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BARRIERLESS ELECTRODE PROCESSES

L. I. Krishtalik

The slow discharge theory, developed and substantiated by the work of Frumkin and his school, satisfactorily describes the basic features of a large number of electrochemical processes (see, for example, Ref. 1). The concepts which had been originally used to describe the discharge of hydrogen ions were shown to be widely applicable to all types of reaction, such as the electrochemical desorption of adsorbed hydrogen, the reduction of anions and neutral molecules, etc. In recent years it has been shown that the basic ideas of the slow discharge theory imply the existence (in a few limiting cases) of new types of electrode reactions showing a number of interesting features [2-4]. The present review article aims to discuss these limiting cases.

The most distinguishing feature of electrochemical reactions is the variation of their activation energy with potential: as the electrode departs from its equilibrium potential in the cathodic (or the anodic) direction, the activation energy of the corresponding electrode process decreases. This behaviour is most conveniently described by the relation

$$A = A_0 - \alpha\eta F, \qquad (1)$$

where A is the activation energy at an overvoltage η (real activation energy values [5] will be used throughout), and A_0 is the activation energy at the equilibrium potential. The transfer coefficient α is found experimentally to be constant over a range of potentials, and its value is often close to 1/2.

If the activation energy of the forward reaction decreases with increase of overvoltage, the activation energy for the reverse reaction must increase

$$A' = A_0' + \beta\eta F. \qquad (2)$$

It can be shown thermodynamically† that at a given potential $\alpha + \beta = 1$.

Relationships involving activation energy values are conveniently visualised with the help of a potential energy diagram. Fig. 1 shows a cross-section of the potential energy surface along the reaction coordinate. Curve *2* corresponds to a higher potential than curve *1*. Since the energy of the activated transition state increases more slowly with potential than does the energy of the initial state, the difference between the two, i.e. the activation energy, decreases.

Consider a discharge reaction (cathodic, say). Since its activation energy is finite at any given potential, and since it decreases with increase of overvoltage, it must ultimately tend to zero at a high enough overvoltage. Under these conditions the reaction rate will be a maximum, and further increase in potential will not affect the current. In other words, for a non-activated process such as this we can write $\alpha = 0$. But for the reverse ionisation reaction we find $\beta = 1$ at these potentials. The potential curves for this case are shown in Fig. 1 as curves *3* and *4* .

Imagine now that the overvoltage is decreased. This raises the activation energy for discharge, but at the same time the activation energy for ionisation is lowered. At a sufficiently low cathodic (i.e. at a sufficiently high anodic) potential the activation energy vanishes. Under these conditions $\beta = 0$ and $\alpha = 1$. The shape of the corresponding potential energy diagram is shown by curves *5* and *6* of Fig. 1.

Unlike non-activated processes, the processes for which $\alpha = 1$ (or $\beta = 1$) require a considerable activation energy. However, and in contrast to normal discharge processes, this activation energy is equal to the heat of the fundamental reaction step, and the activation energy for the reverse processes is zero‡. On a potential diagram this process does not show the familiar hump of the

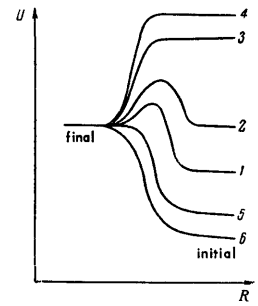


Fig. 1. Potential energy diagram for normal (curves 1 and 2), non-activated (curves 3 and 4), and barrierless discharge (curves 5 and 6).

† We are confining the discussion to one-electron processes.

‡ We must stress once again that we are considering the real activation energy, so that the heat of the fundamental step is a real heat, i.e. a quantity which does not include the latent equilibrium heat of the overall electrode process. We could have based the whole discussion on ideal activation energies, but this would not affect the results.

activational barrier, and therefore we have introduced the term "barrierless" to describe processes of this type[2].

Thus, every electrode process can be expected, in principle, to occur in three forms: barrierless, normal, and non-activated. The polarisation curve, ignoring complications resulting from other stages of the reaction, should have the shape shown in Fig. 2.

Whether or not a current–voltage relation of this form can be observed in practice depends first and foremost on the position of the curve in Fig. 2 with respect to the equilibrium potential. Thus, if the transition from $\alpha = 1$ to $\alpha = 1/2$ occurs below the equilibrium potential (the case denoted by the letter *a* in Fig. 2), barrierless discharge cannot be observed since the reverse (ionisation) reaction predominates below the equilibrium potential. This case appears to be a very common one. However, if the break in the polarisation curve occurs above the equilibrium potential (case *b* of Fig. 2) barrierless discharge becomes accessible to direct observation.

To carry out a barrierless process it is essential that the fundamental reaction step be accompanied by heat absorption, because an activation energy is essentially a positive quantity. In other words, the energy level of the final state must lie above that of the initial state.

It follows that for the slow discharge of hydrogen ions, say, a barrierless process can in principle be observed only with metals which adsorb hydrogen poorly. This is because for these cathodes the energy level of the final state of the slow step — adsorbed hydrogen and a water molecule on the electrode surface — lies well above the energy level corresponding to molecular H_2 in the gas phase and water in the bulk. At the equilibrium potential this latter state is practically at the same level as the initial state — H_3O^+ ions in the double layer. (As before, we are ignoring the latent equilibrium heat of the process.) These energy relations are illustrated in Fig. 3.

On the other hand, for the slow electrochemical desorption of hydrogen the barrierless process is possible in principle only if the energy of the metal–hydrogen bond is large. In this case the final state is a physically adsorbed H_2 molecule, whose energy level is close to that of gaseous hydrogen, and the energy of the initial state (which includes an adsorbed H atom) is lower, the higher the heat of adsorption of hydrogen.

In addition to the above criterion for the realisation of a barrierless process, it is essential that the activation barrier in the normal discharge region should not be too

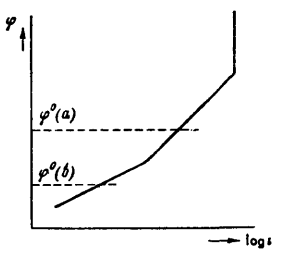


Fig. 2. Idealised polarisation curve (the current corresponding to reaction in one direction only is plotted as abscissa).

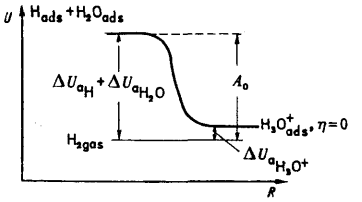


Fig. 3. Potential energy profile for barrierless discharge of H_3O^+ ions at the equilibrium potential; ΔU_a is the adsorption energy of the species indicated, and A_0 is the apparent real activation energy at the equilibrium potential; the horizontal line denotes the energy level corresponding to gaseous H_2.

high, i.e. that the activation energy of the reverse reaction should vanish before the potential has decreased too much. Earlier tentative calculations[6] of the height of activation barriers justify the belief that the barrierless process should be observable on metals with a high hydrogen overvoltage. A comparison of activation energy data for normal discharge on mercury with plausible values for the heat of adsorption of hydrogen on this cathode leads to the same conclusion.

These were the basic considerations used in formulating an experimental study of the hydrogen overvoltage of mercury under conditions likely to lead to barrierless discharge. However, before proceeding to a discussion of the experimental results, it may not be out of place to consider the characteristic features of the kinetics of this new type of electrode reaction.

The rate of discharge of hydrogen ions at constant potential and constant double-layer structure is proportional to their concentration (or activity, see below). This statement is, of course, applicable to any discharge process, ordinary as well as barrierless. However, if we compare the processes at constant overvoltage rather than at constant potential an entirely different set of relations applies. An increase in the concentration of species undergoing discharge, e.g. H_3O^+ ions, lowers the equilibrium potential, and therefore the rate at constant overvoltage increases as $C_{H_3O^+}^{1-\alpha}$ instead of as $C_{H_3O^+}$. For normal discharge $\alpha = 1/2$, and the current density is proportional to $C_{H_3O^+}^{1/2}$. For barrierless discharge, however, $\alpha = 1$, and the rate of reaction at constant overvoltage becomes independent of concentration: the accelerating effect on the reaction of the greater number of species undergoing discharge is exactly compensated by the retardation due to the lowering of the equilibrium potential.

A similar situation exists as regards the effect of the ψ_1-potential. A negative shift of the ψ_1-potential accelerates the discharge, on the one hand, due to the increased surface concentration of H_3O^+ ions, but, on the other hand, it retards the discharge by decreasing the potential jump across the dense part of the double layer. In normal discharge the former effect predominates, because the ψ_1-potential appears with the coefficient $\alpha = 1/2$ in the expression for the retarding effect. In barrierless discharge $\alpha = 1$, and these two effects exactly compensate each other.

Whereas the conclusion that overvoltage is independent of concentration of the discharging species applies equally

to the discharge of ions and to the oxidation–reduction of molecules, exact compensation of the ψ_1-effects can occur only in the reduction of a singly charged cation (or in the oxidation of a singly charged anion). In other cases the effects of the ψ_1-potential on the surface concentration and on the potential jump may not be mutually compensating.

We should stress that lack of dependence of the overvoltage on $C_{H_3O^+}$ and on the structure of the double layer is not at all inconsistent with the assumption of a slow discharge step. Thus, if we examine the rate of hydrogen evolution at constant potential we find that it is proportional to the concentration of H_3O^+ ions. But if it were possible to compare overvoltages in different solutions at constant surface concentration of hydrogen ions, the effect of the ψ_1-potential would be very clearly revealed.

The features of barrierless discharge discussed above can be described by the following equation, which we had previously derived[2] on the basis of the theory of absolute reaction rates:

$$i = \varepsilon \frac{kT}{h} \frac{\varkappa}{\gamma^{\neq}} 10^{15} a_{H_2O} P_{H_2}^{1/2} (1-\theta) \exp\left\{-\frac{1}{RT}\left[\Delta H_{a_H} + \right.\right.$$
$$\left.\left. + \Delta H_{a_{H_2O}} + T\left(\frac{1}{2} S^0_{H_2} - \Delta S^0_{a_{H_2O}}\right) - \eta F\right]\right\} \quad (3)$$

Here ϵ is the electronic charge, $\varkappa$ is the transmission coefficient, $\gamma^{\neq}$ is the activity coefficient of the activated complex, a_{H_2O} is the activity of water, θ is the coverage of the surface by adsorbed hydrogen (for mercury $\theta \ll 1$), the subscript a after ΔH and ΔS indicates that these quantities refer to the adsorption process, and the superscript 0 denotes standard values. The remaining symbols have their usual meaning.

We shall now introduce some refinements into this equation.

It follows from the above discussion and from Eqn. (3) that the overvoltage under conditions of barrierless discharge is practically independent of the composition of the solution: this, as well as $\alpha = 1$ (i.e. $b = 59$ mV), is the most characteristic criterion of slow barrierless discharge. For normal discharge, we know that the overvoltage can be very sensitive to the composition of the solution.

The lower the polarisation curve for normal discharge, the higher is the current density and the overvoltage at which it intersects the branch corresponding to barrierless discharge, i.e. the more easily can the phenomenon be demonstrated experimentally. We have therefore examined the hydrogen overvoltage of mercury in concentrated solutions of salts having a strongly adsorbable anion (iodide and bromide), because the overvoltage for normal discharge is lowest in solutions of this type.

The experimental procedure has already been described in detail[3]. Since it was essential that the results at low current densities be reliable and not distorted by effects such as depolarisation by oxygen, special care had to be taken in the purification of materials and solutions. To improve the efficiency of the electrolytic purification of the solution, we used a relatively thin layer of liquid which was vigorously stirred. This procedure enabled us to obtain satisfactorily reproducible polarisation curves free from depolarisation drift down to current densities of 10^{-7}, $10^{-7.5}$, and 10^{-8} A cm^{-2} for iodide, bromide, and chloride solutions respectively.

Some typical polarisation curves are shown in Fig. 4. Their shape is entirely in keeping with the suggested

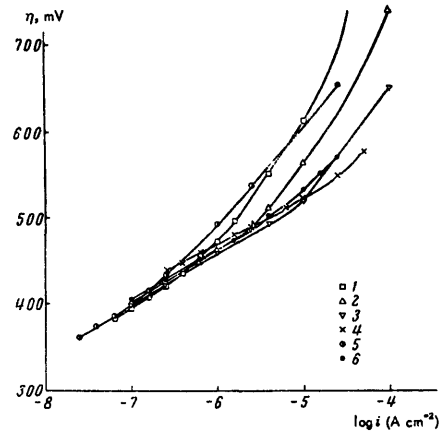


Fig. 4. Polarisation curves for solutions of the following composition (M):
1) 3.2 KI, 0.15 HCl; 2) 3.2 KI, 0.45 HCl; 3) 6 KI, 0.55 HCl; 4) 3 KI, 0.9 HCl, 1.3×10^{-3} $N(Bu)_4Br$; 5) 6.6 NaBr, 0.85 HCl; 6) 11.8 LiBr, 0.1 HCl.

theory of the transition from barrierless to normal discharge§. The sharp inflection of the curves and the transition to a lower value of b have been shown[3] to be not due to any conceivable experimental error, and can be taken as a firmly established fact.

The situation described above has been observed in 23 solutions of KI of different composition, covering a range of KI concentration from 0.8 to 6.0 M and a range of HCl concentration from 0.1 to 1.2 M, three of which contained tetrabutylammonium salts in concentration 10^{-4}–1.3×10^{-3} M. Three solutions contained 6.5–11.8 M LiBr and 0.1–0.9 M HCl; two solutions contained 6.6 and 7 M NaBr and 0.85 M HCl. In every case the b coefficient for the lower branch of the curve was close to 60 mV: the lowest value observed was 52 mV, the highest 63 mV, and in 21 out of 28 experiments b varied between 55 and 60 mV. The average value for all the experiments was $b = 58.5$ mV, which effectively coincides with the theoretical value of 59.1 mV.

In the upper part of the curves (the region of normal discharge) we observe a strong dependence of the overvoltage upon solution composition, including acid concentration, concentration of the adsorbable anion, and concentration of added tetrabutylammonium salt¶. For the range of solution compositions examined in our work, the difference in overvoltage over this region can be 200 mV or higher. On the other hand, in the region where $b = 60$ mV all the curves lie within a band of about 20 mV, and 18 out of the 28 curves lie within 10 mV. There is no apparent relationship between the overvoltage and the composition of the solution. The scatter of the curves obtained with different solutions is of the same order of magnitude as the scatter of the curves obtained in different experiments for a solution of a given composition. We can conclude,

§ The high slope of the top part of some of the curves in iodide solutions is due to the well-known, large shift of the ψ_1-potential in these solutions on approaching the point of zero charge.

¶ This has been shown[7] to intensify the adsorption of I^- very considerably when the surface is positively charged.

therefore, that in the region where $b \simeq 60$ mV the overvoltage is effectively independent of the composition of the solution.

The value $b = 58.5$ mV and the lack of dependence of the overvoltage on solution composition are in complete agreement with the predictions of the theory, and enable us to state that slow barrierless discharge of H_3O^+ ions takes place on mercury at low current densities.

Various authors have observed slopes of the order of 60 mV in their semilogarithmic plots for different cathodes. However, their interpretations (which are not strictly substantiated even for their particular systems) are clearly not applicable to the mercury cathode.

Thus, Thomas[8] ascribes this slope to a logarithmic hydrogen adsorption isotherm, which is clearly not the case for mercury. Equally improbable (for the case of mercury) is the assumption of slow surface diffusion of the adsorbed hydrogen or slow detachment of the hydrogen from stable adsorption sites[9]. A different explanation, put forward by Bockris and coworkers[9], associates the appearance of a low value of b with a change in ψ_1-potential near the point of zero charge. This argument is unconvincing on general grounds[10], and in our particular system it is refuted also by the fact that the inflection in the curve occurs well away from the point of zero charge (up to 0.4 V in concentrated HCl, see Ref. 4), and in a region where the shape of the polarisation curve for normal discharge has already become stabilised (see Fig. 4).

We had previously shown[11] that a slope of 59 mV should be observed if the slow step is non-activated electrochemical desorption, and discharge and ionisation are effectively at equilibrium. However, this explanation does not apply to the present problem, since it predicts a strong dependence of the overvoltage on solution composition.

Thus, of all the mechanisms discussed in the literature which predict $b = 59$ mV, the barrierless discharge mechanism alone accounts for the whole of the experimental data.

The value $\alpha = 1$ implies that over the same region of potential $\beta = 0$, i.e. the ionisation proceeds as a non-activated process. Therefore, although no direct demonstration has yet been given of non-activated electrochemical processes, the present results can be taken as an indirect proof of the existence of such processes. It follows that the general kinetic features of any arbitrary electrode reaction can be expressed, in all probability, by a curve of the type given in Fig. 2. Whether or not any particular portion of the curve is experimentally accessible, however, depends on the quantitative aspects of each individual case.

An important feature of the barrierless discharge of hydrogen ions, the fact that its rate is independent of the concentration of H_3O^+ and of the ψ_1-potential, enables us to use this phenomenon to solve certain general problems not otherwise readily handled.

There has been some discussion[12] of the screening effect of tetraalkylammonium cations on the discharge of other ions. In normal discharge, the strong influence of these cations on the ψ_1-potential (and therefore on the overvoltage) can mask their screening effect if, of course, this effect is not very large. In barrierless discharge ψ_1-effects are absent, but any screening effects should make themselves felt as in normal discharge. According to our results, addition of tetrabutylammonium salts has practically no effect on the overvoltage. There is, in fact, a very small increase in potential, particularly at the lowest current densities, but it is of the order of 10–15 mV and therefore borders on experimental error. This question needs further study, but it is clear in any case that the screening effect in the discharge of hydrogen ions is relatively small.

A more interesting problem is that of the kinetic activity factor. Frumkin and Iofa[13] found that the overvoltage attending hydrogen evolution from concentrated acid solutions of chlorides at constant concentration of acid and Cl^- ions (i.e., according to those workers[13], under conditions of practically constant ψ_1-potential) remains unchanged when the Li^+ cations are replaced by K^+, in spite of the large difference in the activity coefficient of H_3O^+ ($\gamma_{H_3O^+}$) in these solutions. They concluded that, as $\gamma_{H_3O^+}$ changes, the activity coefficient of the activated complex ($\gamma^{\neq}$) also changes so as to produce compensation. The ratio $\gamma^{\beta}_{H_3O^+}/\gamma^{\neq}$, which appears in the equation for normal slow discharge, was thus found to be equal to unity.

However, strictly speaking, the kinetic activity factor is not confined to the ratio $\gamma^{\beta}_{H_3O^+}/\gamma^{\neq}$. The equation for discharge, both normal and barrierless, includes also the activity of water raised to the power α†, so that the full expression for the kinetic activity factor should be $\gamma^{\beta}_{H_3O^+}\gamma^{\alpha}_{H_2O}/\gamma^{\neq}$. Usually γ_{H_2O} is close to unity, and this correction has no significant effect on the precision of the kinetic activity factor. It is very important in principle, however, because the results of Frumkin and Iofa have been generalised by Temkin[14] to include temperature variation (see below).

A rigid experimental evaluation of the effects associated with the activity of water is practically out of the question for normal discharge. Thus, appreciable departures of γ_{H_2O} from unity occur only in very concentrated solutions, in which the error in estimating the ψ_1-effect due to specific adsorption is obviously much greater than any likely potential shift arising from water activity effects. In barrierless discharge, on the other hand, where no ψ_1-effect occurs, the conditions for demonstrating the effect of the activity of water are quite favourable.

To this end, we have studied the overvoltage in very concentrated, acidified solutions of LiBr in which the activity of water was very low (0.1 or less) although the mole fraction was higher than 0.6. If the overvoltage had been directly determined by the activity of water, we should have expected the overvoltage under these conditions to be 50–60 mV higher than in the 3–4 N solutions of KI. In fact, as Fig. 4 shows, the two sets of curves are indistinguishable within experimental error. If, on the other hand, we expect to find only an effect determined by the mole fraction of water, the resulting increase in overvoltage is only 6–8 mV, i.e. a quantity of the order of the experimental error and therefore difficult to observe. Thus, we may conclude that the activity coefficient of water has no effect on hydrogen overvoltage under conditions of barrierless discharge. Hence, following Frumkin and Iofa, we state that $\gamma_{H_2O}/\gamma^{\neq} = 1$. Extending this result, and that of Frumkin and Iofa, to any arbitrary hydrogen ion discharge process, we can write the following approximate equation:

$$\gamma^{\neq} = \gamma^{\beta}_{H_3O^+}\gamma^{\alpha}_{H_2O} \quad \text{or} \quad RT \ln \gamma^{\neq} = \beta RT \ln \gamma_{H_3O^+} + \alpha RT \ln \gamma_{H_2O}. \qquad (4)$$

† This factor allows for the effect of the activity of water on the equilibrium potential.

For barrierless discharge it is easy to verify that $\gamma^{\neq} \simeq \gamma_{H_2O}$. Thus, the distinguishing feature of barrierless discharge is that the activated and the final states are identical: the highest point of the potential energy profile occurs just at the final state. The final state for the discharge of oxonium ions consists of an adsorbed hydrogen atom and a water molecule in the double layer. The activity coefficient of the adsorbed hydrogen is unity (small θ), and therefore the activity coefficient of adsorbed water ($\gamma_{H_2Oads} \simeq \gamma_{H_2O}$) must be adopted as the activity coefficient of the transition state. Thus, the identity of the final and activated state have led us to the same conclusion as the experimental data on overvoltage in very concentration solutions.

Temkin[14], using the analogy between the transfer of a species from a concentrated to a dilute solution and the transfer of a species from one solution to another, and treating water at two not very different temperatures as two distinct solvents, found the entropy of the activated complex. According to Frumkin and Iofa[13], $RT\ln\gamma^{\neq} \simeq \beta RT\ln\gamma_{H_2O^+}$, i.e. $\Delta G^{\neq} \simeq \beta\Delta G^0_{H_3O^+}$, where ΔG is the change in standard Gibbs free energy attending the transfer of the species from the ideal to the real solution. Assuming that this relationship applies also to transfer from one temperature to another, dividing by ΔT, and letting $\Delta T \to 0$, we obtain

$$S^{\neq} \simeq \beta S^0_{H_3O^+}. \quad (5)$$

An analogous argument for barrierless discharge, based on the equality $\gamma^{\neq} \simeq \gamma_{H_2O}$, leads to

$$S^{\neq} \simeq S^0_{H_2O}. \quad (6)$$

An expression of the type of (6) can also be obtained by an alternative approach, without resorting to the above approximation for the activity coefficients or to the analogy between change of temperature and change of solvent. As we have already pointed out, the activated complex for barrierless discharge coincides with the final state, i.e. with an adsorbed H atom and H_2O molecule. Hence

$$S^{\neq} = S^0_{H_{ads}} + S^0_{H_2O_{ads}}. \quad (7)$$

$S^0_{H_{ads}}$ includes only the vibrational contribution. Since the vibrational frequencies of practically all chemical H bonds are fairly high‡, the corresponding partition function is close to unity and $S^0_{H_{ads}}$ is almost zero. Therefore

$$S^{\neq} = S^0_{H_2O_{ads}}. \quad (7a)$$

Since $\Delta S^0_{\alpha_{H_2O}}$ is not large§,

$$S^{\neq} \simeq S^0_{H_2O}. \quad (6)$$

‡ We shall show below that the energy of the adsorption bond is of the order of 30 kcal, which corresponds to a vibrational frequency of ~1100 cm^{-1}, i.e. $S^0_{H_{ads}} \simeq 0.06$ e.u.

§ $\Delta G^0_{\alpha_{H_2O}}$ can be calculated as $10^{-15}N(\sigma_{Hg/H_2O} - \sigma_{Hg})$, where N is Avogadro's number, 10^{-15} is the area in cm^2 occupied by a water molecule in the surface layer, σ_{Hg/H_2O} is the mercury–water interfacial tension, and σ_{Hg} is the surface tension of mercury. On differentiating this expression with respect to temperature, we find $\Delta S^0_{\alpha_{H_2O}}$. Using data on the temperature dependence of the surface tension of mercury[15] and of the interfacial tension at the electrocapillary maximum[16], we obtained $\Delta S^0_{\alpha_{H_2O}} = -1.15$ e.u. One could justifiably question how accurately this value, which applies to the adsorption of water at the potential of the point of zero charge, describes the state of the water molecule formed on discharge of an H_3O^+ ion. However, the order of magnitude is undoubtedly correct, and $\Delta S^0_{\alpha_{H_2O}}$ is much smaller than $S^0_{H_2O} = 16.72$ e.u.[17]

We have pointed out that the relationships between the activity coefficients found experimentally for normal and for barrierless discharge can be generalised in the form of Eqn. (4). Applying the same treatment to this generalised form, we find

$$S^{\neq} \simeq \beta S^0_{H_3O^+} + \alpha S^0_{H_2O}. \quad (8)$$

Eqn. (8) differs from Temkin's Eqn. (5) by a term containing the entropy of water. As was stated above, the starting expression for $\gamma^{\neq}$ used by Temkin makes no allowance for the activity coefficient of water, which is practically equal to unity in most cases. Allowing for this factor introduces an additional term into the expression for the entropy of the activated complex. In fact, Eqn. (8) states that the entropy of the activated complex has a value intermediate between the entropies of the initial ($H_3O^+ + e_{met}$) and of the final ($H_2O + H_{ads}$) states. (It is assumed that $Se_{met} \simeq 0$ and $S_{H_{ads}} \simeq 0$.) This conclusion appears reasonable, since the activated complex corresponds to a configuration intermediate between the initial and the final state. It is well known that the entropy of an activated complex is not in general equal to the mean of the entropies of the initial and the final states. However, in the present case [as pointed out by Temkin[14] in connection with Eqn. (5)] the entropy terms associated with the vibrational partition functions for the activated complex and for species in the initial and in the final state are quite small, and the entropy of the activated complex is almost entirely determined by its interaction with the solvent, as expressed by Eqn. (8).

If the entropy of the activated complex is taken to be the mean of the corresponding values for the initial and the final state, it is more correct to write Eqn. (8) in the form

$$S^{\neq} = \beta S^0_{H_2O^+_{ads}} + \alpha S^0_{H_2O_{ads}}. \quad (8a)$$

For $\alpha = 1$ and $\beta = 0$, this expression reverts to (7a), i.e. the expression obtained directly for the entropy of the activated complex under conditions of barrierless discharge.

For non-activated discharge, the transition state coincides with the initial state, whence it follows that

$$S^{\neq} = S^0_{H_2O^+_{ads}}. \quad (9)$$

But Eqn. (9) can also be obtained directly from (8a) by putting $\alpha = 0$ and $\beta = 1$.

The fact that Eqn. (8a) gives the right results, verified by an independent method, in the limiting cases, leads us to believe that the generalisation of experimental results used in its derivation is also reasonable, and that Eqn. (8a) can also be used in the case of $\alpha = \beta = 1/2$, i.e. for normal discharge.

In the derivation of the kinetic Eqn. (3) given above we took account of the identity of the activated and the final state[2], in particular as regards the value of the entropy of the activated complex [according to (7a)], but we had not brought out the significance of the kinetic activity factor. After introduction of the necessary refinements, the equation takes the following form (the ratio $\gamma_{H_2O}/\gamma_{H_2O\,ads}$ is assumed to be unity):

$$i = \varepsilon\frac{kT}{h}\varkappa 10^{15} x_{H_2O} p_{H_2}^{1/2}(1-\theta)\exp\left\{-\frac{1}{RT}\left[\Delta H_{a_{H_2O}} + \Delta H_{a_H} + T\left(\frac{1}{2}S^0_{H_2} - \Delta S^0_{aH_2O}\right) - \eta F\right]\right\}. \quad (10)$$

The real activation energy A is determined from the slope of the plot of $\ln i$ against $1/T$ at constant overvoltage [5]¶.

The corresponding expression for A is obtained by differentiating Eqn. (10):

$$A = -R\left(\frac{\partial \ln i}{\partial 1/T}\right)_{\eta} = \Delta H_{a_{H_3O}} + \Delta H_{a_H} - \eta F + RT. \qquad (11)$$

From (10) and (11) we find the real pre-exponential factor K:

$$K = \varepsilon \frac{kT}{h} e\varkappa\, 10^{15} x_{H_3O} p_{H_2}^{1/2} (1-\theta) \exp\left(-\frac{{}^1/_2 S^0_{H_2} - \Delta S^0_{a_{H_3O}}}{R}\right). \qquad (12)$$

Fig. 5, in which a number of typical plots of $\log i$ against $1/T$ are shown for different solutions, satisfactorily confirms that the linear relationship is obeyed. Values of K and A were obtained from the experimental linear plots. These values were recalculated by means of Eqn. (1) for the equilibrium potential, i.e. for $\eta = 0$. In all, we obtained 16 independent sets of data: one for a solution of LiBr, two for NaBr, and the rest for KI (two of them with addition of tetrabutylammonium salts). The mean of all the experimental values is $\log K = 3.0\ (\pm 0.4)$ and $A_0 = 22.9\ (\pm 0.5)$ kcal × × mole^{-1}. (The figures in brackets denote the mean deviations from the average.)

Eqn. (12) allows us to calculate the pre-exponential term if we make the usual assumption of a transmission coefficient $\varkappa = 1$ (adiabatic process). All the necessary constants are known, and ΔS_{H_2O} has been evaluated above. (Even if the error in this estimate is of the same order of magnitude as the value itself, the error introduced into the calculation of K is smaller than the experimental error.) The result of this calculation is $\log K = 5.7$. Thus we must record a discrepancy between theory and experiment in excess of the experimental error.

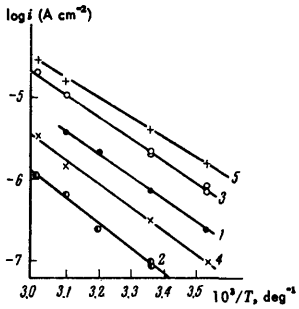


Fig. 5. Temperature variation of the current at constant overvoltage for solutions of different composition (M): 1) 11.8 LiBr, 0.1 HCl, η = 460 mV; 2) 7 NaBr, 0.85 HCl, η = 400 mV; 3) 4.2 KI, 0.45 HCl, η = 470 mV; 4) 3 KI, 0.9 HCl, 1.3×10^{-3} N(Bu)$_4$Br, η = 500 mV; 5) same solution, η = 440 mV.

For normal discharge, Temkin [14] found $\log K = 2.6-3.3$ (for two different solutions) from the data of Iofa and Mikulin [18]; using the data of Post and Hiskey [19], he obtained $\log K = 4$. Thus, the pre-exponential factor for normal discharge is not very different from the value obtained by us for barrierless discharge (the difference being of the order of magnitude of the experimental error).

Temkin's calculation [14] gave $\log K = 5$, the agreement between this and the experimental value being thought fully satisfactory. The small discrepancy was ascribed, with some reservations, to the effect of tunnelling by the proton. If, however, we use Eqns. (8) or (8a) to calculate the pre-exponential factor instead of the expression used by Temkin [Eqn. (5)], a procedure which we now believe to be more justifiable, the pre-exponential term becomes much larger, and $\log K$ takes the value 6.7–6.8. The value of K obtained by this calculation is an order of magnitude larger than the theoretical value for barrierless discharge.

Thus, the discrepancy between theory and experiment is very significant both for normal and for barrierless discharge. It cannot be ascribed to the tunnel effect, since under conditions of barrierless discharge there is no potential barrier through which a proton could penetrate. The tunnel effect may possibly occur to some extent in normal discharge — the disagreement between theory and experiment is perhaps somewhat more serious in this case — but it is quite impossible to draw any definite conclusions from the data which have been discussed.

It should be noted that at least in barrierless discharge the discrepancy between theory and experiment is not associated with any assumptions made in the evaluation of the properties of the activated complex: in this case exact calculation was possible without any need for additional hypotheses. The cause of the discrepancy must be sought, therefore, in the approximations which underlie the theory of absolute reaction rates.

We have reported above our value ($A_0 = 22.9$ kcal × × mole^{-1}) for the activation energy for barrierless discharge at the equilibrium potential. As shown by Eqn. (11), and by the potential diagram of Fig. 3, this value enables us to calculate the adsorption energy of hydrogen, a quantity which has not so far been experimentally accessible because of the very low adsorbability of hydrogen on mercury.

Eqn. (11) includes the quantity $\Delta H_{a_{H_2O}}$. This can be found from the data on σ_{Hg/H_2O} and σ_{Hg} and their temperature variation, used above to evaluate $\Delta S^0_{a_{H_2O}}$. The result is $\Delta H_{a_{H_2O}} = -1.0$ kcal mole^{-1}, and the error in this value has little effect on any subsequent conclusions.

Using the experimental value of A_0 and the above estimate of $\Delta H_{a_{H_2O}}$, we find $\Delta H_{a_H} = 23.3$ kcal mole^{-1}. The error is hardly more than 1.5 kcal (assuming that the error in $\Delta H_{a_{H_2O}}$ is of the order of magnitude of the value itself). From a knowledge of the heat of adsorption of hydrogen and of its heat of dissociation [17], we can calculate the energy of the Hg–H adsorption bond. This turns out to be 29 kcal, a value close to a previous estimate based on a number of analogies and tentative calculations [2, 6, 20].

A case of great interest is that in which neutral molecules rather than H_3O^+ ions undergo barrierless discharge. We noted the phenomenon [4] in the evolution of hydrogen on

¶ Since the comparison of i at different temperatures is made at constant concentration of H_3O^+ in the bulk (but not at the surface), the activation energy determined in this way is termed apparent, and does not include a term for the adsorption energy of H_3O^+ (see Fig. 3).

mercury from concentrated solutions of HCl and strongly acidified, concentrated solutions of KI.[4] Under these conditions the discharge of neutral molecules of the acid is predominant. The composition of the solution now has a significant effect: as was said at the beginning of this article, the effects of the ψ_1-potential on the potential drop across the fixed part of the double layer and on the surface concentration of reducible species are mutually compensating only in the case of singly charged cations. With neutral molecules the second factor is not operative. It is evident from Fig. 6 that the addition of tetrabutylammonium ions, which assist the action of I^-, raises the overvoltage quite significantly in the barrierless discharge region, as should be the case for the discharge of neutral molecules. In weakly acid solutions, however, where H_3O^+ ions are discharged, tetrabutylammonium ions have practically no effect on the overvoltage (Fig. 4). This example shows clearly that a change in the structure of the double layer affects the barrierless discharge process as much as any other discharge process, and that it is only because of the compensation of two opposing effects that the phenomenon is not directly observable in the barrierless discharge of hydrogen ions.

In addition to the evolution of hydrogen on mercury, considered here, there are other electrode reactions for which a barrierless process is likely.

Various authors[9,21-27] have observed a Tafel b constant close to 60 mV, changing to a slope of over 100 mV at higher current densities, in the evolution of hydrogen from acid solutions at a silver cathode. The effect of solution composition on overvoltage was not studied in sufficient detail by those workers. Bockris and Conway[23] found that the overvoltage in pure 0.01 N HCl and in a KCl (or $BaCl_2$) electrolyte is quite different over the region where $b \simeq 120$ mV, but is practically indistinguishable in the region of $b \simeq 60$ mV, as required by the barrierless discharge mechanism. Admittedly, the slope of ~ 60 mV was not detected in another series of experiments reported in the same paper. Disagreement at the top end of the curves, and exact agreement at the bottom end, has been reported also[9] for 0.1 N and 0.4 N HCl.

This reaction is being investigated by V. I. Bystrov in our laboratory. From preliminary results, it appears that change of pH has a powerful effect on hydrogen overvoltage in the region where $b \simeq 120$ mV, but at lower potentials ($b \simeq 60$ mV) the effect is very much weaker. On the whole, the situation seems to indicate slow barrierless discharge changing to normal discharge at higher potentials.

Even less is known about hydrogen evolution at cathodes of Au,[28] W,[9] and Mo,[28] and under certain conditions Pt [9] and Rh,[29] for which a slope of $b \simeq 60$ mV has also been reported. It is not possible to reach a firm conclusion, but only to point out that, with strongly hydrogen-adsorbing metals such as W and Mo, barrierless electrochemical desorption is most likely[2]. For the platinum metals we cannot exclude the possibility of an adsorption-electrochemical mechanism, in which the reaction rate is determined by the rate of electrochemical desorption of hydrogen atoms adsorbed on the cathode from the gas phase[11,30]. This electrochemical desorption could be barrierless[2].

Hydrogen evolution does not appear to be the only type of reaction in which the barrierless process is realised. Thus, the present writer and Rotenberg[31] have observed a perfectly sharp break in the polarisation curves for the anodic evolution of chlorine on graphite (see Fig. 7), the slope at the lower end of the curve corresponding to 60 mV. (The experimental slope is higher by a factor of two because of the peculiar current distribution in the porous electrode; the relation between the apparent and the true slope in porous electrodes is discussed, for example, in Ref. 32.) It is important to note that, in keeping with the theory, the addition of SO_4^{2-} anions and Fe^{3+} cations (both of which are adsorbed on graphite) has practically no effect on the lower part of the polarisation curves, whereas their effect in the region of $b \simeq 110$ mV, where we suppose that normal discharge is proceeding, is quite appreciable. Polarisation curves of similar shape have also been observed under somewhat different conditions[33,34].

The phenomena occurring during anodic evolution of oxygen are more obscure. Several authors[35-38] have

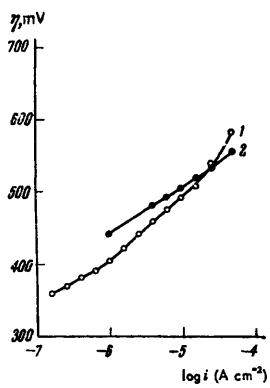


Fig. 6. Effect of tetrabutylammonium ions on the overvoltage in strongly acid KI solutions:
1) 2.2 M KI, 4 M HCl; 2) same solution, + 1×10^{-3} M $N(Bu)_4Br$.

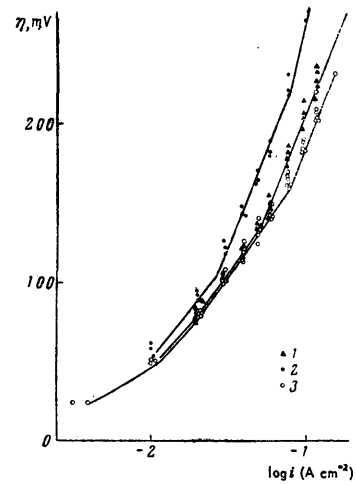


Fig. 7. Polarisation curves for the evolution of chlorine on graphite:
1) 4.4 M Cl^-, 1.5 M H^+; 2) solution 1 with addition of 0.2 M Na_2SO_4; 3) solution 1 with addition of 0.1 M $FeCl_3$.

reported slopes of the order of 60–70 mV on Au, Cu, and Co anodes, but an unambiguous discussion of these results is not possible as yet. Bardina[39] has obtained some interesting results in our laboratory on the anodic oxidation of high-temperature pyrolytic carbon below the equilibrium oxygen potential. We believe that these results can be most satisfactorily explained in terms of barrierless electrochemical desorption of CO_2 accompanying the discharge of OH^- ions.

A slope of ~ 60 mV has been frequently observed in the anodic evolution of nitrogen from azide solutions on anodes of different materials[40-42]. The variation of potential with azide concentration[40,41] corresponds exactly with the requirements of barrierless discharge (or electrochemical desorption). However, another explanation is possible, based on the shape of the adsorption isotherm of nitrogen[42]. A choice between these possibilities must await further experimental work.

In conclusion, we can state that the existence of barrierless discharge in the evolution of hydrogen on mercury is a firmly established fact. A barrierless process offers the most plausible explanation of the features of hydrogen evolution on silver and chlorine evolution on graphite: we may hope that current investigations will finally resolve this problem. Furthermore, there are numerous data which justify the belief that many other electrode reactions can occur by the barrierless mechanism.

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THEORY OF THE MACROSCOPIC KINETICS OF HETEROGENEOUS AND HOMOGENEOUS-HETEROGENEOUS SYSTEMS

V. G. Levich

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