HYDROGEN OVERVOLTAGE.

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The history of electrochemical kinetics is closely bound with the study of the mechanism of hydrogen overvoltage. This is due both to the great practical importance of the reaction of hydrogen evolution and to the belief in its probable simplicity. The latter, to be true, on the whole has not been confirmed by experiment and to the present day we have no complete picture of the successive stages of this reaction. However, many of its characteristics can be regarded as firmly established. In the present paper we wish mainly to communicate some new results pertaining to this field, in addition to those published in several papers in recent years.[1, 2, 3]

(*a*) Proof that the Rate-determining Stage of the Reaction of Hydrogen Evolution on Cathodes with a High Overvoltage — in particular on Mercury — is the Discharge of the Hydrogen Ion on the Metal Surface unoccupied by Adsorbed Hydrogen.

In this respect considerable interest attaches to a determination of the amount of electrochemically-active substance on the electrode surface from the variation of the potential with time after the current has been interrupted. Hickling and Salt [4] determined potential decay curves and came to conclusions incompatible with the above point of view. The method of extrapolation used by these investigators has been criticised by the present author.[1] In the Karpov Institute of Physical Chemistry, Fedotov recently developed an oscillographic method of registering the potential decay curve on a mercury electrode starting from 5×10^{-5} sec.

[1] Frumkin, *Acta Physicochim.*, 1943, **18**, 23.
[2] Jofa and Frumkin, *ibid.*, 1943, **18**, 183.
[3] Frumkin and Aladjalova, *ibid.*, 1944, **19**, 1.
[4] Hickling and Salt, *Trans. Faraday Soc.*, 1941, **37**, 450; *ibid.*, 1942, **38**, 474.

after breaking the circuit. The electrode capacity can be calculated from such measurements without any additional assumptions only if the overvoltage η varies with the time according to a linear law. For this to be so, it is necessary that the variation of the potential be small compared with RT/F, since in this case the rate of the electrochemical reaction on the electrode after the current has been cut off remains practically constant independently of its mechanism. If these conditions are satisfied then the capacity of the polarised electrode can be calculated by the formula :

$$C = \frac{i_0 t}{\Delta\eta} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where i_0 is the c.d. at the moment of breaking the current, t the time and $\Delta\eta$ the change in the overvoltage. If $\Delta\eta$ is not small compared with RT/F then some assumptions must be made in order to determine the capacity. If there is only one slow stage in the cathode process, then, independently of its nature, the state of the cathode and the rate of the cathode process will be single-valued functions of the potential and hence the c.d. of the spontaneous discharge can be found from the value of the steady current at the same cathode potential. In the case of a mercury cathode the latter is determined by Tafel's formula :

$$i = e^{\frac{\eta - a}{b}}$$

where a and b are constants. Hence for the drop in overvoltage we obtain the expression :

$$\Delta\eta = b \ln \left(1 + \frac{i_0 t}{Cb}\right) \quad . \quad . \quad . \quad . \quad (2)$$

In applying eqn. (2) it is necessary to take into consideration the circumstance that at large c.d.'s the determination of η can be vitiated by the ohmic drop of potential in the solution. A suitable correction can be introduced by measuring the resistance or computing it from the paths of the current ; this correction can be avoided if C is calculated using values of $\eta_{observed}$ after two different time intervals t' and t'' from the moment of the current interruption.

Fedotov's experiments were carried out with a comparatively large liquid mercury cathode and the c.d. was limited by the condition that the entire surface of the cathode must be uniformly polarised. With i ranging from 5×10^{-5} to 5×10^{-3} he obtained for C values, 18 to 20 μF/cm.^{2}. In other words, even at comparatively large overvoltages the capacity of the double-layer retains its normal value. Thus only ions of the double-layer are detected on the mercury cathode, but not adsorbed hydrogen atoms, the appearance of which would cause a considerable increase in the electrode capacity. This result is in agreement with others previously obtained [1] and is of fundamental importance. Indeed, at small coverage of the surface by adsorbed hydrogen it is possible to draw the unambiguous conclusion that the experimentally observed relation between η and ln i is incompatible with any other interpretation except that according to which the slow stage of hydrogen evolution on mercury is the discharge stage.

Several authors have advanced the hypothesis that on cathodes with considerable overvoltage atomic hydrogen evaporates into the solution ; this can be detected, e.g., by the reduction of WO_3 suspended in the electrolyte.[5] In this connection the mechanism of the reduction of WO_3 at the surface of a polarised electrode was recently analysed by Bagotzky and Jofa,[6] who found that reduction sets in only when the particles of WO_3 come into immediate contact with the electrode surface and spreads due to the electronic conductance of WO_3 by a mechanism similar to the

[5] Kobosev and Nekrassov, *Z. Elektrochem.*, 1930, **36**, 529.
[6] Bagotzky and Jofa, *Compt. rend., U.R.S.S.*, 1946, **53**, 443.

ordinary action of local elements. Theoretical computations also show that free atomic hydrogen should be expected to appear only at potentials considerably more cathodic than can be realised under normal conditions of electrolysis. It would be incorrect, however, to conclude from the negative results of these experiments that free radicals never appear in the bulk of the solution in electrolytic processes. On the contrary, in other cases, active intermediate products probably can leave the electrode surface and go over into the volume, although this has not yet been proven experimentally.

The most immediate result derived from the theory of slow discharge is the relation between c.d. and the hydrogen ion concentration in the surface layer $(H^+)_s$. This question was again taken over in an investigation recently carried out by Bagotzky in the Electrochemistry Laboratory, Moscow University. If the rate of the over-all process is determined by the rate of the elementary act of discharge of H^+ ions on the metal surface then, regardless of the mechanism of this act, there must be a relation :

$$i = [H^+]_s f(\phi - \psi_1) \quad . \quad . \quad . \quad . \quad (3)$$

where ϕ is the cathode potential and ψ_1 the potential at the point of location of the centre of the hydrogen ion being discharged. Since according to experimental data, the extent of surface covered by hydrogen ions is small, then

$$[H^+]_s = [H^+]e^{-\frac{\psi_1 F}{RT}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In order to bring eqn. (3) into agreement with the experimental data obtained in 0·1 N. HCl solution, which is in many respects a most convenient object for measurements, it is necessary to put

$$f(\phi - \psi_1) = \exp. \frac{[-(\phi - \psi_1) - a]F}{2RT} \quad . \quad . \quad . \quad (5)$$

where $a = 1{\cdot}460$ (at 20°).

Substituting (4) and (5) into (3) and introducing the overvoltage η instead of the potential ϕ, we obtain

$$\eta = a + \frac{2RT}{F} \ln i + \psi_1 - \frac{RT}{F} \ln [H^+] \quad . \quad . \quad (6)$$

Eqn. (6) was first verified experimentally by Levina and Sarinsky ; [7] they compared the variation of η upon the addition of $LaCl_3$ to HCl solution with the corresponding variation of ψ_1 computed according to Stern's theory. However, as has been shown by measurements of the capacity of a Hg-electrode carried out by Vorsina and Frumkin,[8] in the presence of multivalent cations the double-layer has a more complicated structure than can be accounted for by Stern's theory.* In Bagotzky's investigation the variation of η with the concentration of HCl and the addition of KCl was compared with eqn. (6). ψ_1 was calculated according to Gouy's theory taking into account the finite radius of the ions and putting the capacity of the Helmholtz part of the double-layer equal to 19 μF cm.$^{-2}$. That means that the centres of all the ions are located in the diffuse part of the double-layer which begins at a finite distance from

* The suggestion of Breyer and Gutmann [9] that the anomalous trend of the capacity curves in solutions containing multivalent cations obtained in the experiments of Vorsina and Frumkin is due to the discharge of these ions, is founded on misconception since the observed maxima on the curves lie at potentials at which the possibility of such discharge is excluded ; this was also verified in the experiments by the magnitude of the current passing through the electrode.

[7] Levina and Sarinsky, *Acta Physicochim.*, 1937, **7**, 485.

[8] Vorsina and Frumkin, *ibid.*, 1943, **18**, 242.

[9] Breyer and Gutmann, *Trans. Faraday Soc.*, 1946, **42**, 654.

the electrode surface. This method gives for the variation of ψ_1 with the concentration values which differ little from those obtained by Stern's method of computation. The results of some of Bagotzky's measurements are illustrated in Fig. 1 and 2 for a number of solutions containing HCl and KCl in various concentrations (circles) together with the values of η calculated from eqn. (6).

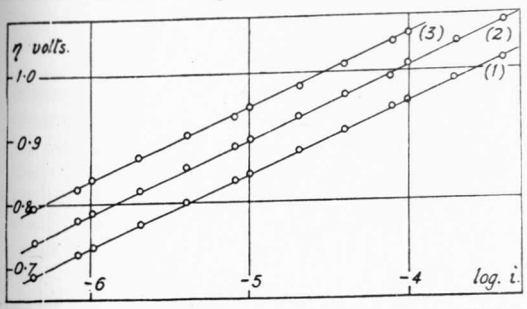

FIG. 1.—Overvoltage against c.d. curves in HCl + KCl, [HCl] + [KCl] = 0·1 N.

(1) [HCl] = 0·1 N ;
(2) [HCl] = 0·01 N. ;
(3) [HCl] = 0·001 N.

Full-line curves—computed by the formula :

$$\eta = 1{\cdot}460 + \psi + 0{\cdot}116 \log i - 0{\cdot}058 \log [H^+].$$

o—experimental points.

It thus appears that if agreement between the theory and experiment for 0·1 N. HCl is obtained by suitably choosing a and the dependence $f(\phi - \psi_1)$, then eqn. (6) gives the overvoltage for all other solutions with great accuracy; this proves the correctness of the main assumption of the theory, according to which the reacting particle is the hydrogen ion in the double-layer and the slow stage of the reaction the discharge of this ion. This conclusion does not depend on the theoretical interpretation of the dependence of i on $(\phi - \psi_1)$. The agreement between the theory and experiment is invalidated if the total concentration of the solution exceeds 0·3 N. As appears from Fig. 1, at constant total concentration of the solution and constant i the quantity η varies with $[H^+]$ approximately as $-\boldsymbol{RT/F} \ln [H^+]$. The range of values of $[H^+]$ for which the validity of this conclusion can be proved can be considerably broadened if the potential of the half-wave of the H^+ ion determined with the dropping electrode is used.

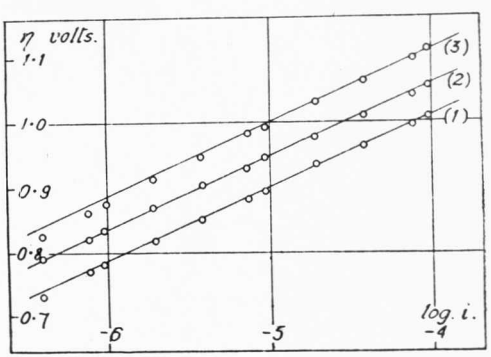

FIG. 2.—Overvoltage against c.d. curves in 0·001 N. HCl in the presence of KCl.

(1) [HCl] + [KCl] = 0·01 N. ;
(2) [HCl] + [KCl] = 0·1 N. ;
(3) [HCl] + [KCl] = 1·0 N.

Full-line curves—computed by the formula :

$$\eta = 1{\cdot}760 + \psi_1 + 0{\cdot}116 \log i - 0{\cdot}058 \log [H^+].$$

o—experimental points.

It is noteworthy that in the case of a mercury electrode the value of the coefficient $b = \boldsymbol{RT/\alpha F}$ in the term containing $\ln i$ in Tafel's equation corrected for the influence of the ψ_1 term gives for α the value 1/2 with an accuracy up to 0·01. It must be conceded that up to date no one has been able to explain why α, in this case at least, is so close to 1/2 and remains constant over such a wide range of potentials. It appears to the author that since the paper by Horiuti and Polanyi,[10] no considerable progress has been made in the interpretation of the coefficient α.

We thought it necessary to dwell in greater length on the verification

[10] Horiuti and Polanyi, *Acta Physicochim.*, 1935, **2**, 505.

f the conclusions following from eqn. (6) since there exists a widespread pinion that the reacting particle is the water molecule and not the ydrogen ion.[11] This concept which is confirmed in the case of hydrogen volution from alkaline solutions on a Ni-electrode [12] and probably also n a Hg-electrode [13] cannot, however, be applied to acid solutions.[14]

In strong acid solutions at concentrations exceeding N , a considerable owering of the overvoltage is observed as compared with the value haracteristic of dilute solutions. The data on the behaviour of solutions f HCl, HBr, H_2SO_4 and $HClO_4$ on a Hg-electrode are summarised in a aper by Jofa and Frumkin.[2] Jofa [15] investigated concentrated acid olutions on a Pb-electrode and Sindjukov [16] solutions of H_2SO_4 and HCl n a Ni-electrode. The overvoltage in H_2SO_4 and H_3PO_4 on a Hg-lectrode was also investigated by Bethune and Kimball.[17] However, heir values for the H_2SO_4 solutions lie considerably lower than those ound by Jofa ; this we believe is due to insufficient care in avoiding ontaminations in the solution and on the surface of the mercury electrode. As was shown by Jofa and Frumkin,[2] the lowering of the overvoltage is losely related to the penetration of anions into the double-layer in oncentrated solutions. The latter can be detected by measuring the lectrocapillary curves and gives rise to considerable negative ψ_1-potentials. The ψ_1-potentials vary linearly with the logarithm of the activity. Ershler ttempted to develop a quantitative theory of the structure of the double-ayer in concentrated acid solutions which would explain this linear ependence.[18] The nature of the bond between the anions and hydrogen ons at the electrode surface in concentrated solutions cannot, however, e considered established, and it is possible that it is not always purely lectrostatic. At any rate, we cannot agree with Bethune and Kimball, who wish to establish a direct relation between the decrease in the over-oltage and the appearance of undissociated acid molecules in the solution. The magnitude of the overvoltage drop is determined not by the bulk roperties of the solution, but by the composition of the surface layer. This follows especially clearly from the fact that the overvoltage drop n $HClO_4$ and H_2SO_4, as well as in HCl and HBr at not too high con-entrations, decreases strongly with increase in the c.d. and hence, in the egative charge of the surface. Thus in 8 N. $HClO_4$ the decrease in η s compared with 0·1 N. $HClO_4$, when log i varies from -5 to -1, reduces rom 0·22 to 0·08 V. At such a total concentration of the acid the con-entration of undissociated $HClO_4$ molecules, judging by the Raman effect,[19] s still very small. In concentrated solutions of HCl the electrode potential ffects the overvoltage drop considerably less, which perhaps indicates he presence of undissociated HCl molecules in the surface layer. It may lso be that the difference in the influence of the electric field of the double ayer is due to the different dimensions of the Cl' and ClO_4' ions.

b) Comparison of the Rates of the Different Stages of Hydrogen Evolution on Cathodes with Low Overvoltage.

On metals such as Pt which adsorb hydrogen well it is possible to make lirect measurements of the rate of H^+ ions. discharge.[20] This was effected

[11] Eyring, Glasstone and Laidler, *J. Chem. Physics*, 1939, **7**, 1053 ; Kimball, Glasstone and Glassner, *ibid.*, 1941, **9**, 91.

[12] Lukovzev, Levina and Frumkin, *Acta Physicochim.*, 1939, **11**, 21 ; Legran nd Levina, *ibid.*, 1940, **12**, 243 ; Lukovzev and Levina, *J. Physic. Chem.* (*Russ.*) in press).

[13] Jofa (unpublished data). [14] Frumkin, *Acta Physicochim.*, 1940, **12**, 481.

[15] Jofa, *J. Physic. Chem.* (*Russ.*), 1945, **19**, 117.

[16] Sindjukov, *Thesis* (Moscow University, 1947).

[17] Bethune and Kimball, *J. Chem. Physics*, 1945, **13**, 53.

[18] Ershler, *J. Physic. Chem.* (*Russ.*), 1946, **20**, 679.

[19] Redlich, *Chem. Rev.*, 1946, **39**, 333.

[20] Dolin and Ershler, *Acta Physicochim.*, 1940, **13**, 747 ; Rosenthal, Dolin nd Ershler, *ibid.*, 1946, **21**, 213.

by means of alternating currents of various frequencies, the current intensity through the platinum electrode being chosen so that the amplitude of oscillation of the electrode potential about a given constant potential did not exceed several millivolts. Under such conditions a platinum electrode with an adsorbed layer of H atoms acts like an admittance composed of a capacitative and a conductance component whose magnitudes vary with the frequency of the current. With increasing frequency the hydrogen layer has no longer time to form and, as a result, the capacitative component of the admittance falls from a value which corresponds to 1200-1400 μF/cm.^{2}, i.e. to the "capacity" of the equilibrium atomic layer (at a frequency of 1-50 c.p.s.) to a value corresponding to 30-40 μF/cm.^{2} (at 3000 c.p.s.), i.e., to the capacity of the double-layer, which does not decrease with further increase of the frequency. As for the conductance, it increases with the frequency tending to a limiting value Π which, as has been shown by Dolin and Ershler,[20] is connected with the rate of discharge of H^+ ions by the simple relation :

$$J_0 = \frac{RT}{F}\Pi$$

where J_0 is the c.d. of H^+ ions discharge on a platinum surface at the given potential under equilibrium conditions, i.e., the quantity usually termed exchange current. Experiments carried out by this method made it possible for the first time to measure directly the rate of discharge of H^+ ions under conditions when the formation of molecular H_2 from adsorbed H atoms was excluded. This was accomplished by carrying out the measurements at potentials slightly more anodic than the reversible hydrogen potential, when the equilibrium concentration of molecular H_2 in the liquid becomes sufficiently small. The dependence of the discharge rate on the concentration of H^+ ions found in the case of acid solutions was in satisfactory agreement with the theory of slow discharge of H^+ ions, i.e. the discharge rate at constant hydrogen equilibrium pressure was approximately proportional to the square root of the concentration of H^+ ions.

With increase in the rate of the main electrochemical reaction of discharge, which occurs upon transition to cathodes with low overvoltage, the kinetics of the over-all reaction of H_2 evolution begins to be affected, generally speaking, by the conditions under which the subsequent stages proceed, such as the formation of molecular hydrogen and its removal from the electrode surface. The slowness of these stages is also made manifest by the penetration of hydrogen into the metal.[21] In the case of a palladium electrode it was shown by Frumkin and Aladjalova [3] that the measured overvoltage is additively composed of two components : the first depends on the slowness of the discharge process (of a hydrogen ion or, in the case of alkaline solutions which were primarily used in their investigation, of a water molecule), while the second is determined by the reversible potential of the hydrogen absorbed on the electrode surface. The latter, however, is in equilibrium not with hydrogen at atmospheric pressure, but rather with hydrogen whose concentration is determined by the rate of diffusion in the solution or by the conditions of the $\alpha \rightleftharpoons \beta$ phase transition characteristic of the system Pd—H. The additivity of the equilibrium potential of adsorbed hydrogen and the discharge overvoltage is characteristic of surfaces on which adsorbed hydrogen possesses certain properties, viz., that its fugacity is proportional to $e^{f\theta}$, where f is a constant and θ the extent of surface covered. This relation agrees with the results of direct measurements of the surface covering of a Pt-electrode as a function of the potential at anodic polarisation.[22] Kinetic relations compatible with such thermodynamic properties were deduced by Temkin.[23]

[21] Frumkin, *Acta Physicochim.*, 1937, **7**, 475.
[22] Frumkin and Šlygin, *ibid.*, 1935, **3**, 781 ; 1936, **5**, 819.
[23] Temkin, *J. Physic. Chem.* (*Russ.*), 1941, **15**, 296.

According to Dolin and Ershler,[24] in the case of a platinum electrode ɔo, the total overvoltage of H_2 evolution can be divided into two comɔnents, one determined by the discharge overvoltage, the other by the ıte of diffusion of molecular hydrogen. The first component depends ı the concentration approximately in accordance with the conclusions f the theory of slow discharge (the rate of discharge at constant overɔltage in the presence of an excess of a foreign electrolyte is approximtely proportional to the square root of $[H^+]$); in alkaline solutions, howver, the observed dependence on the concentration does not agree with ıe theory. This latter circumstance has not as yet been explained.

As Dolin and Ershler have shown, their conclusions are confirmed by ɔmparison of the rate of discharge of H^+ ions measured by the method escribed above, with the rate of evolution of molecular hydrogen corɛcted for concentration polarisation in the solution. At first sight a ɔmparison of the rate of discharge with the rate of gas evolution appears ifficult since the former is measured at a potential slightly more anodic ıan the reversible hydrogen potential, inasmuch as only under such ɔnditions the evolution of H_2 can be excluded. The comparison, howver, becomes possible due to the previously mentioned properties of dsorbed layers of H on Pt. At medium covering of the Pt surface by dsorbed hydrogen the rate of discharge on the equilibrium electrode ɛases to depend on the potential due to mutual compensation of the pposed influences of potential and change in adsorption energy on ɔvering as shown by Temkin.[20, 23] Such a comparison leads to the conlusion that in the case of HCl solutions the rate of discharge of H^+ ions nd the total rate of evolution of H_2 are almost the same. In other soluɔns (H_2SO_4, and especially NaOH) the rate of the first stage is greater ıan the rate of formation of molecular hydrogen; there is, however, far-reaching parallelism in the way the two processes are affected by number of factors (composition and concentration of the solution, oisoning of the electrode). It may be that in this case during the volution of molecular H_2 only a part of the electrode surface is utilised ɔr discharge due to the limitation of the kinetics by the following stage f recombination. This question demands further investigation.

A detailed investigation was made of the process of hydrogen evolution n nickel in acid and alkaline solutions.[12] The overvoltage was measured s a function of the c.d. at cathodic and anodic polarisation with large nd small c.d.'s, and as a function of the composition of the solution; the ariation of the potential with the time after breaking the current and he behaviour of the electrode in alternating current were also investigated. 'he material obtained is too abundant to be discussed in detail here. The est agreement with experiment is obtained on the basis of the following cheme. On the greater part of the Ni-electrode the slowest stage is he discharge of the hydrogen ion or, in alkaline solution, of the water ıolecule. At the same time there exists an area, comprising but a small ɔart of the surface, for which the rate of the process is limited by the stage f recombination,

$$H + H = H_2.$$

t must also be assumed that surface diffusion between the two kinds of ɹreas is a slow process. With a lowering of the concentration of the acid ɔr alkali the discharge rate at a given overvoltage decreases and, as a esult, the reaction on the second type of areas increases in relative imɔortance. In alkaline solutions at concentrations of alkali exceeding ɔo^{-2} N., all the conclusions from the theory of slow discharge concerning he dependence of the overvoltage on the concentration are well borne ɔut; at lower concentrations of alkali with an excess of foreign electrolyte ɔresent, the overvoltage becomes nearly independent of the concentration

[24] Dolin and Ershler, *Acta Physicochim.*, (in press).

when the hydrogen atoms recombination is the slowest stage. It is essential, however, that even on the areas on which the discharge is the slowest stage, the rate of the following stages of removal of hydrogen atoms is not infinitely great compared with the discharge; as a result with an increase in the overvoltage on the Ni-electrode adsorbed hydrogen accumulates in increasing amounts. This can be detected in measurements of the electrode potential decay after the interruption of the polarising current.

In the case of small covering of the electrode surface definite conclusions regarding the reaction mechanism can be drawn from the value of the coefficient b in Tafel's equation. This becomes difficult at large covering since the same value of b can correspond to different mechanisms depending on the way the surface covering affects the free energy of the activated complex. Horiuti and Jkusima [25] have proposed a more general relation which can be used to determine the reaction mechanism. Denote by $\vec{J}$ and $\overleftarrow{J}$ the true values of the cathodic and anodic currents. Then the measured current i is evidently equal to

$$i = \vec{J} - \overleftarrow{J}.$$

At $i = 0$, $\vec{J} = \overleftarrow{J} = J_0$, where J_0 is the "exchange current" under equilibrium conditions.

According to Horiuti and Jkusima

$$\frac{\vec{J}}{\overleftarrow{J}} = e^{\frac{\eta n F}{RT}} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where n is the number of protons in the activated complex. It follows from eqn. (8) that for small values of η

$$i = \frac{\eta n F}{RT} \cdot J_0$$

and, hence,

$$\left(\frac{\partial \eta}{\partial i}\right)_{i=0} J_0 = \frac{RT}{nF} \quad . \quad . \quad . \quad . \quad (9)$$

Eqn. (9) is closely related to eqn. (7). The value of J_0 can be extrapolated from measurements of i at higher overvoltages at which $\overleftarrow{J} \ll \vec{J}$ or it can be directly measured by means of isotope exchange. Unpublished data of Levina show that both methods give close values of J_0. The criterion (9) was used by Lukovzev and Levina to investigate the reaction mechanism in the case of a Ni-electrode in alkaline solutions.[12] It should be observed that an exact determination of $\left(\frac{\partial \eta}{\partial i}\right)_{i=0}$ involves considerable experimental difficulties. The mean of a large number of measurements gives for $\left(\frac{\partial \eta}{\partial i}\right)_{i=0} J_0$ values running from 27 to 15 mv. when the concentration of NaOH varies from 0·3 to 3×10^{-4} N. in the presence of NaCl, which according to eqn. (9) indicates a variation of n from 1 to 2. For a platinum electrode Tolin and Ershler,[24] after correcting the value of η for concentration polarisation, as indicated above, found in this manner $n \sim 1$. It should be observed that Horiuti and Jkusima,[25] using a similar though not quite identical procedure found for Pt in KOH, $n = 2$, whence they concluded that the rate-determining stage of the process is the discharge of the H^+ ion on the H atom with the formation of a H_2 molecule. The cause of the disagreement is as yet not clear.

In general, it can be considered established that for electrodes with

[25] Horiuti and Jkusima, *Proc. Imp. Acad. Tokyo*, 1939, **15**, 39.

low overvoltage, in addition to the slowness of the discharge stage, the slowness of the following stages of the process also begins to tell. It is at present still impossible, however, to establish with finality the comparative quantitative values of the velocity of these stages, in particular to what extent the reaction $H + H^+ + e \rightarrow H_2$ plays a part simultaneously with the removal of hydrogen according to the mechanism : $H + H \rightarrow H_2$.*

(c) Influence of Oxide Films on the Hydrogen Overvoltage.

The problem of the hydrogen overvoltage is complicated by the circumstance that there are a number of additional factors affecting the rate of hydrogen evolution. One of these is the presence of oxide films on the electrode surface. As was shown by Levina and Platonova [26] and Kabanov and Rosenzweig [27] the presence of oxides on a powdered iron electrode in alkaline solutions considerably increases the hydrogen overvoltage. This can be detected by measuring the potential of an iron electrode, preliminarily subjected to anodic oxidation, on cathodic polarisation. According to Kabanov and Rosenzweig, after the reduction of $Fe(OH)_2$ is completed the hydrogen overvoltage is reduced by 0·25 v. In the presence of an oxide film, too, anomalously high values of the coefficient b in Tafel's equation are observed. The overvoltage in these experiments was computed for a constant value of the c.d. corresponding to the reaction of hydrogen formation. The rate of this reaction was determined from the volume of gas evolved. In this case the authors observed the influence of an oxide film which was unstable at the given polarisation, but which made itself felt in the considerable time needed to remove the film.

As has been shown by Kolotyrkin,[28] the hydrogen overvoltage on a lead electrode changes slowly with time. For example, after passing from high to low values of the polarising c.d., one observes a slow increase in the overvoltage. It is possible that these changes in the overvoltage are also determined by the state of oxidation of the surface and are connected with a slow approach to a stationary state of oxidation, corresponding to the given conditions of polarisation. Due to these variations of the overvoltage the curves of potential decay after the polarising current has been interrupted cross one another for currents of different density.

Under different conditions the presence of oxygen on the surface probably leads to a decrease in the overvoltage.

(d) Kinetics of Hydrogen Evolution upon Spontaneous Dissolution of the Metal.

From the viewpoint of practical electrochemistry special significance attaches to the kinetics of hydrogen evolution upon the spontaneous dissolution of metals. The author,[29] and Hammett and Lorch,[30] were apparently the first to apply the laws of the kinetics of the electrochemical evolution of hydrogen in order to explain phenomena observed in the dissolution of metals. They showed that the proportionality between the rate of decomposition of sodium amalgam in buffer solutions and the square root of the concentration of sodium in the amalgam, discovered by Brönsted and Kane [31] follows directly from Tafel's equation. In this

* The former reaction should make the extent of surface covered by hydrogen independent of the polarisation at large c.d.'s.[21] Contrary to the opinion of Hickling and Salt,[4] however, this does not give rise to a limiting overvoltage value, the existence of which is not confirmed by experiment either.

[26] Levina and Platonova, *J. Physic. Chem.* (*Russ.*) (in press).
[27] Kabanov and Rosenzweig, *ibid.* (in press).
[28] Kolotyrkin, *ibid.*, 1946, **20**, 667.
[29] Frumkin, *Z. physik. Chem. A*, 1932, **160**, 116.
[30] Hammet and Lorch, *J. Amer. Chem. Soc.*, 1932, **54**, 2128.
[31] Brönsted and Kane, *ibid.*, 1931, **63**, 3624.

deduction it is assumed that the evolution of hydrogen and the ionisation of the metal are two independent electrochemical reactions related only by the common value of the potential of the metal surface. The notion of two independent electrochemical reactions on the same surface was widely developed by Wagner and Traud.[32] In a number of investigations carried out in Moscow it was shown that the laws of hydrogen evolution on metal surfaces are not changed by a simultaneous dissolution of the metal. Tafel's equation with ordinary values of the coefficients remains in force even at potentials more anodic than the stationary potential of spontaneous dissolution. Naturally, in such cases the rate of hydrogen evolution cannot be computed from the current; it was determined from the volume of gas evolved. The solution of lead and nickel in acids [33] and of iron in alkalies [26, 27] was studied from this viewpoint. Apparent deviations from this conclusion may be noted when insufficiently pure metals are dissolved, due to the circumstance that the dissolution changes the composition of the metal surface and the magnitude of the hydrogen overvoltage. If the indicated relation is borne out, the potential and rate of spontaneous dissolution can be found from the hydrogen overvoltage and the anodic polarisation curve.[33, 34] Special interest attaches to the case when the rate of ion exchange between the metal and the solution at equilibrium potentials is not too great compared with the rate of hydrogen evolution. In this case the potential of dissolution of the metal cannot be regarded as an equilibrium potential with respect to a definite concentration of ions in the solution. Such a case is encountered in the dissolution of iron and nickel in acids.

It is usually assumed that the potential of active iron in alkalies saturated with $Fe(OH)_2$ which corresponds to a hydrogen overvoltage of $\eta = 0{\cdot}045$ is the equilibrium potential of the system Fe, $Fe(OH)_2$, OH'. However, measurements of the hydrogen overvoltage and anodic polarisation of Fe in alkaline solution led Levina and Platonova [26] and Kabanov and Rosenzweig [27] to the conclusion that this potential is in reality only the steady-state potential determined by the kinetics of hydrogen evolution and of the anodic dissolution of iron, whereas the true equilibrium potential of this system is several hundredths of a volt more negative.

I shall not dwell here on the comparison of this interpretation of the dissolution of metals with the interpretation based on the theory of local elements which is usually given in the theory of corrosion; this question has been discussed elsewhere.[34, 35]

It follows from the above that when the potential of dissolution of metals cannot be regarded as an equilibrium potential with respect to the ions in the solution it should vary when substances affecting the kinetics of the cathodic or anodic processes are introduced into the solution. Kusnezov [36] investigated the action of a large number of organic compounds (corrosion inhibitors) on the steady state potential of dissolution of iron in acids; his findings are in agreement with the viewpoint here developed.

Although the discharge of hydrogen ions and the ionisation of the metal in the process of dissolution of a metal in aqueous systems are undoubtedly as a rule statistically independent, in principle cases are possible when both processes occur simultaneously in one elementary act. It would be very interesting to draw the line between two such types of reactions.

[32] Wagner and Traud, *Z. Elektrochem.*, 1938, **44**, 391.
[33] Frumkin and Kolotyrkin, *Acta Physichochim.*, 1941, **14**, 469; Kolotyrkin and Frumkin, *Compt. rend., U.R.S.S.*, 1941, **33**, 445, 450.
[34] Frumkin, *Trans. 2nd Meeting on Metal Corrosion* (Academy of Sciences, 1940), **1**.
[35] Levich and Frumkin, *Acta Physicochim.*, 1943, **18**, 325.
[36] Kusnezov, *J. Physic. Chem. (Russ.)* (in press).

Conclusions.

It can be shown by a number of independent methods that in the case of hydrogen evolution on mercury from acid solutions the slowest stage of the reaction is the discharge of the hydrogen ion which completely determines the kinetics of the overall reaction. In the case of cathodes with low overvoltage the rate of the discharge stage can be determined experimentally too ; however, besides this stage the kinetics is also affected by the subsequent stages, such as the formation of hydrogen molecules, or the diffusion of molecular hydrogen in the solution. The presence of oxide films on the surface of metals has a marked influence on hydrogen overvoltage. The hydrogen overvoltage remains unchanged when the anodic process and dissolution of the metal occur simultaneously thus making it possible from measurements of hydrogen overvoltage and anodic polarisation of the metal to draw conclusions regarding the steady-state potential and the rate of dissolution of the metal.

Résumé.

On montre, par diverses méthodes indépendantes, que l'étape la plus lente dans le dégagement de l'hydrogène, sur le mercure à partir de solutions acides, est la décharge des ions hydrogène et ceci détermine complètement la cinétique de la réaction d'ensemble. Avec des cathodes à faible survoltage, la cinétique est alors affectée par la formation suivante de molécules d'hydrogène ou par la diffusions de l'hydrogène moléculaire dans la solution. On discute comment des films d'oxydes influencent le survoltage d'hydrogène et on montre comment, dans certaines conditions, les mesures de ce survoltage et de la polarisation anodique du métal permettent de tirer des conclusions, en ce qui concerne le potentiel de l'état stationnaire et la vitesse de dissolution du métal.

Zusammenfassung.

Eine Reihe von voneinander unabhängigen Methoden haben ergeben, dass die Entladung der Wasserstoffionen die langsamste Stufe der Wasserstoffabscheidung von Säurelösungen an Quecksilber ist und die Kinetik der Gesamtreaktion völlig bestimmt. Bei Kathoden mit kleiner Überspannung wird die Kinetik auch durch die darauffolgende Wasserstoffmolekülbildung oder Diffusion des molekularen Wasserstoffs in der Lösung beeinflusst. Die Wirkung von Oxydfilmen auf die Wasserstoffüberspannung wird besprochen und es wird gezeigt, auf welche Weise, unter gewissen Umständen, Messungen der Wasserstoffüberspannung und der anodischen Polarisation des Metalls zu Schlussfolgerungen über das Gleichgewichtspotential und die Auflösungsgeschwindigkeit des Metalls führen können.

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