Kinetics of Processes on the Platinum Electrode[1].

II. The rate of discharge of H-ions and the rate of the over-all process of hydrogen evolution on platinum

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I. Introduction

In the preceding paper it has been shown that by measuring the capacity and the ohmic component of the electrode conductivity one can directly measure the absolute rate of the stage of discharge and ionization of hydrogen. It turns out that the ohmic component of the electrode conductivity when measured with a current of a sufficiently high frequency, is equal to the rate of discharge and ionization of adsorbed hydrogen multiplied by $\frac{F}{RT}$.

It will now be interesting to compare the rate of the discharge and ionization stage with the rate of the over-all process $2H^{\cdot} \rightleftarrows H_2$ and thus to decide experimentally the question whether the overvoltage on platinum is determined by the stage of discharge of H-ions.

In so far as the data available in the literature on the overvoltage on platinum are extremely contradictory, they could not be used for our object. It was desirable to investigate the rates of the discharge stage and of the over-all process under conditions as uniform as possible. For this purpose the measurements of the overvoltage on platinum were carried out under conditions quite identical with those of the measurements of capacity with an alternating current.

Since the measurements of the rate of the discharge and ionization stage were carried out at potentials lying close to the reversible

[1] P. Dolin and B. Ershler, Part I. Acta Physicochimica URSS, **13**, 747 (1940).

hydrogen potential, the comparison with the rate of the over-all process has obviously no sense unless at potentials close to the hydrogen potential. Our overvoltage measurements were accordingly carried out in the region of small polarizations both on the anodic and cathodic sides.

II. Experimental results

The apparatus employed in our measurements is shown in Fig. 1 It only differs from the apparatus used in measuring the capacity by the

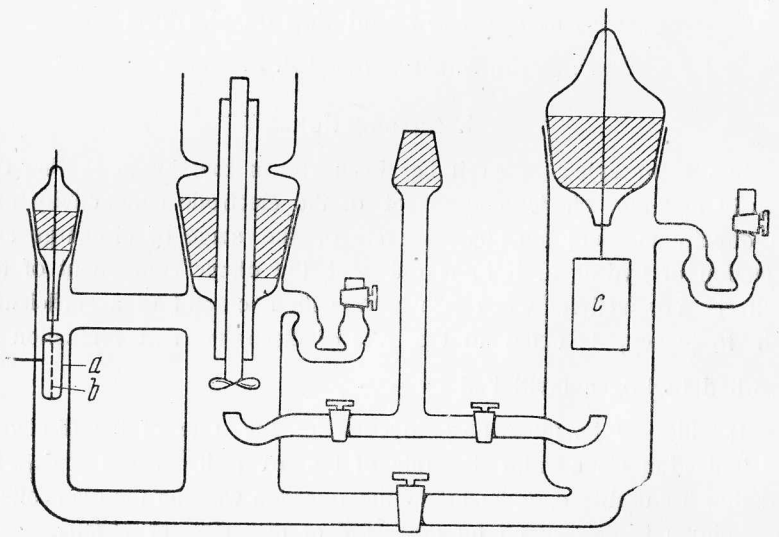

Fig. 1.

presence of a stirrer provided for the purpose of stirring the solution surrounding the electrode *a*. The number of revolutions of the stirrer was brought to 2000 per minute and more, and it was found that beginning approximately with 1000 revolutions per minute the influence of the concentration polarization completely vanished.

The polarization was measured with reference to a hydrogen electrode *c* in the same solution by the compensation method.

The overvoltage was studied in *N* HCl, *N* NaOH, 0.05 *N* NaOH + + *N* Na_2SO_4 and, with a poisoned electrode, in HCl. To ascertain

whether all the experimental conditions were the same as in the measurements with an alternating current, the same apparatus, before measuring the overvoltage, was used for determining the curves of the capacity and ohmic component of conductivity in *N* HCl at a frequency of 375 c. p. s. Comparison of these curves with the corresponding curves of the first series of measurements shows that the conditions under which the measurements were carried out were in both cases the same.

In *N* HCl the measurements of the overvoltage were carried out with a current density ranging from 2×10^{-5} to 1.5×10^{-3} A/cm.^{2} in the case of cathodic polarization, and from 2×10^{-5} to $4.7 \times \times 10^{-4}$ A/cm.^{2} in that of anodic polarization.

The overvoltage curves were taken with the electrode cleaned by anodic polarization directly before the measurements, with the same electrode two hours after cleaning, and with the poisoned electrode[2].

The results of the measurements are represented by the curves in Fig. 2. The same figure shows the curves obtained by Hammett under similar conditions. As can be seen from Fig. 2, our data coincide practically completely with those of Hammett[3].

Curve *I*, obtained directly after anodic cleaning of the electrode, shows that over the range of current densities mentioned above, the relation between the overvoltage η and the current density i has a linear character. Taking advantage of this circumstance we introduce the conception of the resistance of the electrode with respect to direct current, defined by the following expression:

$$R_d = \frac{\eta}{i}.$$

In the case of the cleaned electrode in HCl $R_d = 5.6\,\Omega$.

It is clear that the quantity $\frac{1}{R_d}$ is characteristic of the rate of the over-all process just as the limiting value of the ohmic component of the electrode conductivity is characteristic of the rate of the stage of discharge of H-ions.

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[2] The poisoning of the electrode was carried out in the same way as in the capacity measurements (p. 657).

[3] Hammett, J. Am. Chem. Soc., **46**, 7 (1924).

On the curves obtained two hours after the anodic cleaning of the electrode the interval of current densities in which the $\eta - i$ relation is linear is considerably narrower than in the preceding case, while the slope of these curves, which is characterized by the quantity R_d,

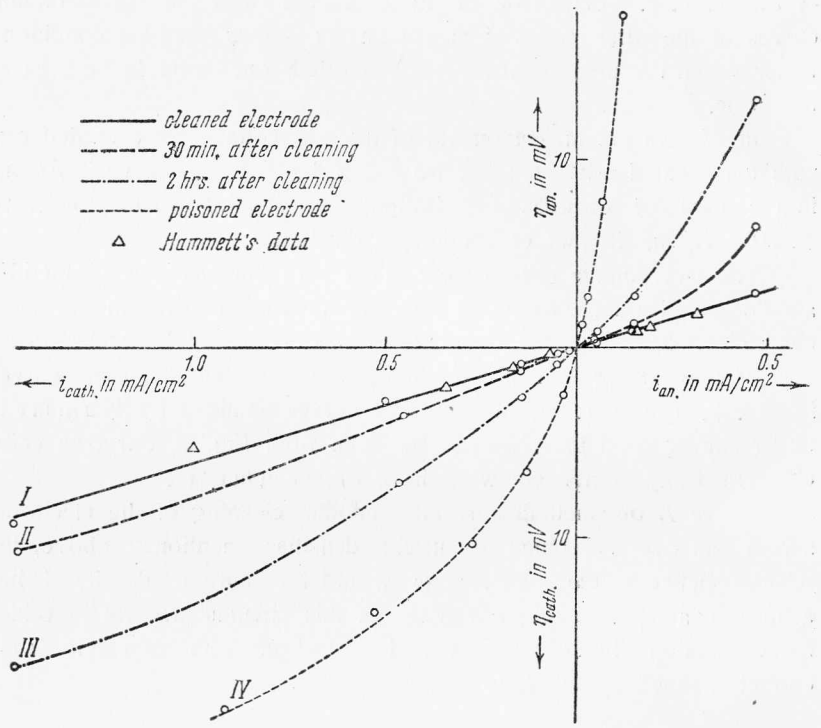

Fig. 2. Overvoltage curves for N HCl.

is considerably larger. In the case of the poisoned electrode, in the same interval of current densities in which the measurements were carried out, no linear relation between η and i was observed. However, if R_d is calculated for smaller current densities, the value 92 Ω is obtained. The value of R_d for the poisoned electrode is thus approximately 16 times that for the cleaned one.

Now in the case of the same poisoning of the electrode, the rate of the discharge and ionization stage is 10 times smaller. Taking into account the fact that the poisoning of the surface is difficult to reproduce quantitatively, we can conclude that the poisoning of the electrode surface equally affects the over-all reaction of hydrogen evolution and the separate stage of the discharge of H-ions.

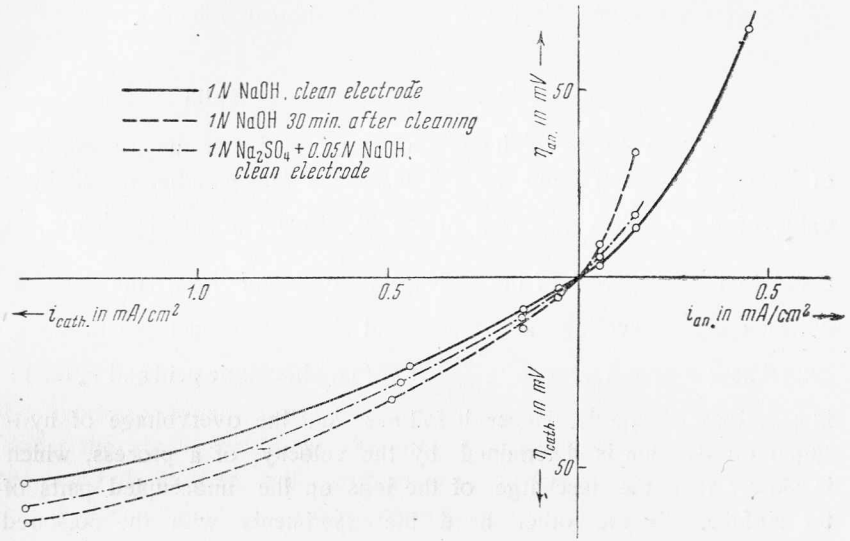

Fig. 3. Overvoltage curves for NaOH.

The overvoltage curves for alkali solutions are plotted in Fig. 3. From Fig. 3 it can be seen that the range of current densities where the relation of η to i is linear is considerably narrower in NaOH than in a solution of HCl. Over the range of current densities where η varies linearly with i the resistance $R_d = \frac{\eta}{i}$ is equal to 55 Ω.

Table 1

Electrode	r in Ω	R_d in Ω
N HCl, non-poisoned electrode .	0.21	5.6
N HCl, poisoned electrode . . .	2.0	92
N NaOH, non-poisoned electrode	5.0	55

The values of R_d which characterize the rate of the over-all process $2H^{\cdot} \rightleftarrows H_2$ and those of r, characterizing the rate of the discharge and ionization stage $H_3O^{\cdot} + (Pt) + e \rightleftarrows (Pt)H$ in HCl, NaOH and with the poisoned electrode in HCl are compared in Table 1. The values of r are given for the reversible hydrogen potential.

III. Discussion of experimental results

It has been shown in the preceding paper that if the overvoltage of hydrogen is determined by the discharge stage alone, the limiting value of the ohmic component of the electrode conductivity $\frac{1}{r}$ must be equal to the reciprocal of the resistance $\frac{1}{R_d}$ found from the relation between the overvoltage and the current density for small polarizations. Experiment shows that $z_1 = \frac{1/r}{1/R_d} = 27$ in hydrochloric acid and $z_2 = 11$ in solutions of NaOH. Hence it follows that the overvoltage of hydrogen on platinum is determined by the velocity of a process, which is slower than the discharge of the ions on the unoccupied parts of the surface. On the other hand the experiments with the poisoned surface show that the poisoning produces approximately the same influence both on the rate of the discharge and ionization reaction and on the rate of the over-all process. The same result is observed on transition from acid to alkali solutions. Moreover, the experiments of Kabanow[4], who has measured the overvoltage on platinum at very large current densities, have shown that in the case of platinum the removal of hydrogen from the surface cannot be wholly secured by the recombination mechanism. We accordingly assume that in the case of platinum the overvoltage is determined by the rates of two stages: the discharge of H-ions on unoccupied parts of the surface and the discharge of H-ions on the adsorbed hydrogen atoms with the formation of hydrogen molecules. These reactions take place mainly in acids. In the case of alkalies the reactions of discharge are mainly determined not by H-ions, but by the molecules of water. It is quite possible and even certain that the removal of hydrogen from the surface is secured not only by the electrochemical reaction mentioned

[4] B. Kabanow, Acta Physicochimica URSS, **5**, 193 (1936).

above, but also by the simultaneously proceeding recombination reaction. We shall confine our calculations, however, to a simpler scheme, leaving the latter reaction out of account. For platinum we thus assume the same overvoltage mechanism which has been developed by Frumkin[5,6] for Ni. In accordance with what has been stated above we shall, in deriving the relation between η and i, use the concept of heterogeneity of the surface. As a characteristic of heterogeneity the linear relation of the differential heat of adsorption to the degree of covering will be taken. As has been shown in the preceding paper, such a characteristic of the heterogeneity of the surface is equivalent to taking into account the repulsive forces. Expressions for the overvoltage in which the repulsive forces were taken into account were derived by Okamoto and Hirota[7,8] for Ni. These autors based their calculations on the recombination mechanism of the overvoltage.

We shall start from the assumption of a complete mobility of the hydrogen atoms adsorbed on the surface and shall put $\alpha = \beta = 1/2$. Under the above conditions the rates of the reactions which proceed on the electrode in acids will be determined by the following expressions.

I. The rate of discharge of H-ions on the unoccupied part of the surface with the formation of adsorbed atoms:

$$K_1 [H^{\cdot}] e^{-\frac{\varphi F}{2RT}} \frac{1}{p^{1/2}}. \qquad (1)$$

II. The rate of discharge of H-ions on adsorbed hydrogen atoms with formation of hydrogen molecules

$$K_2 [H^{\cdot}] e^{-\frac{\varphi F}{2RT}} p^{1/2}. \qquad (2)$$

III. The rate of ionization of adsorbed atoms with formation of H-ions

$$K_3 e^{\frac{\varphi F}{2RT}} p^{1/2}. \qquad (3)$$

[5] A. Frumkin, Acta Physicochimica URSS, **7**, 475 (1937).
[6] P. Lukowzew, S. Lewina and A. Frumkin, Acta Physicochimica URSS, **11**, 21 (1939).
[7] J. Horiuti and G. Okamoto, Sci. Pap. Inst. Phys. Chem. Res., **28**, 231 (1936).
[8] Okamoto, Horiuti and Hirota, Sci. Pap. Inst. Phys. Chem. Res., **29**, 223 (1936).

IV. The rate of adsorption of molecular hydrogen with formation of adsorbed atoms and H-ions

$$K_4 [H_2] e^{\frac{\varphi F}{2RT}} \frac{1}{p^{1/2}}. \tag{4}$$

Here, as before, p denotes the pressure of the atomic hydrogen gas which is in equilibrium with the hydrogen adsorbed on the surface. If complete surface diffusion exists, p is the same over the whole surface.

The derivation of formulae (1) and (3) has been given in the preceding paper. The derivation of (2) and (4) can be explained in the following way: the rate of reaction II is proportional to the rate of desorption of atomic hydrogen from the surface. The latter is determined according to Temkin's formula $v = K_d p^{1/2}$. It must moreover be taken into account that the desorption process is accompanied by the discharge of H-ions, the rate of this discharge being influenced both by the concentration of the H-ions and by the electric field of the double layer. The latter circumstance was accounted for in expression (2) by the factors $[H^+]$ and $e^{-\frac{\varphi F}{2RT}}$ respectively. In a similar way, if one takes into account that reaction IV means simultaneously the adsorption of hydrogen and its ionization, expression (4) is obtained.

In a steady state, with a direct current, $p = \text{const.}$,

$$K_1 [H^+] e^{-\frac{\varphi F}{2RT}} \frac{1}{p^{1/2}} - K_2 [H^+] e^{-\frac{\varphi F}{2RT}} p^{1/2} -$$

$$- K_3 e^{\frac{\varphi F}{2RT}} p^{1/2} + K_4 [H_2] e^{\frac{\varphi F}{2RT}} \frac{1}{p^{1/2}} = 0. \tag{5}$$

Hence we find that

$$p = \frac{K_1 [H^+] + K_4 [H_2] e^{\frac{\varphi F}{RT}}}{K_2 [H^+] + K_3 e^{\frac{\varphi F}{RT}}}. \tag{6}$$

From the equilibrium conditions

$$K_1 [H^+] e^{-\frac{\varphi_0 F}{2RT}} \frac{1}{p_0^{1/2}} = K_3 e^{\frac{\varphi_0 F}{2RT}} p_0^{1/2}$$

and

$$K_2 [H^+] e^{-\frac{\varphi_0 F}{2RT}} p_0^{1/2} = K_4 [H_2] e^{\frac{\varphi_0 F}{2RT}} \frac{1}{p_0^{1/2}},$$

where p_0 is the pressure corresponding to the equilibrium hydrogen potential, we get:

$$e^{\frac{\varphi_0 F}{RT}} = \frac{K_1 [H^+]}{K_3} \frac{1}{p_0}, \tag{7}$$

$$e^{\frac{\varphi_0 F}{RT}} = \frac{K_2 [H^+]}{K_4 [H_2]} p_0, \tag{8}$$

$$e^{\frac{\varphi_0 F}{RT}} = \left(\frac{K_1 K_2}{K_3 K_4 [H_2]} \right)^{1/2} [H^+], \tag{9}$$

and

$$p_0 = \left(\frac{K_1 K_4 [H_2]}{K_3 K_2} \right)^{1/2}. \tag{10}$$

The cathodic current is determined by the expression

$$i_c = 2 \left[K_1 [H^+] e^{-\frac{\varphi F}{2RT}} \frac{1}{p^{1/2}} - K_3 e^{\frac{\varphi F}{2RT}} p^{1/2} \right] =$$

$$= \frac{2 \left[K_1 [H^+] e^{-\frac{\varphi F}{2RT}} - K_3 e^{\frac{\varphi F}{2RT}} p \right]}{p^{1/2}}. \tag{11}$$

Substituting in equation (11) the expression for p from (6), we obtain after reduction

$$i_c = \frac{2 \left[K_1 K_2 [H^+]^2 e^{-\frac{\varphi F}{2RT}} - K_3 K_4 [H_2] e^{\frac{3\varphi F}{2RT}} \right]}{p^{1/2} \left(K_2 [H^+] + K_3 e^{\frac{\varphi F}{RT}} \right)}. \tag{11a}$$

We shall consider expression (9) and replace φ by $\varphi_0 - \eta$; if η is small, the exponential terms in equation (11a) can be expanded in power series. Confining ourselves to the first two terms we get after reduction

$$i_c = 4 \frac{F}{RT} \frac{K_3 K_4 [H_2] e^{\frac{3\varphi_0 F}{2RT}}}{p^{1/2} \left[K_2 [H^+] + K_3 e^{\frac{\varphi_0 F}{RT}} \right]} \eta. \tag{11b}$$

If now $[H_2]\, e^{\frac{\varphi_0 F}{RT}}$ is taken from expression (8) and $e^{\frac{\varphi_0 F}{RT}}$ from expression (7) we obtain from equation (11b)

$$i_c = \frac{4S\eta}{1 + \frac{K_1}{K_2 p_0}}, \tag{11c}$$

where $S = \frac{F}{RT}\left(K_1 K_3 [H^+]\right)^{1/2}$ is the coefficient in the equation for the overvoltage according to the theory of slow discharge in the case of a heterogeneous surface with a small η, assuming that the degree of covering during the process of polarization remains constant ($p = \text{const.}$).

In fact we obtain in this case

$$i_1 = K_1 [H^+]\, e^{-\frac{\varphi F}{2RT}} \frac{1}{p_0^{1/2}} - K_3\, e^{\frac{\varphi F}{2RT}} p_0^{1/2}. \tag{12}$$

From the equilibrium conditions we find

$$p_0 = \frac{K_1 [H^+]}{K_3} = e^{-\frac{\varphi_0 F}{RT}}. \tag{13}$$

Taking advantage of the fact that $\varphi_0 - \varphi = \eta$ is small and substituting in equation (12) the expression for p_0 from equation (13), we obtain after expanding the exponential terms of equation (12) in power series

$$i_1 = \frac{F}{RT}(K_1 K_3 [H^+])^{1/2}\, \eta = S\eta. \tag{14}$$

Substituting now in equation (11c) the quantity p_0 from equation (10) we finally obtain:

$$i_c = \frac{4S\eta}{1 + \left(\frac{K_1 K_3}{K_2 K_4 [H_2]}\right)^{1/2}} = \frac{4S\eta}{1 + L}. \tag{15}$$

It is easy to see that in the case of alkaline solutions, where the discharge reaction involves mainly water molecules, equation (15) preserves exactly the same form, but the coefficient S in this case is proportional not to the square root of the concentration of H^+-ions, but to the square root of the concentration of OH'-ions.

The quantity L is easily found by comparing the rate of the discharge and ionization reaction with the rate of the over-all process. In fact if one takes into account that the coefficient S is equal to the limiting value of the ohmic component of the electrode conductivity $\frac{1}{r}$, and the coefficient $\frac{4S}{1+L}$ to the reciprocal of resistance $\frac{1}{R_d}$ found from the overvoltage curves, the quantity L for N HCl can be determined in the following way:

$$\frac{1/R_d}{1/r} = \frac{0.18}{4.85} = \frac{4}{1+L};\quad L_{HCl} = 107.$$

In N NaOH the quantity L is equal to 42.0.

Using the conception of the mechanism of hydrogen overvoltage on platinum developed above we shall derive the expression for the exchange velocity.

Let A, B, C and D denote the reaction rates I, II, III and IV respectively; the exchange velocity v will then be determined by the following expression:

$$v = D\frac{C}{C+B} + D =$$

$$= K_4 [H_2]\, e^{\frac{\varphi_0 F}{2RT}} p_0^{-1/2} \left(\frac{K_3\, e^{\frac{\varphi_0 F}{2RT}} p_0^{1/2}}{K_3\, e^{\frac{\varphi_0 F}{2RT}} p_0^{1/2} + K_2 [H^+]\, e^{-\frac{\varphi_0 F}{2RT}} p_0^{1/2}} + 1 \right). \tag{16}$$

With the help of equations (8) and (15) this can be transformed into the form

$$v = (K_4 K_2 [H_2][H^+])^{1/2} \frac{2 + \frac{1}{L}}{1 + \frac{1}{L}}. \tag{16a}$$

As can be seen from the calculation given above, one can with sufficient approximation neglect the quantity $\frac{1}{L}$; then it follows from equation (16a) that the exchange rate is proportional to the square root of the hydrogen pressure. This relation was experimentally observed by Horiuti and Polanyi[9].

Equation (16a) can easily be transformed with the help of equations (14) and (15) to the following form:

$$v = \frac{RT}{F}\frac{S}{1+L}\left(2 + \frac{1}{L}\right). \tag{17}$$

[9] Horiuti and Polanyi, Mem. Proc. Manch. Liter. and Phil. Soc. **78**, 47 (1933—34).

Comparing now equation (17) with the expression $\frac{1}{R_d} = \frac{4S}{1+L}$ we get:

$$v = \frac{1}{R_d}\frac{RT}{2F}\left(1 + \frac{1}{2L}\right). \qquad (18)$$

Using the quantity L one can easily determine to what extent, with rise of cathodic polarization, the reaction of ionization of adsorbed hydrogen (reaction III) influences the degree of covering of the surface which is established in accordance with the ratio of the rates of discharge on the free and covered surface regions (reactions I and II). We can thus determine the potential range beyond which the rate of the ionization reaction (III) can be neglected in comparison with the rate of the discharge reactions (I and II).

For this purpose we shall find the ratio of the rate of reaction II to that of reaction II:

$$n = \frac{K_3 e^{\frac{\varphi F}{2RT}} p^{1/2}}{K_2 [H^+] e^{-\frac{\varphi F}{2RT}} p^{1/2}} = \frac{K_3}{K_2 [H^+]} e^{\frac{\varphi_0 F}{RT}} e^{\frac{-\eta F}{RT}} = L e^{\frac{-\eta F}{RT}} \qquad (19)$$

and[10]

$$\lg n = \lg L - \frac{\eta F}{2.3\,RT}. \qquad (19a)$$

For N HCl we have

$$\lg n = 2.03 - 17.3\,\eta,$$

and for N NaOH

$$\lg n = 1.62 - 17.3\,\eta.$$

Table 2 contains the values of n calculated in this way for the region of cathodic overvoltage.

One can see from Table 2 that with $\eta = 0.17$ V. in N HCl and with $\eta = 0.15$ V. in N NaOH the rate of reaction III is already 10 times smaller, than that of reaction II. The influence of the ionization of hydrogen molecules (reaction IV) vanishes at still smaller cathodic potentials because the rate of this reaction at the reversible potential is considerably smaller than that of reaction III.

The terms in the expression

$$p = \frac{K_1 [H^+] + K_4 [H_2]\, e^{\frac{\varphi F}{RT}}}{K_2 [H^+] + K_3 e^{\frac{\varphi F}{RT}}}$$

containing the factor $e^{\frac{\varphi F}{RT}}$ can consequently be neglected, beginning from potentials — 0.17 V. in N HCl and — 0.15 V. in N NaOH. Hence

$$p = \frac{K_1}{K_2}$$

Table 2

η	n	
	N HCl	N NaOH
0.0	108	42
0.05	14.6	5.9
0.1	2.0	0.78
0.15	0.27	0.11
0.17	0.12	0.48
0.19	0.056	

which means that with further increase of cathodic polarization p remains constant and depends on the ratio $\frac{K_1}{K_2}$ alone. This circumstance was assumed by Frumkin in the derivation of overvoltage formulae for metals which adsorb hydrogen. We are now able to define for platinum the potential range for which this assumption is correct in so far as the influence of the recombination can be disregarded.

Conclusions

1. The overvoltage of hydrogen was measured on platinum over the range of current densities from 2×10^{-5} A/cm.^{2} to 1.5×10^{-3} A/cm.^{2} in the cathodic region and from 2×10^{-5} A/cm.^{2} to 4.7×10^{-4} A/cm.^{2} in the anodic region in solutions N HCl, N NaOH, 0.05 N NaOH + + N Na_2SO_4 and on a poisoned electrode in N HCl.

2. It was found that the rate of the discharge stage is 27 times as large in HCl and 11 times as large in NaOH, as the rate of the over-all process $2H^+ \rightleftarrows H_2$ at the reversible hydrogen potential.

3. In agreement with this and other facts it is supposed that the overvoltage on platinum is determined by the rates of two reactions — the discharge of H-ions on free and covered regions of the electrode

[10] Formula (19a) holds for such values of the potential for which the isotherm of hydrogen adsorption on platinum preserves its logarithmic shape. This has been confirmed experimentally up to the reversible hydrogen potential. In the case of more cathodic potentials no experimental check exists. The above calculation has thus only a preliminary character.

surface with formation of an adsorbed atom and a molecule of hydrogen, respectively, and also by the rate of the inverse reactions. From this, an equation giving the relation of η to i for a heterogeneous surface in the region of small overvoltages is derived. The possibility of a removal of hydrogen atoms from the surface by recombination was disregarded in these calculations.

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Received
September 10, 1940.