

by the galvanometer, confirming the validity of the assumptions made. The difference is due to the fact that the measured space-charge density was less than expected because of inertial and gravitational settling of the particles and also, apparently, to a lesser extent due to insufficient uniformity of the concentration of the particles in the chamber recorded by the counter.

The author wishes to thank M. G. Evreinov, M. N. Olevskii, and M. V. Maslennikov for discussion of this work.

SUMMARY

1. When a generator of uniformly charged particles is switched on, a steady-state space-charge density is rapidly established in the chamber.
2. A new method, based on the use of an electric field strength transducer, has been applied for the measurement of the space-charge density and its distribution with respect to mobilities. The convection current and its distribution with respect to mobilities may be calculated from such measurements.

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Received 18th April 1960

EFFECT OF ADSORBED ATOMIC HYDROGEN ON THE HYDROGEN OVERVOLTAGE

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The effect of adsorbed hydrogen on the evolution of hydrogen has been frequently studied, both theoretically and experimentally¹⁻³. In most cases the theoretical

examination of the problem was confined to the case where $\alpha = 0.5$,¹ which, as will be shown below, constitutes a serious limitation. The kinetic equations have been derived in the present work using a somewhat more general version of the procedure proposed by Temkin⁴, who employed the activated-complex method.

The following three stages are at present regarded as possible in the evolution of hydrogen from acid solutions:

discharge:



recombination:



electrochemical desorption:



For stage (I) we have

$$\mu_t = \mu_{H^+} + \mu_e, \quad (1)$$

where μ_t is the chemical potential of the activated complex in the reaction, μ_e the chemical potential of the electron ($\mu_e = -FE$, E being the electrode potential), μ_{H^+} the chemical potential of the hydrogen ion, and μ_H the chemical potential of the adsorbed hydrogen.

If the electrode surface is non-uniform, then for the uniform sections s we have, according to Temkin⁴,

$$\mu_t^s = \mu_t^{s0} + RT \ln \frac{\theta_t^s}{(1-\theta_t^s)}, \quad (2)$$

$$\mu_{H^+}^s = \mu_{H^+}^{s0} + RT \ln a_{H^+}, \quad (3)$$

$$\mu_H^s = \mu_H^{s0} + RT \ln \frac{\theta_H^s}{1-\theta_H^s}, \quad (4)$$

where θ_t^s and θ_H^s are the degrees of coverage of sections s with the activated complex and atomic hydrogen respectively.

According to the assumption made previously⁴, the following relations hold for any form of the hydrogen adsorption isotherm:

$$\mu_H^{s0} = \mu_H^0 + RT\varphi(s), \quad (5)$$

$$\mu_t^{s0} = \mu_t^0 + \alpha'_1 \mu_e + \alpha'_2 RT\varphi(s), \quad (6)$$

where $\varphi(s)$ is a function of the parameter s , characterising the energetic non-uniformity of the surface; $0 < \alpha'_2 < 1$ shows that the distribution of the energy of the activated complex on the surface is similar to the distribution of atomic hydrogen; $0 < \alpha'_1 < 1$ shows that the activated complex includes only part of the free energy of the electron, which the latter possessed before the completion of the fundamental reaction stage, assuming that the free energy of the electron becomes zero after this stage. From the physical significance of α'_1 and α'_2 , it follows that they are not necessarily equal. On substituting Eqns. (2)–(6) in (1), we obtain the following expressions:

for the forward reaction (I)

$$\theta_t^s = \exp \left(- \frac{(\mu_t^0 - \mu_{H^+}^0)}{RT} \right) \exp \left(\frac{(\alpha'_1 - \alpha'_2) \mu_e}{RT} \right) \exp [- \alpha'_2 \varphi(s)] a_{H^+} (1 - \theta_H^s); \quad (7)$$

for the reverse reaction (I)

$$\theta_H^s = \exp \left(- \frac{(\mu_H^0 - \mu_t^0)}{RT} \right) \exp \left(- \frac{\alpha'_1 \mu_e}{RT} \right) \exp [(1 - \alpha'_2) \varphi(s)] \theta_t^s. \quad (8)$$

From Eqns. (7) and (8), it is easy to find, in the usual

way³, the expressions for the velocities of the forward ($\vec{\omega}$) and reverse ($\bar{\omega}$) reactions (I) on sections s :

$$\vec{\omega} ds = \chi L \frac{kT}{h} \exp\left(-\frac{\mu_{H^+}^0 - \mu_{H^+}}{RT}\right) \exp\left(\frac{(1 - \alpha'_1) \mu_e}{RT}\right) \exp[-\alpha'_2 \varphi(s)] (1 - \theta_H^0) ds, \quad (9)$$

$$\bar{\omega} ds = \chi L \frac{kT}{h} \exp\left(-\frac{\mu_{H^+}^0 - \mu_{H^+}}{RT}\right) \exp\left(\frac{-\alpha'_1 \mu_e}{RT}\right) \exp[(1 - \alpha'_2) \varphi(s)] \theta_H^0 ds, \quad (10)$$

where χ is the transmission coefficient of the reaction, L the number of adsorption sites on the surface, k and h are the Boltzmann and Planck constants respectively, R is the gas constant, T the absolute temperature, and $\mu_{H^+}^0 = \mu_{H^+}^0 - RT$.

Eqns. (9) and (10) essentially describe, in a differential form, the effect of adsorbed hydrogen on the rate of reaction (I). To obtain integral expressions for the rates, it is necessary to integrate Eqns. (9) and (10) with respect to s from 0 to 1. As shown by Temkin⁴, even when $\varphi(s)$ is a linear function, Eqns. (9) and (10) cannot be integrated in terms of elementary functions, if the variation of $\varphi(s)$ is small when s varies from 0 to 1.

Putting $\varphi(s) = 0$ in Eqns. (9) and (10), we readily obtain the following expressions for the forward and reverse rates of reaction (I) on a uniform surface:

$$\vec{\omega}_0(I) = k_0(I) (1 - \theta_H) \exp\left(\frac{\mu_{H^+}}{RT}\right) \exp\left(-\frac{\alpha' FE}{RT}\right), \quad (11)$$

$$\bar{\omega}_0(I) = k_0(I) (1 - \theta_H) \exp\left(\frac{\mu_{H^+}^0}{RT}\right) \exp\left(\frac{\beta' FE}{RT}\right), \quad (12)$$

where $1 - \alpha'_1 = \alpha'$ and $\alpha' + \beta' = 1$.

For a uniform surface, we have

$$\frac{\theta_H}{1 - \theta_H} = \exp\left(\frac{\mu_H - \mu_H^0}{RT}\right) = \exp\left(\frac{F(\eta_p - \eta_{pc})}{RT}\right), \quad (13)$$

where $\mu_H^0 = \mu_{H^+}^0$ is the chemical potential of the adsorbed hydrogen in the standard state ($\theta_H = \frac{1}{2}$) and μ_{H_2} the chemical potential of gaseous hydrogen:

$$F\eta_p = \mu_H - \frac{1}{2}\mu_{H_2}; \quad F\eta_{pc} = \mu_H^0 - \frac{1}{2}\mu_{H_2}. \quad (14)$$

On substituting (13) in (12), we obtain

$$\bar{\omega}_0(I) = k_0(I) (1 - \theta_H) \exp\left(\frac{\mu_H}{RT}\right) \exp\left(\frac{\beta' FE}{RT}\right).$$

At equilibrium $\theta_H = \theta_r$, $\mu_H = \frac{1}{2}\mu_{H_2}$, and $E = E_r$. Hence remembering that

$$\mu_{H^+} - \mu_H = F(E_r - \eta_p), \quad (15)$$

we find

$$\vec{\omega}_0 = k_0(I) (1 - \theta_H) \exp\left(\frac{\beta' \mu_{H^+} + \alpha' \mu_H}{RT}\right) \exp\left(\frac{\alpha' F(\eta_k - \eta_p)}{RT}\right), \quad (16)$$

$$\bar{\omega}_0 = k_0(I) (1 - \theta_H) \exp\left(\frac{\beta' \mu_{H^+} + \alpha' \mu_H}{RT}\right) \exp\left(\frac{-\beta' F(\eta_k - \eta_p)}{RT}\right), \quad (17)$$

where $\eta_k = E_r - E$ is the measured hydrogen overvoltage.

According to Eqns. (16) and (17), the exchange current at the equilibrium potential is given by

$$i_0^* = k_0(I) (1 - \theta_r) \exp\left(\frac{\beta' \mu_{H^+} + \alpha' \frac{1}{2} \mu_{H_2}}{RT}\right). \quad (18)$$

On substituting (18) in (16) and (17), we finally obtain

$$\vec{\omega}_0(I) = i_0^* \frac{1 - \theta_H}{1 - \theta_r} \exp\left(\frac{\alpha' F \eta_p}{RT}\right) \exp\left(\frac{\alpha' F(\eta_k - \eta_p)}{RT}\right), \quad (19)$$

$$\bar{\omega}_0(I) = i_0^* \frac{1 - \theta_H}{1 - \theta_r} \exp\left(\frac{\alpha' F \eta_p}{RT}\right) \exp\left(\frac{-\beta' F(\eta_k - \eta_p)}{RT}\right). \quad (20)$$

To derive equations for the rates of reaction (I) on non-uniform surfaces ($\vec{\omega}_H$, $\bar{\omega}_H$), it is necessary to integrate

Eqns. (9) and (10) with respect to s from 0 to 1. This can be done as in the calculation of the rates of adsorption and desorption⁵. Integration yields the following expressions for the forward and reverse rates of reaction (I) [$\vec{\omega}_H(I)$ and $\bar{\omega}_H(I)$ respectively]:

$$\vec{\omega}_H(I) = k_H(I) \exp\left(\frac{\mu_{H^+} - \alpha'_1 \mu_H}{RT}\right) \exp\left(\frac{\beta'_1 \mu_e}{RT}\right), \quad (21)$$

$$\bar{\omega}_H(I) = k_H(I) \exp\left(\frac{\beta'_2 \mu_H}{RT}\right) \exp\left(\frac{-\alpha'_1 \mu_e}{RT}\right), \quad (22)$$

$$k_H(I) = J_0 \chi L \frac{kT}{h} \exp\left(-\frac{\mu_{H^+}^0 - \alpha'_1 \mu_H^0}{RT}\right); \quad \alpha'_1 + \beta'_1 = \alpha'_2 + \beta'_2 = 1, \quad (23)$$

where J_0 is a constant whose significance has been explained by Temkin⁴. Temkin showed that Eqns. (9) and (10) can be integrated for any isotherm in which the function $\varphi(s)$ undergoes infinite change and satisfies the condition $\frac{d}{ds} [RT \exp \varphi(s) / RT] \gg 0$.

Expressing μ_e in terms of the electrode potential and using Eqn. (14), it is easy to convert Eqns. (21) and (22) to the following form:

$$\vec{\omega}_H(I) = i_H^* \exp\left(\frac{F(\alpha'_1 - \alpha'_2) \eta_p}{RT}\right) \exp\left(\frac{\alpha'_1 F(\eta_k - \eta_p)}{RT}\right), \quad (24)$$

$$\bar{\omega}_H(I) = i_H^* \exp\left(\frac{F(\alpha'_1 - \alpha'_2) \eta_p}{RT}\right) \exp\left(\frac{-\beta'_1 F(\eta_k - \eta_p)}{RT}\right), \quad (25)$$

where

$$i_H^* = k_H(I) \exp\left[\frac{\beta'_1 \mu_{H^+} + (\alpha'_1 - \alpha'_2) \frac{1}{2} \mu_{H_2}}{RT}\right]. \quad (26)$$

Similarly we can obtain the following expressions for the forward and reverse rates of stage (II) (recombination).

For a uniform surface:

$$\vec{\omega}_0(II) = i_0^{**} \left(\frac{1 - \theta_H}{1 - \theta_r}\right)^2 \exp\left(\frac{2F\eta_p}{RT}\right), \quad (27)$$

$$\bar{\omega}_0(II) = i_0^{**} \left(\frac{1 - \theta_H}{1 - \theta_r}\right)^2, \quad (28)$$

where

$$i_0^{**} = k_0(II) (1 - \theta_r)^2 \exp\left(\frac{\mu_{H_2}}{RT}\right). \quad (29)$$

For a non-uniform surface:

$$\vec{\omega}_H(II) = i_H^{**} \exp\left(\frac{2\alpha' F \eta_p}{RT}\right), \quad (30)$$

$$\bar{\omega}_H(II) = i_H^{**} \exp\left(\frac{-2\beta' F \eta_p}{RT}\right), \quad (31)$$

where

$$i_H^{**} = k_H(II) \exp\left(\frac{\alpha' \mu_{H_2}}{RT}\right). \quad (32)$$

In the same notation we have the following expressions for stage (III) (electrochemical desorption).

For a uniform surface:

$$\vec{\omega}_0(III) = i_0^{***} \left(\frac{1 - \theta_H}{1 - \theta_r}\right) \exp\left(\frac{\beta'' F \eta_p}{RT}\right) \exp\left(\frac{-\alpha'' F(\eta_k + \eta_p)}{RT}\right), \quad (33)$$

$$\bar{\omega}_0(III) = i_0^{***} \left(\frac{1 - \theta_H}{1 - \theta_r}\right) \exp\left(\frac{\beta'' F \eta_p}{RT}\right) \exp\left(\frac{-\beta'' F(\eta_k + \eta_p)}{RT}\right), \quad (34)$$

where

$$i_0^{***} = k_0(III) (1 - \theta_r) \exp\left(\frac{\beta'' \mu_{H^+} + (1 + \alpha'') \frac{1}{2} \mu_{H_2}}{RT}\right). \quad (35)$$

For a non-uniform surface:

$$\vec{\omega}_H(III) = i_H^{***} \exp\left(\frac{F(\alpha''_2 - \alpha''_1) \eta_p}{RT}\right) \exp\left(\frac{\alpha''_1 F(\eta_k + \eta_p)}{RT}\right), \quad (36)$$

$$\bar{\omega}_H(III) = i_H^{***} \exp\left(\frac{F(\alpha''_2 - \alpha''_1) \eta_p}{RT}\right) \exp\left(\frac{\beta''_1 F(\eta_k + \eta_p)}{RT}\right), \quad (37)$$

where

$$i_H^{\circ\circ} = k_H (\text{III}) \exp \left(\frac{\beta_1 \mu_{H_2} + (\alpha_1 + \alpha_2) \frac{1}{2} \mu_{H_2}}{RT} \right). \quad (38)$$

Using Eqn. (13), we obtain

$$\frac{1 - \theta_H}{1 - \theta_r} = \frac{1 + \exp(-F\eta_{pc}/RT)}{1 + \exp[F(\eta_p - \eta_{pc})/RT]}, \quad (39)$$

since the overvoltage η_p is zero at the equilibrium potential. The value of η_{pc} characterizes the adsorption capacity of the metal. Obviously in the range where θ varies from 0 to ~ 0.1

$$\frac{1 - \theta_H}{1 - \theta_r} \approx 1. \quad (40)$$

Eqn. (39) simplifies greatly when $\theta > 0.9$. It is readily seen that in this case it becomes

$$\frac{1 - \theta_H}{1 - \theta_r} \approx \exp \left(\frac{F(\eta_{pc} - \eta_p)}{RT} \right) \quad (0.9 < \theta < 1); \quad (41)$$

substitution of Eqns. (40) and (41) in (19) and (20), (27) and (29), and (33)–(35) yields the kinetic equations for the stages in the evolution of hydrogen on uniform surfaces in terms of η_k and η_p respectively for the cases where $\theta < 0.1$ and $\theta > 0.9$.

In the range where θ varies from 0.1 to 0.9, the kinetic equations in terms of the same variables can be found as follows¹. Eqns. (19), (20), (27)–(29), and (33)–(35) contain products of the form

$$\frac{1 - \theta_H}{1 - \theta_r} \exp \left(\frac{\alpha F \eta_p}{RT} \right), \quad (42)$$

where $0 < \alpha \leq 1$.

According to Eqn. (13), we have

$$\frac{1 - \theta_H}{1 - \theta_r} \exp \left(\frac{\alpha F \eta_p}{RT} \right) = \frac{\theta_H^2 (1 - \theta_H)^{1-\alpha}}{\theta_r^2 (1 - \theta_r)^{1-\alpha}} = k_c \approx \text{const}; \quad (43)$$

in the subsequent treatment k_c will refer only to the case where $\alpha = 0.5$. Thus kinetic equations, in terms of η_k and η_p only, for the evolution of hydrogen on uniform surfaces, for the case where $0.1 < \theta < 0.9$, can be found from Eqns. (19) and (20), (27)–(29), and (33)–(35) by replacing terms of the type of (42) by terms containing k_c and η_p .

Effect of Adsorbed Hydrogen on the Evolution of Hydrogen on Uniform Surfaces

We shall assume that the evolution of hydrogen takes place in two successive stages, the first of which will always be stage (I) and the second may be either stage (II), or, as shown by Frumkin and Aladzhhalova for palladium, diffusion of molecular hydrogen from the electrode to the solution (slow stage). In the latter case the kinetics of the second stage both on uniform and non-uniform surfaces are described by the following equations:

$$\omega (\text{IV}) = i^{\circ\text{IV}} \exp \left(\frac{2F\eta_p}{RT} \right), \quad (44)$$

$$\omega (\text{IV}) = i^{\circ\text{IV}}, \quad (45)$$

since the recombination stage is assumed to be rapid under these conditions and consequently $\mu_{H_2} = 2\mu_H$; $i^{\circ\text{IV}}$ is obviously independent of the degree of coverage of the metal with hydrogen and is wholly determined by the concentration and diffusion coefficient of molecular hydrogen in the solution.

If the anodic process can be neglected in the second stage, then Eqns. (27) and (45) yield the relation between η_k and η_p :

$$\eta_p = \frac{\alpha_1}{2} \eta_k + \frac{RT}{2F} \ln \frac{i_0^{\circ\circ}}{i_0^{\circ\circ}}. \quad (46)$$

When η_p becomes greater than η_{pc} and $\theta > 0.9$, the following expression is obtained for the applied current by substitution of (41) in (27):

$$i = \tilde{\omega}_0 (\text{II}) = i_0^{\circ\circ} \left(\frac{2F\eta_{pc}}{RT} \right). \quad (47)$$

It is readily seen that in this case the effect of the adsorbed hydrogen results in the appearance of a limiting current². Under these conditions the relation between η_p and η_k is given by Eqn. (19). Substituting (41) in (19) and setting the result equal to (47), we find

$$\eta_p = \alpha_1 \eta_k + \frac{RT}{F} \ln \frac{i_0^{\circ\circ}}{i_0^{\circ\circ}}. \quad (48)$$

When $\eta_p > \eta_{pc}$ and diffusion of hydrogen[†] is the second stage, there can be no limiting current. If η_k and η_p ($\theta > 0.9$) are sufficiently large, then according to Eqns. (19), (41), and (45), the relation between η_k and η_p is given by

$$\eta_p = \frac{\eta_{pc}}{3} + \frac{RT}{3F} \ln \frac{i_0^{\circ\circ}}{i_0^{\circ\circ}} + \frac{\alpha_1}{3} \eta_k. \quad (49)$$

Furthermore, it follows from Eqns. (19) and (42) that

$$\alpha_1 \eta_k - \eta_p = \frac{RT}{F} \ln \frac{i}{i_0^{\circ\circ}} - \eta_{pc}. \quad (50)$$

When $0.1 < \theta < 0.9$, we obtain the following expression for the discharge stage from Eqns. (43) and (19)–(20):

$$\tilde{\omega}_0 (\text{I}) = k_c i_0^{\circ\circ} \exp \left(\frac{F(\alpha' - 0.5) \eta_p}{RT} \right) \exp \left(\frac{\alpha' F (\eta_k - \eta_p)}{RT} \right), \quad (51)$$

$$\tilde{\omega}_0 (\text{I}) = k_c i_0^{\circ\circ} \exp \left(\frac{F(\alpha' - 0.5) \eta_p}{RT} \right) \exp \left(\frac{-\beta' F (\eta_k - \eta_p)}{RT} \right). \quad (52)$$

Neglecting the anodic process, we have

$$\eta_k - \eta_p = \frac{RT}{\alpha' F} \ln i - \frac{RT}{\alpha' F} \ln (k_c i_0^{\circ\circ}) - \frac{\alpha' - 0.5}{\alpha'} \eta_p. \quad (53)$$

Frumkin and Aladzhhalova¹ demonstrated experimentally that Eqn. (53) holds for the evolution of hydrogen on palladium in alkaline media and $\alpha = 0.5$. Comparison of Eqn. (53) with Eqns. (50) and (19) shows that, assuming the palladium surface to be uniform, Eqn. (53) can be valid only when θ varies between 0.1 and 0.9 and $\Delta\eta_p$ does not exceed 55–60 mV. In the case $0.1 < \theta < 0.9$ the equations for the diffusional stage [Eqns. (45) and (46)] remain unchanged and, according to (27) and (28), the kinetic equations for the recombination stage become

$$\tilde{\omega}_0 (\text{II}) = i_0^{\circ\circ} (k_c)^2 \exp \left(\frac{F\eta_p}{RT} \right), \quad (54)$$

$$\tilde{\omega}_0 (\text{II}) = i_0^{\circ\circ} (k_c)^2 \exp \left(-\frac{F\eta_p}{RT} \right). \quad (55)$$

In the same experiments it was shown that the relation between η_p and the current density follows equations of the type of (45) and (46). Thus Frumkin and Aladzhhalova believe that in the evolution of hydrogen on a uniform palladium surface the second stage can only be diffusional.

[†] The process during saturation with hydrogen of the electrolyte layer near the electrode is considered.

Neglecting anodic processes, the relation between η_k and η_p can be easily found from Eqns. (51) and (54):

$$\eta_p = \frac{2}{3} \alpha' \eta_k + \frac{2}{3} \frac{RT}{F} \ln \left(\frac{i_0^{\alpha'}}{k_s i_0^{\alpha''}} \right). \quad (56)$$

Comparison of Eqn. (56) with Eqns. (46) and (49) shows that on transition from the range $\theta < 0.1$ to $0.1 < \theta < 0.9$ and to $\theta > 0.9$, the relation between η_p and η_k remains linear, but the corresponding slopes change in the proportions $\frac{1}{2} : \frac{2}{3} : \frac{1}{3}$.

We shall now assume that the evolution of hydrogen involves stages (I) and (III). In this case the applied current is equally distributed between the two stages. We shall assume further that η_{pc} is large. If $\eta_k - \eta_p$ is also large, then anodic processes can be neglected in both stages. So long as $\eta_p < \eta_{pc}$, the quantity $(1 - \theta_H)/(1 - \theta_T)$ can be assumed to be unity and the following expressions are obtained from Eqns. (33) and (19) ($\theta < 0.1$):

$$\eta_k = \frac{RT}{\alpha' F} \ln \frac{i}{2i_0^{\alpha'}}, \quad (57)$$

$$\eta_p = \frac{(\alpha' - \alpha'')}{\alpha'} \frac{RT}{F} \ln i + \frac{RT}{F} \ln \frac{(2i_0^{\alpha'})^{\alpha''/\alpha'}}{(2i_0^{\alpha''})}, \quad (58)$$

$$\eta_p = (\alpha' - \alpha'') \eta_k + \frac{RT}{F} \ln \frac{i_0^{\alpha'}}{i_0^{\alpha''}}. \quad (59)$$

With the same assumptions, for $\eta_p > \eta_{pc}$, it is easy to show, by substituting (41) in (33) and (19), that ($\theta > 0.9$)

$$\eta_k = \frac{RT}{\alpha' F} \ln \frac{i}{2i_0^{\alpha'}} - \frac{\eta_{pc}}{\alpha'}, \quad (60)$$

$$\eta_p = \frac{(\alpha' - \alpha'')}{\alpha''} \frac{RT}{F} \ln i + \frac{RT}{F} \ln \frac{2i_0^{\alpha'}}{(2i_0^{\alpha''})^{\alpha'/\alpha''}} - \frac{\alpha' - \alpha''}{\alpha''} \eta_{pc}, \quad (61)$$

$$\eta_p = (\alpha' - \alpha'') \eta_k + \frac{RT}{F} \ln \frac{i_0^{\alpha'}}{i_0^{\alpha''}}. \quad (62)$$

In the case $0.1 < \theta < 0.9$, substitution of (43) in (33) and (19) readily yields

$$\eta_k = \frac{2}{\alpha' + \alpha''} \frac{RT}{F} \ln i - \frac{1}{\alpha' + \alpha''} \frac{RT}{F} \ln (4k_s^2 i_0^{\alpha''} i_0^{\alpha'}), \quad (63)$$

$$\eta_p = \frac{2(\alpha' - \alpha'')}{\alpha' + \alpha''} \frac{RT}{F} \ln i - \frac{2}{\alpha' + \alpha''} \frac{RT}{F} \ln \frac{(2k_s i_0^{\alpha'})^{\alpha''}}{(2k_s i_0^{\alpha''})^{\alpha'}}, \quad (64)$$

$$\eta_p = (\alpha' - \alpha'') \eta_k + \frac{RT}{F} \ln \left(\frac{i_0^{\alpha'}}{i_0^{\alpha''}} \right). \quad (65)$$

The following points emerge from an examination and comparison of Eqns. (53)–(59) and (60)–(62).

1. On transition from small to large coverages with atomic hydrogen, the slope of the Tafel plot changes, being determined at small coverages by the value of α' , which refers to the discharge stage, at moderate coverages by the value of $(\alpha' + \alpha'')/2$, and at large coverages by the value of α'' , which refers to the electrochemical desorption stage. At low coverages the slope yields the exchange current $i_0^{\alpha'}$, referring to the discharge stage, and at large coverages it yields a current which depends on η_{pc} as well as on $i_0^{\alpha''}$ and $i_0^{\alpha'}$.

2. Like η_k , η_p varies linearly with $\ln i$; η_p , and consequently θ_H , increases when $\alpha' > \alpha''$ and decreases when $\alpha' < \alpha''$.

3. For any degree of coverage, η_p is linearly related to η_k , the coefficients of the equation remaining the same.

In conclusion we shall note that when the discharge stage is rapid, it follows from Eqns. (19) and (20) that always $\eta_p = \eta_k$ and consequently the evolution of hydrogen in this case follows the formulae referring to stages (II), (III), and the diffusional stage, in which η_p must be replaced by η_k .

Effect of Adsorbed Atomic Hydrogen on the Evolution of Hydrogen on Non-Uniform Surfaces

We shall show that the kinetic equations for the evolution of hydrogen on non-uniform surfaces, without any limitation to the variation in $\Delta\eta_p$, are fully consistent with the experimental data obtained by Frumkin and Aladzhalova in an investigation of hydrogen overvoltage on palladium in alkaline solutions. According to their findings, $\eta_k - \eta_p \gg RT/F$. From Eqns. (24), we obtain for this case the expression

$$\eta_k = \frac{RT}{\alpha' F} \ln \frac{i}{i_H^{\alpha'}} + \frac{\alpha_2'}{\alpha_1'} \eta_p. \quad (66)$$

From a comparison of Eqns. (66) and (53), it is readily seen that the former will be consistent with experiment when $\alpha_2' = \alpha_1'$. This assumption also explains the following fact observed by Frumkin and Aladzhalova. Palladium is permeable to hydrogen, the rate of diffusion being high, so that the chemical potentials and the rates of evolution of the adsorbed hydrogen on the polarised and diffusional sides of the electrode are the same. Consequently η_p^d and η_p^s must be equal, η_p^d being the value of η_p on the diffusional side and η_p^s its value on the polarised side. It was found experimentally that

$$\eta_p^d = \frac{\alpha_2'}{\alpha_1'} \eta_p^s = \frac{RT}{2F} \ln \left(\frac{i}{2i_0^{\alpha'}} + 1 \right). \quad (67)$$

This equation becomes $\eta_p^d = \eta_p^s$, provided that $\alpha_1' = \alpha_2'$. Experiment shows that in acid solutions $\eta_k - \eta_p$ is small compared with RT/F , so that the anodic processes can be neglected at all values of i . On substituting $\alpha_1' = \alpha_2' = 0.5$, found experimentally, in Eqns. (24) and (25) and solving the latter for η_k , we obtain

$$\eta_k = \frac{2RT}{F} \ln \left[\frac{i}{2i_H} + \sqrt{\left(\frac{i}{2i_H} \right)^2 + 1} \right] + \eta_p.$$

A relation of this type, involving the sum of η_p and a term depending on i , was obtained for η_k in the experiments of Frumkin and Aladzhalova. An analogous expression also follows from Eqns. (52) and (53) for $\alpha' = 0.5$.

We shall now assume that the evolution of hydrogen on a non-uniform surface comprises stages (I) and (III). It can be readily shown, by Eqns. (24) and (36), that when $\eta_k - \eta_p \gg RT/F$, then

$$\eta_k = \frac{\alpha_2' + \alpha_3''}{\alpha_1' \alpha_2' + \alpha_3' \alpha_1'} \frac{RT}{F} \ln \left[\frac{i}{(2i_H^{\alpha'})^{\alpha_1'/(\alpha_1' + \alpha_2')}} (2i_H^{\alpha''})^{\alpha_3''/(\alpha_3'' + \alpha_1'')} \right], \quad (68)$$

$$\eta_p = \frac{\alpha_1' - \alpha_1''}{\alpha_1' \alpha_2' + \alpha_3' \alpha_1'} \frac{RT}{F} \ln \left[\frac{i}{(2i_H^{\alpha'})^{\alpha_1'/(\alpha_1' - \alpha_1'')}} (2i_H^{\alpha''})^{-\alpha_1''/(\alpha_1' - \alpha_1'')} \right], \quad (69)$$

$$\eta_p = \frac{\alpha_1' - \alpha_1''}{\alpha_2' + \alpha_3'} \eta_k + \frac{RT}{(\alpha_2' + \alpha_3')} \ln \left[\frac{i_H^{\alpha'}}{i_H^{\alpha''}} \right]. \quad (70)$$

Eqns. (68)–(70) are fully analogous to Eqn. (46). It should be noted that in this case η_p increases with increase in i only when $\alpha_1' > \alpha_1''$.

A somewhat unexpected result is obtained when the exchange currents $i_H^{\alpha'}$ and $i_H^{\alpha''}$, defined by Eqns. (26) and (38), are substituted in Eqn. (68):

$$\eta_k = \frac{RT}{\alpha F} \ln i - \frac{RT}{F} \ln p^{1/2} - \frac{1-\alpha}{\alpha} \frac{RT}{F} \ln a_{H^+} + \text{const}, \quad (71)$$

where

$$\alpha = \frac{\alpha_1' \alpha_2'' + \alpha_2' \alpha_1''}{\alpha_2' + \alpha_2''}. \quad (72)$$

Formally, Eqn. (71) is identical with the expression for η_k in the slow-discharge stage on uniform metal surfaces when the degree of coverage with atomic hydrogen is zero. According to Eqn. (26), the exchange current for the discharge stage on non-uniform surfaces is proportional to the pressure of hydrogen raised to the power $(\alpha_1' - \alpha_2')/2$; Eqn. (71) shows that, for a two-stage mechanism, the exchange current depends on the hydrogen pressure raised to the power $\alpha/2$.

As in the case of uniform surfaces, when the discharge stage is rapid on non-uniform surfaces, always $\eta_k = \eta_p$ [see Eqns. (24) and (25)].

In conclusion the author wishes to express his profound gratitude to Prof. A.N. Frumkin for valuable advice and detailed discussion of this work.

SUMMARY

1. A new form of kinetic equations for the evolution of hydrogen on uniform and non-uniform surfaces, reflecting the effect of adsorbed hydrogen on this process for all known principal mechanisms of the evolution of hydrogen, has been given [Eqns. (18)–(20) and (21)–(38)].
2. On markedly non-uniform surfaces, the kinetics are identical regardless of the type of the adsorption isotherm for atomic hydrogen.
3. Evolution of hydrogen is retarded by adsorbed hydrogen to the greatest extent on uniform surfaces, when recombination is the slow stage. A limiting current may occur. In the remaining cases only an increase in the Tafel plot is possible, without, however, the attainment of values characteristic of a limiting current.
4. At large overvoltages, during evolution of hydrogen on uniform and non-uniform surfaces by the electrochemical desorption mechanism, the change in the amount of adsorbed hydrogen with increase in the polarising current density depends on the relation between α' and α'' , where α' refers to the discharge stage and α'' to the electrochemical desorption stage. When $\alpha' > \alpha''$, the amount of adsorbed hydrogen increases.
5. At large overvoltages on uniform and non-uniform surfaces the relation between the hydrogen overvoltage and the chemical potential of the adsorbed atomic hydrogen is linear for all mechanisms.

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Received 30th May 1960

INVESTIGATION OF THE MECHANISM OF THE OXIDATION OF MERCAPTOACETIC ACID USING SULPHUR-35. I. ROLE OF SULPHIDE IN THE OXIDATION

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The mechanism of the oxidation of thiocarboxylic acids by molecular oxygen has interested research workers for a long time. Study of the kinetics of the oxidation of mercaptoacetic acid at various pH values under aerobic and anaerobic conditions has established that the first intermediate oxidation product, dithiodiacetic acid, catalyses the reaction¹. The mechanism of the initiation of oxidation was first investigated in Refs. 2–7, in which the process was shown to consist in dehydrogenation of mercaptoacetic acid, and the suggestion was made that, apart from the disulphide, hydrogen peroxide is formed, and oxidises the mercapto-group. The presence of hydrogen peroxide in the solution is actually observed^{8,9} but this is not a direct proof, since it can also be formed in secondary reactions, from organic peroxides.

The disulphide first formed can undergo further change at higher pH values. Different views have been put forward concerning the mechanism of this reaction. It has been suggested that the primary act is hydrolysis of the dithiodiacetic acid with formation of sulphenic and mercaptoacetic acids^{10–12}. Since the sulphenic acid is very unstable, it reacts with oxygen and is converted to sulphinic acid. In the opinion of some workers it disproportionates into mercaptoacetic and sulphinic acids. According to Schöberl¹³, disproportionation takes place in a different way: oxalic acid and inorganic sulphide (both isolated from the reaction mixture) are formed in addition to the mercaptoacetic acid. Study of the hydrolysis of dithio-compounds, using models of different structures, reveals that hydrogen sulphide may be split off from the thiol which is formed, and even precipitation of sulphur may ensue¹⁴. In the presence of organic oxidants, one or two oxygen atoms are added to the –S–S– bond of the dithio-compound, after which hydrolysis yields a thiol and a sulphenic acid^{15,16}. The sulphenic acid is probably stabilised by the elimination of hydrogen sulphide.

Thus previous work has been concerned with the dehydrogenation of mercaptoacetic acid and the further changes undergone by dithiodiacetic acid. Only the formation of inorganic sulphide during the oxidation has been demonstrated. Until recently the mechanism of the formation and oxidation of sulphide had not been established, nor in general the role of the sulphur compounds which are formed.

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