KINETICS OF IONIZATION OF MOLECULAR HYDROGEN ON PLATINUM ELECTRODES

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The ionization of molecular hydrogen on a platinum electrode is of considerable interest. Yet, in studying its mechanism one encounters many difficulties, particularly in the case of smooth electrodes. Thus, the high sensitivity of a platinum surface to the experimental conditions (preliminary treatment of the electrode, purity of solutions, etc.) interfere considerably with the reproducibility of experimental data. On top of that, the ionization of hydrogen on platinum proceeds very rapidly. Therefore, under ordinary conditions of polarization and mixing, the rate of the over-all process is limited by the diffusion of hydrogen towards the electrode surface. Consequently, the large number of works completed [1-20] still has not provided any unequivocal results with regards to the mechanism of this reaction.

In this work we have investigated the kinetics of hydrogen ionization on a rotating Pt-disc electrode in various solutions, by recording its polarization curves. The solutions used in this work contained high concentrations of hydrogen (or OH^-) ions, considerably in excess of the dissolved H_2 concentration; therefore, we could disregard any changes in the hydrogen-ion concentration in the layer adjacent to the electrode, which might have been caused by the flow of current. We chose a rotating disc electrode since some of its properties [21] made it most convenient to investigate the transition from the diffusion to the kinetic range. Some of the results obtained had already been published [16].

EXPERIMENTAL

A schematic representation of the apparatus is shown in Fig. 1. Polarization of the investigated electrode 1 was carried out in the central part of the electrolytic cell with the help of two supporting electrodes 2 made of platinized platinum. Before being placed into the cell the electrolyte in vessel 4 was saturated with hydrogen and carefully purified through adsorption on a platinized Pt-net. A hydrogen electrode in the same electrolyte 3 was used for reference. The elctrode was rotated by means of an arrangement whose construction, due to the small dimensions of the rotating components of the microseal 9, made it possible to achieve high rates of rotation (up to 20,000 rpm) without disturbing the air-tight system. The shaft was driven by a 200 W"Synchronous"electric motor. The investigated electrode consisted of a platinum disc attached to the tip of a nickel shaft and fused to a glass tube in such a way that only the lower surface of the Pt-disc was exposed to the solution. The investigated geometrical area was 0.196 cm^2. According to the data obtained from charge curves,the virtual surface of the platinized electrode exceeded the visible one by 25-30 times.

In order to achieve reproducible results we alternately subjected the electrode to anodic and cathodic polarization in a carefully purified 1 N H_2SO_4 solution saturated with hydrogen. The pure solutions were prepared in the way described in [16].

As was already pointed out in [16], with increased rotational velocity the ionization of hydrogen on a smooth Pt-electrode approached a certain limiting value. In order to attain this limit we measured the polarization curves for the ionization of molecular hydrogen on a smooth Pt-electrode at high rotational velocities (in the range from4,000 to 20,000 rpm) in 1 N H_2SO_4, 1 N HCl, 1 N HBr, and 1 N KI + 0.1 N HCl solutions. Such curves obtained in 1 N H_2SO_4 are shown in Fig. 2. In the cases of 1 N HCl,1 N HBr, and 1 N KI + 0.1 N HCl the curves looked about the same. The maximum current density in H_2SO_4 was 3.85 ma/cm^2, HCl 2.18 ma/cm^2,

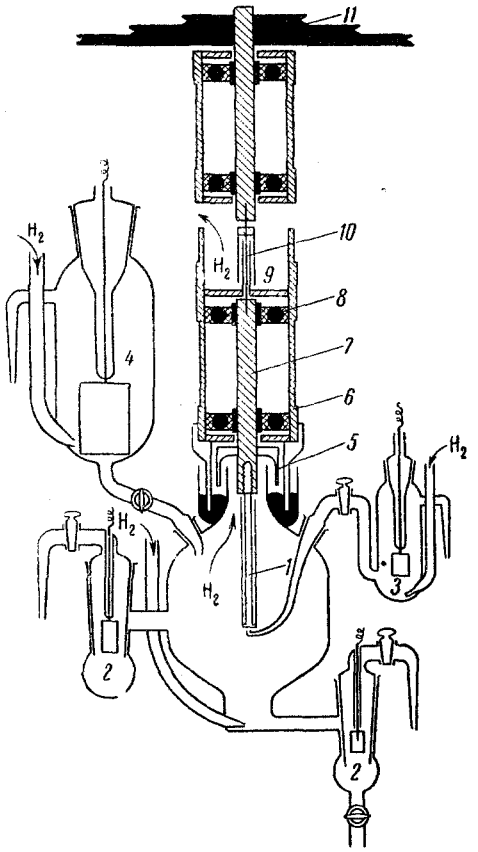

Fig. 1. Polarization apparatus. 1) Rotating platinum-disc electrode; 2) supporting electrode; 3) reference electrode; 4) vessel used to purify the investigated solutions and saturate them with hydrogen; 5) attached mercury seal; 6) metal cylinder; 7) brass shaft; 8) ball bearing; 9) liquid microseal; 10) steel pin; 11) pulley.

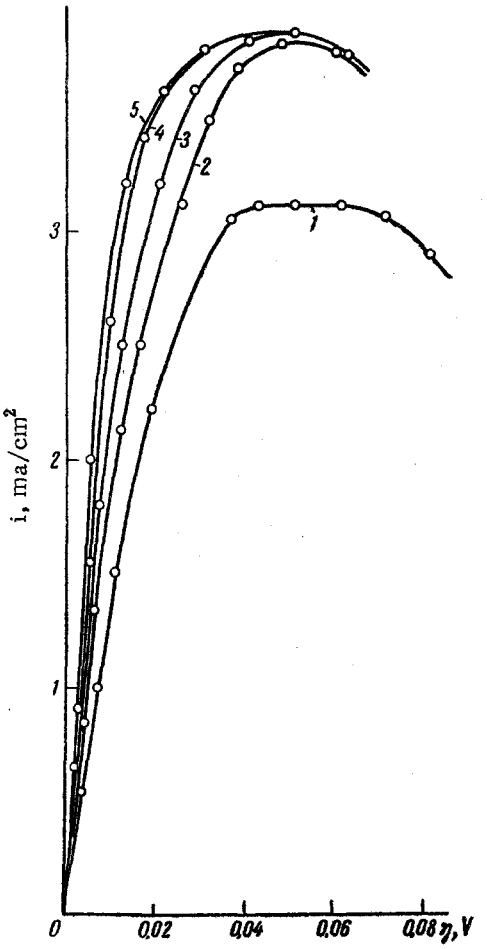

Fig. 2. Ionization curves of molecular hydrogen on a smooth Pt-electrode in 1 N H_2SO_4.
1) At 2,400 rpm; 2) 8,000 rpm; 3) 10,000 rpm; 4) 15,000 rpm; 5) 20,000 rpm.

HBr 1.56 ma /cm², and in 1 N KI + 0.1 N HCl 0.48 ma /cm². The maximum current at high rotational velocities was attained at $\eta \sim 45$ mV. At η = = 45 ± 5 mV in the case of 1 N H_2SO_4 and 1 N HCl the current remained constant (± 1%) for 15-20 min. In the case of 1 N HBr during the same time interval we observed a decrease approaching 8%. To obtain reproducible results we measured the curves at approximately constant rate of impressing the voltage (20-25 mV/min).

If we let the ordinate denote the currents corresponding to various electrode rotational velocities at η = 45 mV and the abcissa, the square root of the number of electrode revolutions per second ($m^{1/2}$), then on a smooth platinum electrode in 1 N H_2SO_4, 1 N HCl, and 1 N HBr, we will obtain the curves shown in Fig. 3.

As may be seen in Fig. 3, at low electrode rotational velocities the graph of i vs $m^{1/2}$ is a straight line; such a functional dependence is characteristic of processes whose kinetics are determined by the rate at which the reagents diffuse towards the electrode surface [21]. At high revolutions the current density is independent of the number of revolutions, but depends on the kinetics of the process itself. Graphically this is represented by a straight line parallel to the abcissa.

When the (i, η) curves were determined on the platinized electrode in solutions of sulfuric and hydrobromic acids, it turned out that the behavior of the platinized Pt-electrode with respect to hydrogen ionization was very similar to that of the smooth one. However, one required very high revolutions (15,000-20,000 rpm) in order to

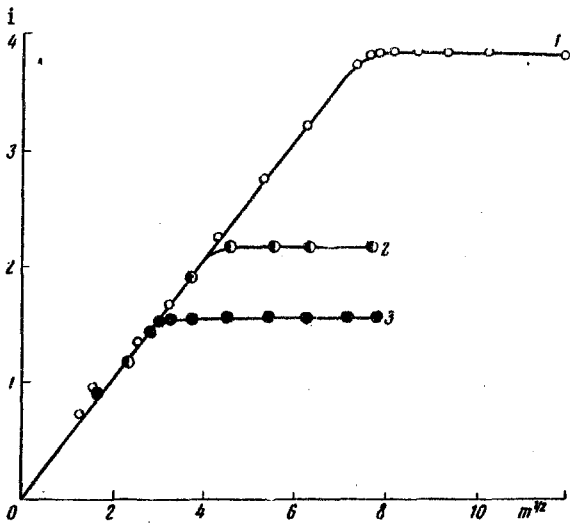

Fig. 3. Maximum current (η = 45 mV) as a function of the no. of electrode revolutions.
1) 1 N H_2SO_4; 2) 1 N HCl; 3) 1 N HBr (m = number of revolutions per second).

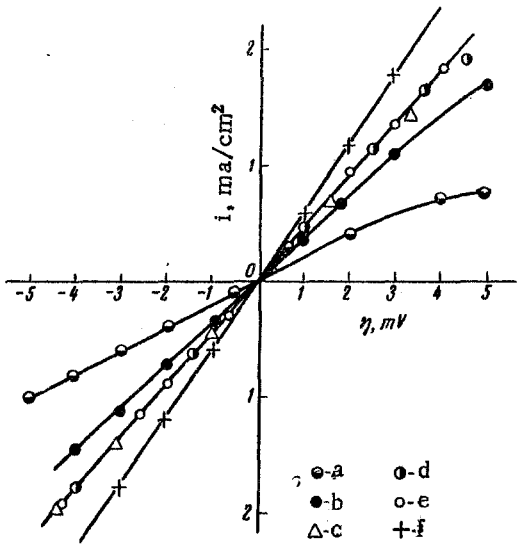

Fig. 4. Molecular hydrogen ionization curves at an electrode rotational velocity of 20,000 rpm.
a) 1 N HBr, voltage impressed at the rate of 25-30 mV/min; b) 1 N HCl, 25-30 mV/min; c) 1 N HBr, 150-200 mV/min; d) 1 N HCl, 150-200 mV/min; e) 1 N H_2SO_4, 25-30 mV/min; f) 1 N H_2SO_4, 25-30 mV/min. Curves a, b, c, d, and e are on a smooth electrode, f on a platinized electrode.

TABLE

1 N solution	Rate of impressing the voltage, in mV/min	R_η
HBr	25-30	5.2
HBr	150-200	2.2
HCl	25-30	2.8
HCl	150-200	2.2
H_2SO_4	25-30	2.2
H_2SO_4	150-200	2.2
NaOH	25-30	59

attain the kinetic limit on the platinized Pt-electrode in sulfuric acid. In the case of HBr the transition from the smooth to the platinized electrode increased the maximum kinetic current. The (i, η) hydrogen-ionization curves and hydrogen-ion-discharge curves on a smooth electrode at 20,000 rpm and at low overvoltages are shown in Fig. 4. In the same figure we have plotted the (i, η) ionization and discharge curves on a platinized Pt-electrode in sulfuric acid at low overvoltages and at the same number of electrode revolutions.

Comparing the curves obtained in 1 N H_2SO_4 on a smooth electrode with the ones on a platinized Pt-electrode, we can see that the hydrogen-ionization rate on the smooth electrode attains, or at least approaches, the kinetic limit, and although the rate of hydrogen transfer to both electrodes is the same, the rate of the over-all process on the smooth electrode is much slower. In the same Figure we can also see that on the smooth electrode the slopes of the HBr and HCl curves partly depend on the rate at which the voltage is impressed. This indicates that after activation the state of the electrode surface changes with time at a rate which depends on the composition of the solution.

From Fig. 4 it is also evident that at low potentials the (i, η) function can be expressed by a straight line. For the sake of comparison it is convenient in this case to use the relationship $\eta/i = R_\eta$, which can be used as the specific rate at potentials close to the reversible hydrogen-electrode potential. In the table we have compared the R_η values in various solutions which were calculated from our measurements on an activated smooth electrode. It is clear that at low polarizations the difference in the nature of the anion shows up in the magnitude of R_η only under conditions where the rate at which voltage is impressed is not too large.

DISCUSSION OF EXPERIMENTAL RESULTS

The high rotational velocities of the electrode enabled us to attain a limit at which the rate of the over-all process was determined by some kinetic step. A comparison between these data and the data on the adsorption of anions on platinum, obtained by Frumkin, Shlygin, and Ershler [22-25], leads to the conclusion that the more the anion is adsorbed, the sooner occurs the kinetic retardation of the process. Wicke and Weblus [14] have already noted that the adsorption of anions on platinum retards the ionization of hydrogen. The transition from the diffusion to the kinetic range takes place in a narrow interval of $m^{1/2}$. Such a sharp transition indicates that the order of reaction is determined by the hydrogen, and is close to zero.

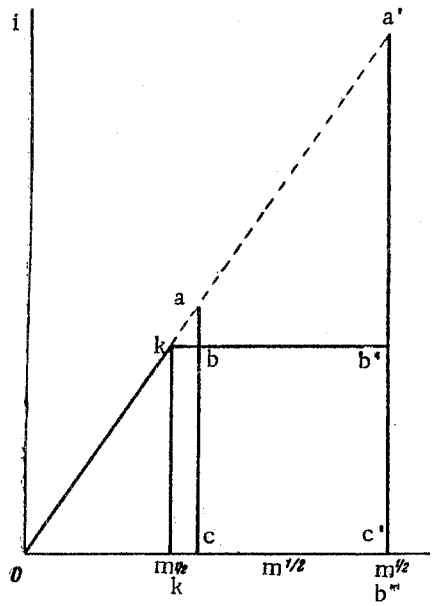

Fig. 5. Diagram illustrating the dependence of i on $m^{1/2}$

Figure 5 gives a schematic representation of the (i, $m^{1/2}$) function at $\eta = 45 \pm 5$ mV. This function is represented by the broken line okb'. As was already mentioned, the ok section corresponds to the diffusion range, while the kb' to the kinetic. It is obvious that in the absence of kinetic limitations the (i, $m^{1/2}$) functions in the rotational velocity range from $m_k^{1/2}$ to $m_b^{1/2}$ would be represented by the dotted line k_a'. In Fig. 5 it may be seen that in the kinetic range the ratio ab/bc increases with increase in $m^{1/2}$. The meaning of this relationship becomes clear if the equation representing the density of the current flowing through the rotating disc electrode [21]

$$i = Am^{1/2}([H_2]_0 - [H_2]_s) = i_d\left(1 - \frac{[H_2]_s}{[H_2]_0}\right) \quad (1)$$

is rewritten in the form

$$\frac{[H_2]_s}{[H_2]_0} = \frac{i_d - i}{i_d},$$

where A = a constant; $[H_2]_0$ = concentration of the dissolved H_2 sufficiently far from the electrode; $[H_2]_s$ = concentration of the dissolved H_2 in a layer adjacent to the electrode; i_d = density of the limiting diffusion current.

It may be seen from Fig. 5 that

$$\frac{[H_2]_s}{[H_2]_0} = \frac{i_d - i}{i_d} = \frac{ac - bc}{ac} = \frac{ab}{ac}.$$

It is evident from this relationship that to each increase in the ab/ac ratio (with increase in $m^{1/2}$ there corresponds an increase in $[H_2]_s\,[H_2]_0^{-1}$, and since the value of $[H_2]_0$ remains constant during the experiment then the increase in the ratio must be due to increased $[H_2]_s$.

Thus, at higher electrode revolutions the current density remains constant in the kinetic region, whereas the hydrogen concentration near the electrode surface ($[H_2]_s$) increases and at $m \to \infty$ it approaches $[H_2]_0$. It is obvious that such a regularity corresponds to a zero-order reaction with respect to H_2.

Let us analyze more carefully the shape of curves which express the (i, $m^{1/2}$) function. If $m^{1/2}$) is small and an insignificant current is flowing through the electrode, i.e., small compared to the exchange current between H_2 and H^+ ions in solution, then $[H_2]_s$ will approach its equilibrium value, in other words $[H_2]_s\,[H]_0^{-1} \sim e^{-(2F\eta/RT)}$. Under such conditions polarization is purely concentration dependent. Using equation (1) we can write the equation

$$i = Am^{1/2}[H_2]_0\left(1 - e^{-\frac{2F\eta}{RT}}\right). \quad (2)$$

At sufficiently low $m^{1/2}$ we can determine i from the value of η by using Equation (2); the computed results

are in good agreement with the experimental data [16]. Equation (2) is in practice applicable only as long as the rate at which H_2 is converted to hydrogen ions is sufficiently large, i.e., at not too large values of η, since at very small values of m Equation (1) ceases to apply.

Now we will try to find the full dependence of i on $m^{1/2}$, since such a function might be needed in the various assumptions concerning the mechansim of this reaction. At first we will assume that η is quite large, so that in the slowest step we can neglect the rate of the reverse (cathode) reaction in comparison with the rate of the direct one (anode).

1) First we will analyze the case where the transition from the molecular to adsorbed atomic hydrogen is the slowest step. On the assumption that the surface is uniform and not extensively covered, the reaction rate (in this case determined by the H_2-absorption rate) should be equal to $K_1 [H_2]_s$.

The conditions of a step-wise reaction demand that

$$i = Am^{1/2}\{[H_2]_0 - [H_2]_s\} = K_1 [H_2]_s \tag{3}$$

By eliminating $[H_2]_s$ in Equation (3) we will get

$$[H_2]^s = [H_2]_0 \frac{1}{1 + \frac{i_a}{i_d}}; \quad i = i_a \frac{1}{1 + \frac{i_a}{i_d}}, \tag{4}$$

where i_a = "limiting adsorption current," equal to $K_1 [H_2]_0$.

From Equation (4) it follows that: at $i_d \ll i_a$, $i = i_d$, and $[H_2]_s/[H_2]_0 \to 0$; at $i_d \gg i_a$, $i = i_a$, and $[H_2]_s \sim [H_2]_0$.

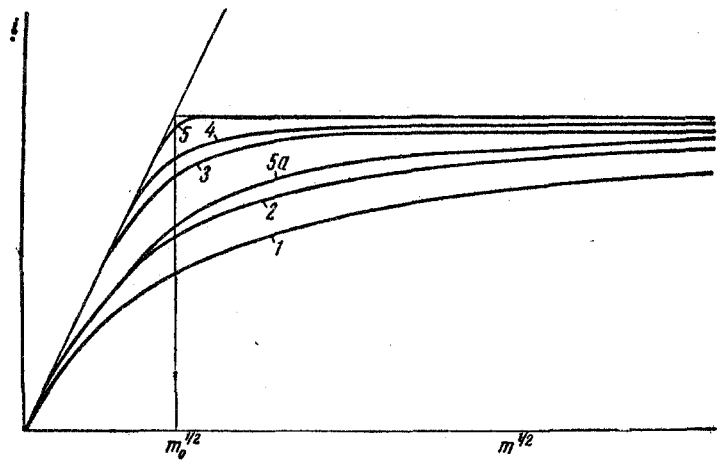

Fig. 6. Theoretical (i, $m^{1/2}$ curves calculated for different reaction schemes.

In order to construct the (i, $m^{1/2}$) function it is convenient to introduce the number m_0; for all the curves in Fig. 6 m_0 is the value of m at which the limiting diffusion current $i_d = Am^{1/2}[H_2]_0$ becomes equal to the limiting kinetic current. For the given special case

$$Am_0^{1/2}[H_2]_0 = i_a.$$

Equation (4) can now be transformed into

$$i = \frac{i_a}{1 + \frac{m_0^{1/2}}{m^{1/2}}} \tag{4a}$$

or

$$\frac{i_a}{i} = 1 + \frac{m_0^{1/2}}{m^{1/2}}. \tag{4b}$$

The (i, $m^{1/2}$) function, expressed by Eq. (4a), is represented by the curve 1 in Fig. 6.

As may be seen on curve 1, the transition from the diffusion range ($i \sim i_d$) to the kinetic ($i \sim i_a$) proceeds very smoothly.

2) Let us now analyze the dependence which is related to the theory of delayed discharge, i.e., ionization under the conditions of a sparsely covered uniform surface and the assumption that there is an equilibrium between the adsorbed atomic and the dissolved molecular hydrogen. It is obvious that with these assumptions the ionization rate for a given η is equal to $K' [H_2]_s^{1/2}$ where K' is a constant, and consequently

$$i = Am^{1/2}\{[H_2]_0 - [H_2]_s\} = K' [H_2]_s^{1/2}, \tag{5}$$

whence

$$i = i_u\left(\sqrt{\frac{i_u^2}{4i_d^2} + 1} - \frac{i_u}{2i_d}\right); \tag{6}$$

here $i_u = K' [H_2]_0^{1/2}$ the limiting "ionization current" of the adsorbed hydrogen. By denoting (as was mentioned before) the value of m at which $i_d = i_u$ by the number m_0, we can use Equation (6) to plot curve 2 (Fig. 6); this curve represents the equation

$$i = i_u\left(\sqrt{\frac{m_0}{4m} + 1} - \frac{m_0^{1/2}}{2m^{1/2}}\right). \tag{7}$$

In constructing curve 2, as well as all the others in Fig. 6, we chose the ordinate scale in such a way that the limiting kinetic current would coincide with the limiting kinetic current on curve 1. In this case the transition from the diffusion to the kinetic range occurs over a somewhat narrower interval of m, narrower than the one analyzed before, but far from the sharp change observed experimentally.

3) Temkin [26, 27] derived several equations based on the ideas of a nonuniform surface with the nonuniformity represented by a logarithmic isotherm; if we use these equations and assume that there is an adsorption equilibrium between H_2 and the H adsorbed on the surface, while the reaction rate is determined by the ionization rate of H atoms, then we will get somewhat better results. With moderately covered surfaces and an overvoltage η the ionization rate will in this case be expressed by the function $K \exp(\beta F/RT)(\eta - \eta_\theta)$, where η_θ = equilibrium potential, corresponding to a covering θ, and β = a constant whose value lies between 0 and 1.

Thus,

$$i = Am^{1/2}([H_2]_0 - [H_2]_s) = K \exp\frac{\beta F}{RT}(\eta - \eta_\theta). \tag{8}$$

And since with the above-made assumptions

$$\eta_\theta = -\frac{RT}{2F}\ln [H_2]_s + \text{const},$$

then it follows from Equation (8) that

$$i = Am^{1/2}([H_2]_0 - [H_2]_s) = K' [H_2]_s^{\beta/2} \tag{9}$$

Equation (9) is a generalized form of Eq. (3) and (5); to solve this equation it is convenient to introduce a new variable $\Phi = [H_2]_s^{\beta/2} [H_2]_0^{-\beta/2}$, then

$$i = K' [H_2]_0^{\beta/2}\Phi = i_u\Phi; \tag{10a}$$

$$m^{1/2} = \frac{i_u\Phi}{A[H_2]_0(1 - \Phi^{2/\beta})} = m_0^{1/2}\frac{\Phi}{1 - \Phi^{2/\beta}} \tag{10b}$$

Here i = limiting "ionization current" equal to $K'[H_2]_0$, and m_0 = the value of m at which the limiting diffusion current $A[H_2]_0 m^{1/2}$ becomes equal to i_u. By varying Φ from 0 to 1 it is easy to construct a curve of i vs $m^{1/2}$ from Equations (10a) and (10b). Curve 3 in Fig. 6 corresponds to $\beta = 0.25$ or $2/\beta = 8$. As is evident, in this case the transition from the diffusion to the kinetic range is also much smoother than in the experiment.

4) The most satisfactory results can be obtained if one assumes that the kinetic stage of the reaction is preceded by the establishment of an equilibrium between the H_2 in solution and the adsorbed hydrogen, with the surface almost completely covered; the kinetic stage may involve the ionization itself or a surface diffusion towards centers on which the ionization occurs. A hypothesis very similar to this one has already been proposed by V. A. Roiter and E. S. Poluyan [7].

We know from charge curves that at atmospheric pressure the area of a Pt-electrode covered by hydrogen does not have the limiting value*. One may assume that the H_2-adsorption rate is large enough only on a portion of the surface, so that under the experimental conditions the remainder does not participate in the reaction due to the low rate of H_2 adsorption; but on the portion that we selected here the exchange between the gaseous phase and the adsorbed atoms proceeds so rapidly that the adsorption equilibrium is preserved and the rate of the over-all process must depend on some subsequent stage. Finally, let us assume that within the limits of this "activated" area all the zones are equivalent with respect to the adsorption energy as well as the rate of the above-mentioned subsequent stage. If we have sufficient anodic polarization and the rate of H^+ discharge can be neglected, the above-mentioned assumptions will give us

$$i = Am^{1/2}\{[H_2]_0 - [H]_s\} = K'\theta = \frac{K'K[H_2]_s^{1/2}}{1 + K[H_2]_s^{1/2}}, \tag{11}$$

where K' = rate constant for the kinetic stage, θ = fraction of the activated area covered up.

From this, if we denote $[H_2]_s^{1/2}[H_2]_0^{1/2}$ by Φ, we will get

$$i = \frac{i_u(1+\gamma)\Phi}{1+\gamma\Phi}, \tag{12}$$

$$m^{1/2} = \frac{1}{A[H_2]_0}\frac{i}{1-\Phi^2} = \frac{m_0^{1/2}}{i_u}\frac{i}{1-\Phi^2}, \tag{12a}$$

where

$$i_u = \frac{K'K[H_2]_0^{1/2}}{1+K[H_2]_0^{1/2}}, \quad \gamma = K[H_2]_0^{1/2}, \quad Am_0^{1/2}[H_2]_0 = i_u.$$

Curve 4 (Fig. 6) was computed from Equation (12) and (12a), by assuming that $\gamma = 10$ and treating Φ as an independent variable which may have any value between 0 and 1.

The choice of a large γ means that when $[H_2]_s = [H_2]_0$ the fraction of area covered is close to 1; for example, at $\gamma = 10$ the limiting area covered is 10/11. Curve 4 (Fig. 6) gives a much sharper transition than did the previous curves; at large γ the transition can be made even more abrupt. Thus at $\gamma = 100$ we get curve 5 (Fig. 6). As one may see from this curve Equations (12) and (12a) could represent the experimental data quite satisfactorily.

Thus the existence of an abrupt transition from the diffusion to the kinetic range at high η can be explained by assuming that the reaction rate is proportional to the fraction of the "activated" area covered and that the adsorption rate on the remaining area can be neglected. Moreover, the "activated" area can be treated in accordance with Langmuir's kinetics by assuming that the fraction covered, θ, is close to 1. Uniform-surface equations give somewhat poorer results. The action of anions can be explained by the fact that the anion adsorption reduces the size of the "activated" surface by lowering the Pt − H bond energy and the H_2-adsorption rate. Consequently the adsorption of anions decreases the over-all molecular-hydrogen ionization rate, although in the case of Br^- it does not reduce but somewhat enhances the ionization rate of adsorbed H_2 [8].

All the calculations made so far were on the assumption that the rate of cathodic reaction can be neglected by comparison with that at the anode. However, if η is not too large in comparison with RT/2F, the cathodic reaction must be taken into account. One can easily verify that it results in a smoother transition from the diffu-

* According to the data of Knorr and co-workers [28] it is quite close to the limiting value.

sion into the kinetic range. Let us now examine from this point of view the mechanism proposed in section 4, which for $\gamma = 10$ and a completely irreversible total reaction gave curve 4 (Fig. 6). In order to take the cathodic reaction into account we have to replace the right side of Equation (11) with $K'K[H_2]_S^{1/2} - K''(1 + K[H_2]_S^{1/2})$. In place of Equation (12) we will now get

$$i = \frac{i_u (1+\gamma)(\Phi - \Phi_r)}{(1+\gamma\Phi)(1-\Phi_r)}, \tag{13}$$

where $\Phi_r = K''/KK' \cdot 1/[H_2]_0^{1/2}$ is the equilibrium value of Φ, i.e., the value of $[H_2]_S^{1/2}\,[H_2]_0^{1/2}$ corresponding to $i = 0$, while the remaining letters have their previous meaning. Equation (12a) obviously retains its form. By varying Φ from Φ_r to 1 in Equation (13) and (12a), we can construct a curve of $\underline{i}$ vs $m^{1/2}$ By taking (same as before) $\gamma = 10$ and $\Phi_r = 10^{-1}/_2$, which corresponds to $\eta = 29$ mV, in place of Curve 4 we will get the Curve 5a (Fig. 6), one with a considerably smoother translation.

At sufficiently low values of η, where $[H_2]_{S,r}$ (the equilibrium value of $[H_2]_S$) differs only slightly from $[H_2]_0$ and consequently from $[H_2]_S$, the $(i, m^{1/2})$ function should fulfill Equation (4a), which would prevent $\underline{i}$ from attaining its limiting value when $m^{1/2}$ is increased*. As we have previously shown, this conclusion (independent of any assumptions about the reaction mechanism) agrees well with the experimental results [16].

The limiting value of $\underline{i}$ at small η can be determined by extrapolating the experimental data to $m^{1/2} \to \infty$. The easiest way to do such an extrapolation is by plotting $1/i$ vs $1/m^{1/2}$. The linear relationship between these two numbers (just as Equation (4b) would demand) indicates the applicability of Equation (4a).

In Fig. 7 we have plotted such graphs for the anodic potentials of: 2.5, 5, 10, 15, 20, and 30 mV. It is apparent from Fig. 7 that at 2.5, 5, and 10 mV the points which correspond to 8000, 10,000 and 20000 rpm lie far below the extrapolated line. Such a deviation can be explained by assuming that at the indicated potentials and electrode revolutions the reaction proceeds in the diffusion range, while beginning with 8000 rpm the fluid flow looses its strictly laminary nature. As is well known, a transition to conditions of turbulent mixing is accompanied by increased current density [13, 21]. Extrapolation was carried out from points which corresponded to rotational velocities not in excess of 6000 rpm. For potentials equal to 20 and 30 mV and at high revolutions the deviations from the line passing through the points at low revolutions have the opposite sign and are related to the deviations of the $(i, m^{1/2})$ function from Equation (4a) at high η values. As is apparent from the graph, this deviation was taken into consideration in the extrapolation.

From the data obtained by extrapolation we constructed the kinetic curve of $\underline{i}$ vs η shown in Fig. 8. As may be seen in Fig. 8, in the interval from -10 to + 10 mV, the (i, η) function of the over-all reaction of hydrogen discharge and ionization on smooth platinum (in the absence of concentration polarization) is a straight line with the slope $R^*\eta = 1.8$. Comparing the value of $R^*\eta$ with the ohmic component of resistance $r = 0.2$ (measured

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* Actually, let $f([H_2])_S$ represent the reaction rate as a function of $[H_2]_S$. By definition $f([H_2])_{S,r} = 0$, and consequently

$$f([H_2]_s) = \{[H_2]_s - [H_2]_{s,r}\} f'([H_2]_{s,r}) = B\{[H_2]_s - [H_2]_{s,r}\},$$

where B is constant for any given η. From this

$$i = Am^{1/2}\{[H_2]_0 - [H_2]_s\} = B\{[H_2]_s - [H_2]_{s,r}\} \tag{14}$$

By eliminating $[H_2]_S$ from equation (14) we get

$$i = \frac{ABm^{1/2}}{Am^{1/2} + B}\{[H_2]_0 - [H_2]_{s,r}\} = i_k \frac{1}{1 + \frac{m_0^{1/2}}{m^{1/2}}}, \tag{15}$$

where i_k is the limiting kinetic current $B\{[H_2]_0 - [H_2]_{S,r}\}$, and $m_0 = B/A$, i.e., the value of $\underline{m}$ at which the limiting diffusion current $Am^{1/2}\{[H_2]_0 - [H_2]_{S,r}\}$ becomes equal to i_k. Equation (15) has a form similar to Equation (4a), which gave Curve 1 (Fig. 6).

by the alternating-current method [8, 9]*) we find that $R*\eta$ exceeds r by approximately one order of magnitude. This means that at potentials close to the equilibrium value the over-all rate of ionization and discharge of the molecular hydrogen is lower by one order of magnitude than the separate ionization and discharge rates of the adsorbed atomic hydrogen.

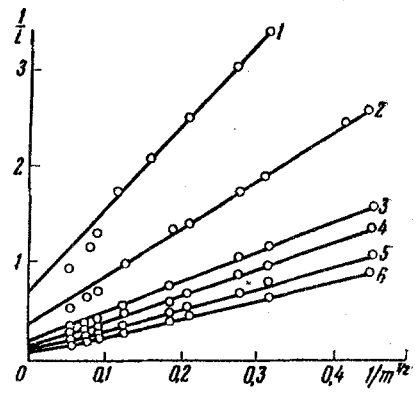

Fig. 7. 1/i as a function of $1/m^{1/2}$ on a smooth Pt-electrode in 1 N H_2SO_4 for η equal to:
1) 2.5 mV; 2) 5 mV; 3) 10 mV; 4) 15 mV; 5) 20 mV; 6) 30 mV (m is the number of revolutions per second).

Such a conflict with the assumption that the ionization of hydrogen on the "activated" portion of the platinum surface is the slow stage does not per se refute this assumption. It can be explained by the fact that the current density, as determined from the relation between the measured current and the visible electrode surface, is always smaller than the current density on the "activated" portion of the electrode. With alternating current measurements, however, the reactivity of adsorbed hydrogen is determined on the whole electrode surface. As was already pointed out a while back, the adsorption may possibly be followed by another slow stage (such as surface diffusion), which would also account for the discrepancy between the over-all rate of molecular hydrogen ionization and the rate of the step involving the ionization of the adsorbed atomic hydrogen.

SUMMARY

1) We have investigated the relationship between the density of hydrogen-ionization current on rotating smooth or platinized Pt-disc electrodes and the overvoltage in: 1 N H_2SO_4, 1 N NaOH, 1 N HBr, and 1 N KI + 0.1 N HCl solutions, in the rotational-velocity range from 120 to 20,000 rpm. High electrode revolutions made it possible to get limiting diffusions and attain the limit at which the hydrogen-ionization rate was determined by the kinetic stage of reaction.

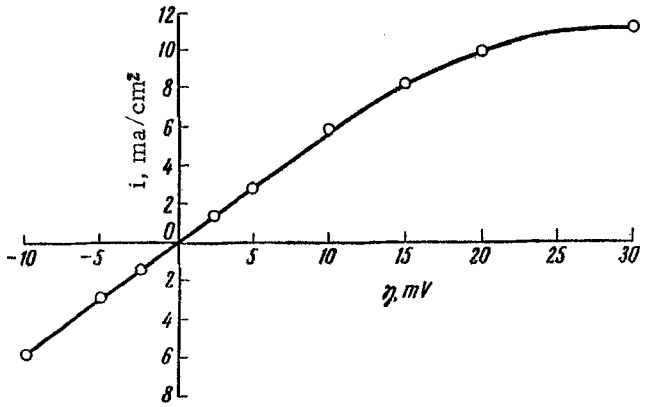

Fig. 8. Kinetic i vs η curve for the ionization of H_2 and discharge of the H^+ ion on a smooth Pt electrode in 1 N H_2SO_4 (constructed from extrapolated data).

2) The reaction was kinetically retarded at lower potentials and the retardation was the more pronounced the higher the anionic adsorbability and the lower the rate of impressing the voltage.

3) At sufficiently positive potentials the transition from the diffusion to the kinetic range occurred over a narrow interval of electrode revolutions (per second), which indicated that the order of the reaction with respect to hydrogen was close to zero.

*Knorr and co-workers [28] give an even smaller value, $r = 3 \cdot 10^{-2}$ in 8 N H_2SO_4.

4) The combined experimental results can be explained by assuming that only an "activated" portion of the surface, where the H_2-adsorption rate becomes large enough, participates in the electrochemical reaction. The "activated" portion of the surface attains an adsorption equilibrium with the molecular hydrogen which corresponds to an appreciably covered surface while the rate of the over-all reaction is determined by the rate of some stage which follows the adsorption; it could, for example, be the ionization of the adsorbed hydrogen or the surface diffusion of atoms from adsorption to ionization centers. Adsorption of anions decreases the size of the "activated" surface.

LITERATURE CITED

[1] O. Sackur, Z. Phys. Chem. 54, 647 (1906).

[2] F. Weigert, Z. Phys. Chem. 60, 513 (1907).

[3] K. Bennewitz, Z. Phys. Chem. 72, 202 (1910).

[4] L. Hammett, J. Amer. Chem. Soc. 46, 7 (1924).

[5] M. Thalinger and M. Volmer, Z. Phys. Chem. (A) 150, 401 (1930).

[6] M. Volmer and H. Wick, Z. Phys. Chem. 172, 429 (1935).

[7] V. A. Roiter and E. S. Poluyan, J. Phys. Chem. 7, 775 (1936).

[8] P. I. Dolin and B. V. Érshler, J. Phys. Chem. 14, 886 (1940).

[9] P. I. Dolin, B. V. Érshler, and A. N. Frumkin, J. Phys. Chem. 14, 907 (1940); Acta Phys. Chim. URSS 13, 779 (1940).

[10] A. N. Frumkin, P. I. Dolin, and B. V. Érshler, J. Phys. Chem. 14, 916 (1940); Acta Phys. Chim. URSS 13, 793 (1940).

[11] J. Horiuti and Ikusima, Proc. Imp. Acad. Tokyo 15, 39 (1939).

[12] N. T. Permitina and A. I.Shlygin, Bull. Acad. Sci. KazSSR, Chem. Ser. 53 (1951).

[13] É. A. Aikazyan and A. I. Fedorova, Proc. Acad. Sci. USSR 86, 1137 (1952).

[14] E. Wicke and B. Weblus, Z. Elektrochem. 56, 169 (1952).

[15] M. Breiter and R. Clamroth, Z. Elektrochem. 58, 493 (1954).

[16] A. N. Frumkin and É. A. Aikazyan, Proc. Acad. Sci. USSR 100, 315 (1955).

[17] M. Breier, C. Knorr, and R. Meggle, Z. Elektrochem. 59, 153 (1955).

[18] C. Knorr, Z. Elektrochem. 59, 647 (1955).

[19] M. Breiter, C. Knorr, and W. Völkl, Z. Elektrochem. 59, 681 (1955).

[20] K. Vetter and D. Otto, Z. Elektrochem. 60, 1072 (1956).

[21] V. G. Levich, Physicochemical Hydrodynamics, 1952, 54 and on.*

[22] A. I. Shlygin and A. N. Frumkin, Acta Phys. Chim. URSS 3, 791 (1935).

[23] A. I. Shlygin and A. N. Frumkin, and V. I. Medvedovskii, Acta Phys. Chim. URSS 4, 911 (1936).

[24] A. N. Frumkin and A. I. Shlygin, Bull Acad. Sci. Chem. Ser. 1936, 773.

[25] B. V. Érshler, Acta Phys. Chim. URSS 7, 327 (1937).

[26] M. I. Temkin, J. Phys. Chem. 15, 296 (1941).

[27] A. N. Frumkin and N. A. Aladzhalova, J. Phys. Chem. 18, 498 (1944); Acta Phys. Chim. URSS 19, 1 (1944)

[28] M. Breiter, H. Kammermaier, and C. Knorr, Z. Elektrochem. 60, 37 (1956).

* In Russian.

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