, 1109 (1939).
10. Z. A. Iofa, *Zhur. Fiz. Khim.*, **13**, 1435 (1939); A. N. Frumkin and Z. A. Iofa, *ibid.*, **18**, 268 (1944).
11. A. M. Azzam, J. O'M. Bockris, B. E. Conway, and H. Rosenberg, *Trans. Faraday Soc.*, **46**, 918 (1950).
12. K. V. Chmutov, "Tekhnika Fiziko-Khimicheskogo Issledovaniya" (Techniques of Physicochemical Research), Goskhimizdat, Moscow, 1954.
13. Tsa Ch'uang-hsin and Z. A. Iofa, *Dokl. Akad. Nauk SSSR*, **125**, 1065 (1959).
14. Tsa Ch'uang-hsin and Z. A. Iofa, *Dokl. Akad. Nauk SSSR*, **123**, 1308 (1959).
15. J. G. N. Thomas, *Trans. Faraday Soc.*, **57**, 1603 (1961).
16. A. N. Frumkin, *Adv. Electrochem.*, **1**, 65 (1961).
17. J. O'M. Bockris, I. A. Ammar, and A. K. M. S. Huq, *J. Phys. Chem.*, **61**, 879 (1957).
18. B. E. Conway, *Canad. J. Chem.*, **37**, 120 (1959).
19. J. O'M. Bockris and B. E. Conway, *Trans. Faraday Soc.*, **48**, 724 (1952).