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Kinetics of Processes on the Platinum Electrode.

I. The kinetics of the ionization of hydrogen adsorbed on a platinum electrode

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I. Introduction

The kinetics of the reaction of the electrochemical evolution and solution of hydrogen, $2H_3O^{\cdot} + 2e \rightleftarrows H_2 + 2H_2O$, and of its individual stages has hitherto been investigated mainly by the method of measuring the overvoltage of hydrogen. The substance of this method is as follows: from the velocity of the over-all reaction it is concluded which particular stage of the over-all process, being the slowest of all stages, determines the overvoltage. In the theory of Tafel[1], for example, it is assumed that the stage determining the overvoltage of hydrogen is the recombination of atoms. According to the theory of Volmer, which has been further developed by Frumkin[2], the stage determining the overvoltage is assumed to be the reaction of the discharge of H-ions.

It has been shown by Frumkin[3] that in the case of mercury, if the absence of adsorbed hydrogen on its surface is taken into account, all the experimental material on the overvoltage of hydrogen obtained in the work of Lewina and Sarinsky[4], can be fully accounted for only from the point of view of the theory of the slow discharge.

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1 J. Tafel, Z. physik. Chem. **50**, 641 (1905).
2 A. Frumkin, Z. physik. Chem., **A 164**, 121 (1933).
3 A. Frumkin, Acta Physicochimica URSS, **7**, 475 (1937).
4 S. Lewina u. W. Sarinsky, Acta Physicochimica URSS, **6**, 491 (1937); **7**, 485 (1937).

In the case of platinum the corresponding experimental material which should enable the mechanism of overvoltage to be established unambiguously is insufficient. The data of different authors are extremely contradictory. Besides, the most interesting data on the influence of the concentration of the electrolyte and neutral salts on the overvoltage are absent for platinum.

The object of the present paper was the study of the kinetics of a particular stage of the over-all process, namely the stage of the discharge of ions and of the ionization of hydrogen atoms adsorbed on platinum by the method of measuring the capacity component and the ohmic component of the conductivity of the electrode (see below) with a current of variable frequency. The experiments were carried out in the interval of potentials from 0.0 to 1.0 V. on the anodic side with respect to the reversible hydrogen potential in the given solution at a hydrogen pressure of one atmosphere.

As will be shown below, under these conditions all the stages of the over-all process, except the stage of hydrogen ion discharge and hydrogen ionization, were excluded.

According to the conception of the platinum electrode developed by Frumkin and Šlygin[5], in the case of slow, *i. e.*, equilibrium charging of the electrode, the quantity of electricity passed through the electrode, must be used in the following way.

Over the potential range from 0.0 to 0.25 V. (in a HCl solution), the current will be used mainly in the process of removing or forming the hydrogen layer adsorbed on the surface of platinum, that is, in the process of discharge and ionization of hydrogen, and to a certain extent for charging of the double layer (the so-called hydrogen region). Over the potential range from +0.4 to +0.8 V. most of the current is used for charging the double layer (the so-called double-layer region). At a potential of +0.8 V. the oxidation of the electrode takes place.

When the current is passed through a platinum electrode which is kept at a potential more anodic than the potential of the reversible hydrogen electrode, that is, under the conditions in which the evolution of gaseous hydrogen is practically excluded, we shall obviously have

[5] A. Šlygin and A. Frumkin, Acta Physicochimica URSS, 3, 791 (1935).

but one stage:

$$H_3O^+ + (Pt) + e \rightleftarrows (Pt)\,H + H_2O.$$

The possibility of investigating the rate of this stage alone can be explained qualitatively with the help of the following reasoning. Let us consider what will happen if the electrode is charged rapidly, that is, under such conditions that the hydrogen film has no time to get into equilibrium with the ions in the double layer.

Let us change the potential of the electrode by $\Delta\varphi$ from a certain equilibrium value φ_r, passing for this purpose a quantity of electricity ΔQ. If the potential of the electrode corresponds to the hydrogen region, the quantity of electricity ΔQ will be used for charging the double layer and for the reaction of ionization of adsorbed hydrogen or discharge of hydrogen ions. We shall assume that the former process proceeds practically instantaneously, while the latter, as any chemical reaction, with a certain finite velocity.

For a certain rate of charging, the hydrogen layer will have no time to get into equilibrium with the ions of the double layer. Consequently, with increased rate of charging a smaller quantity of electricity ΔQ will be required to increase the electrode potential by the same amount $\Delta\varphi$. This means that with increase of the rate of charging the capacity of the electrode decreases. It is clear that the dependence of the capacity of the electrode on the charging rate will be determined by the kinetics of the reaction of discharge and ionization. A convenient method for measuring the rate of charging is provided by applying a current of variable frequency.

In the case of alternating current and an electrical condenser the phase angle between the current and the voltage is equal to 90°. In so far as the condenser is charged practically instantaneously, while the process of discharge and ionization of hydrogen on a platinum electrode proceeds with a finite velocity, the electrode will give a smaller phase shift than an electrical condenser, that is, the phase angle of the electrode will lie in the interval between 0 and 90°. From the theory of alternating currents it is known that if a system gives a phase shift in the interval from 0 to 90°, it can be replaced, in the sense of its behaviour with respect to an alternating current, by a certain complex conductivity consisting of a capacity (reactive) and an ohmic (active) component. With a change in frequency both the capacity and the ohmic component will be changed.

The electrode can thus be treated, in the case of an alternating current, as a complex conductivity composed of two components — the active conductivity, which when referred to unit area we shall call in the sequel the ohmic conductivity, and the reactive conductivity referred to as the capacity conductivity. The capacity component of the electrode, expressed in microfarads per $cm.^2$ will be also called the capacity of the electrode. It must be noted that the resistance of the electrode as metallic conductor is included in the ohmic component; this quantity is, however, so small that it can be neglected in comparison with the resistance due to the slow discharge of the H-ions.

Capacity measurements with the help of an alternating current with a frequency from 1000 to 12 000 c. p. s. have been carried out by Thon[6] for mercury and platinum electrodes. The decrease in the capacity of the electrode with the frequency was ascribed by **Thon** to the limited rate of the ionic exchange.

It will be shown below that the relation of the ohmic and capacity components of the conductivity of a platinum electrode to the frequency enables us to make quantitative conclusions as to the kinetics of the reaction of discharge and ionization of hydrogen.

II. Experimental part

1. Method

The capacity of the electrode was measured with the help of a Wheatstone bridge.

Fig. 1 shows the measuring circuit. The central part of this circuit consisted of a Wheatstone bridge composed of capacities C_1, C_2, C_3, cell and resistance R. The ohmic component of the electrode conductivity was compensated by the resistance R which was connected in parallel with the capacity C_3. Such a connection of the resistance R and capacity C_3 is more convenient because the connection in series of C_3 and R would in certain cases require too small resistances leading to large errors in the measurements. Besides, as will be shown below,

[6] Thon, C. R., **200**, 54 (1935).

in the case of parallel connection of C_3 and R these quantities have a simple physical meaning.

The current of variable frequency was supplied by a valve generator D. For frequencies from 100 to 6000 c. p. s. a telephone was

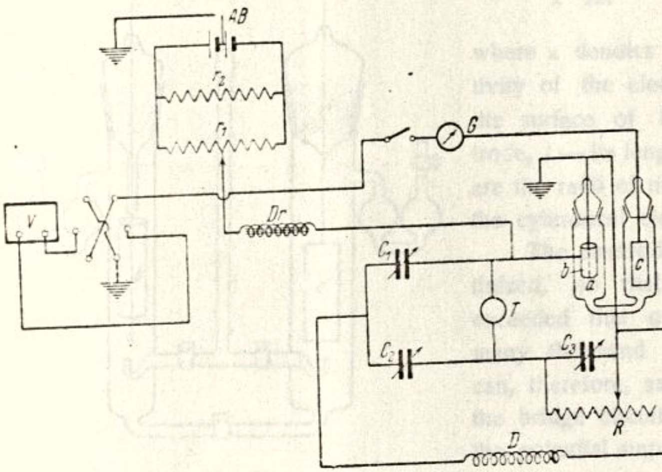

Fig. 1. Diagram of the measuring circuit.

used as zero instrument; at a frequency of 10 c. p. s. the latter was replaced by a galvanometer with a scale from —10 to +10 divisions and a sensitivity of 1×10^{-7} A. The amplitude of the potential applied to the bridge was so chosen as to keep the potential changes on the electrodes tested below 15 mV. Therefore the amplitude of the potential applied to the zero instrument required amplification; this was provided by a two-valve amplifier.

The second part of the circuit served for keeping the test electrode at a constant polarization from the battery AB and for measuring it with reference to the potential of the hydrogen electrode C.

The measuring cell (Fig. 2) consisted of two vessels one of which contained the test-electrode a, and the other the hydrogen electrode c.

A platinum wire 0.1 mm. in diameter and 1.65 cm. in length was used as the test-electrode. The polarization electrode b was a cylinder

3 mm. in diameter; the test-electrode a was placed along its axis. Such a disposition of the electrodes a and b is essential for reducing the error depending on the resistance of the electrolyte. In this case the resistance is determined by the following expression:

$$R_e = \frac{1}{\varkappa} \frac{s}{2\pi l} 2.3 \lg \frac{r_2}{r_1}, \qquad (1)$$

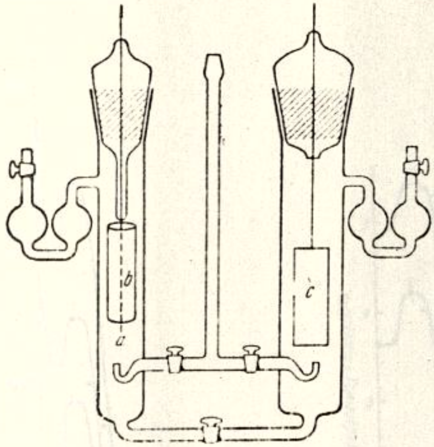

Fig. 2.

where $\varkappa$ denotes the conductivity of the electrolyte, s is the surface of the test-electrode, l — its length, r_1 and r_2 are the radii of the tested and the cylindrical electrodes.

The electrode b was platinized, so that its surface exceeded that of electrode a many thousand times. One can, therefore, assume that in the bridge circuit the drop of the potential amplitude on the tested electrode a alone was practically measured.

The measurements were carried out with the following solutions: N HCl; N H_2SO_4; N NaOH; 0.2 N HCl + N KBr; 0.03 N HCl + N KBr; 0.05 N NaOH + N Na_2SO_4, and, with a poisoned electrode, in N HCl. All the solutions were prepared from chemically pure reagents and purified before the experiment with the aid of a freshly platinized electrode in a hydrogen atmosphere. The test-electrode was etched before the experiment with hot *aqua regia* and, after washing with distilled water, heated in air at a temperature of 700—900°. Directly before the measurements the test-electrode was cleaned by anodic polarization. The measurements were carried out in the following way: at a given frequency the capacity and the ohmic component of the electrode conductivity were measured as functions of the anodic polarization in the interval from 0.0 to 1.0 V. The curves representing the relation of the capacity and of the ohmic component of the electrode conductivity to the polarization at a given frequency will be denoted in the sequel as capacity and ohmic conductivity curves.

2. Experimental results

a. **Capacity and ohmic conductivity curves in different solutions.** The measurements were carried out in a N HCl solution over the frequency range between 10 and 3375

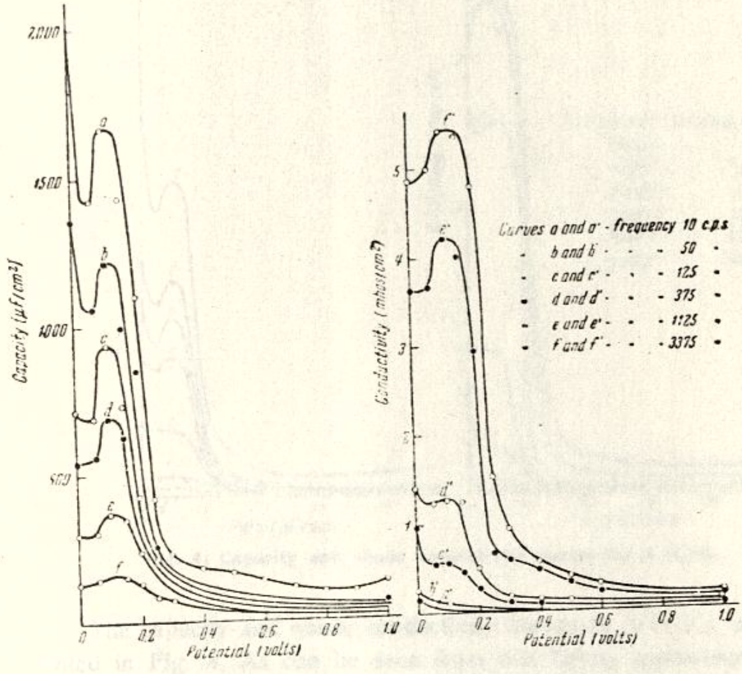

Fig. 3. Capacity and ohmic conductivity curves for N HCl.

c. p. s. The capacity and ohmic conductivity curves in N HCl are plotted in Fig. 3.

From Fig. 3 it may be seen that, if no account is taken of the sharp rise of the curves in the neighbourhood of the reversible hydrogen potential at low frequencies, over the potential range between 0.0 and 0.2 V., the capacity and the ohmic components of the conductivity have approximately a constant value. The variation of these values in this potential interval, which approximately corresponds to the hydrogen region on the charging curve[7], does not exceed 30%. It is well known that at a potential of 0.8 V. in the anodic direction a sharp bend of the charging curve takes place due to the beginning of the electrode oxidation. On the capacity and ohmic conductivity curves in a HCl solution the rise corresponding to the oxidation of the electrode is absent.

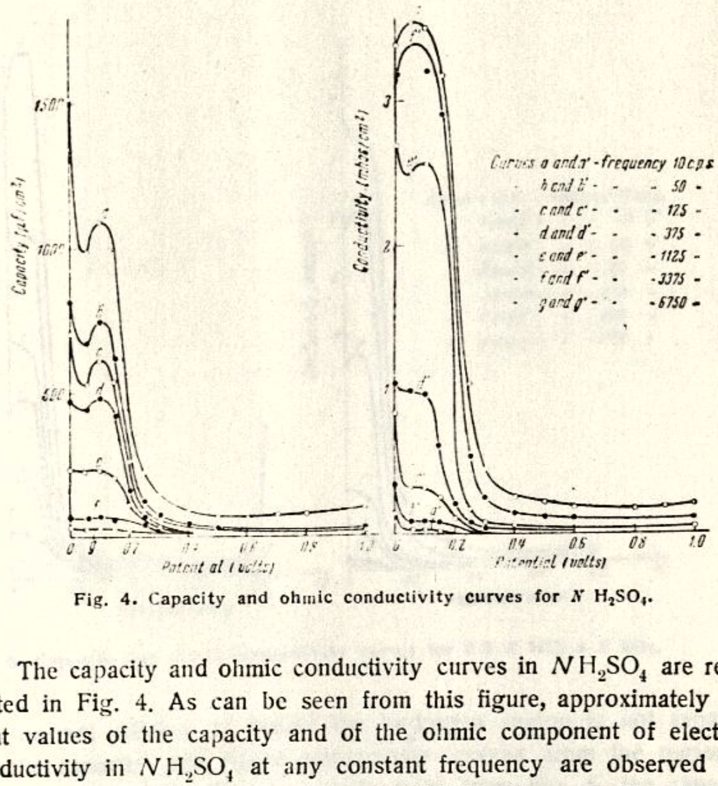

Fig. 4. Capacity and ohmic conductivity curves for N H_2SO_4.

The capacity and ohmic conductivity curves in $N\,H_2SO_4$ are represented in Fig. 4. As can be seen from this figure, approximately constant values of the capacity and of the ohmic component of electrode conductivity in $N\,H_2SO_4$ at any constant frequency are observed over the potential range between 0.0 and 0.15 V. The variation of these quantities in the potential interval considered does not exceed 20%. The rise of the curves at a potential of 0.8 V., which corresponds to the oxidation of platinum, is also absent.

[7] By the term charging curve Frumkin and Šlygin denote the curve giving the relation of the electrode potential to the quantity of electricity passed through the electrode, measured at slow charging of the electrode, that is, under equilibrium conditions.

In the solution $0.2\,N\,HCl + N\,KBr$ (Fig. 5) constant values of the capacity and of the ohmic component of conductivity are observed over the potential range between 0.0 and 0.1 V. At a potential of 0.8 V. at low frequencies a rise of the capacity curves corresponding to the evolution of bromine is observed. At higher frequencies this rise vanishes.

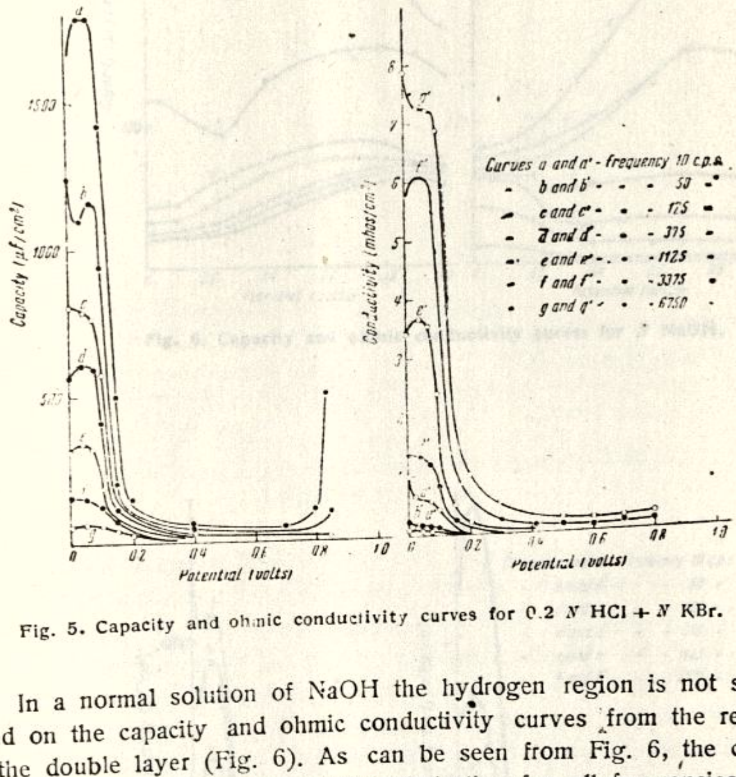

Fig. 5. Capacity and ohmic conductivity curves for 0.2 N HCl + N KBr.

In a normal solution of NaOH the hydrogen region is not separated on the capacity and ohmic conductivity curves from the region of the double layer (Fig. 6). As can be seen from Fig. 6, the capacity rises with increase of anodic polarization for all frequencies; the ohmic conductivity does not vary with increasing polarization at low frequencies, but rises rapidly with increase of potential at high frequencies.

The capacity and ohmic conductivity curves in a $0.5\,N\,NaOH + N\,Na_2SO_4$ solution coincide nearly completely with the corresponding curves in $N\,NaOH$. In the solution $0.03\,N\,HCl + N\,KBr$ the capacity and ohmic conductivity curves (Fig. 7) have the same character as

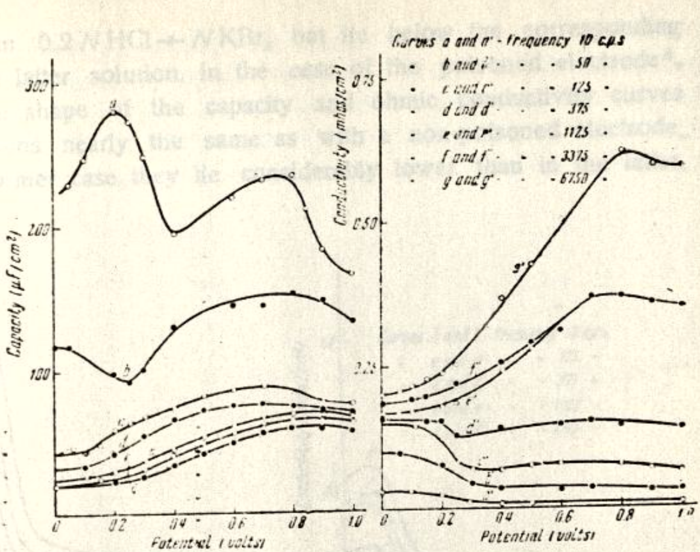

Fig. 6. Capacity and ohmic conductivity curves for N NaOH.

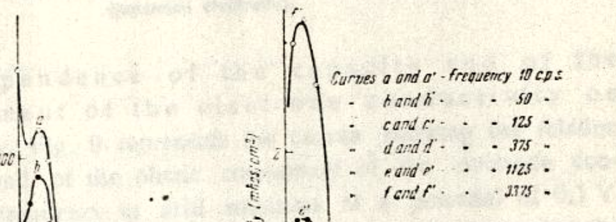

Fig. 7. Capacity and ohmic conductivity curves for 0.03 N HCl + N KBr.

in the solution $0.2\,N\,HCl + N\,KBr$, but lie below the corresponding curves in the latter solution. In the case of the poisoned electrode[8], in $N\,HCl$, the shape of the capacity and ohmic conductivity curves (Fig. 8) remains nearly the same as with a non-poisoned electrode, but in the former case they lie considerably lower than in the latter.

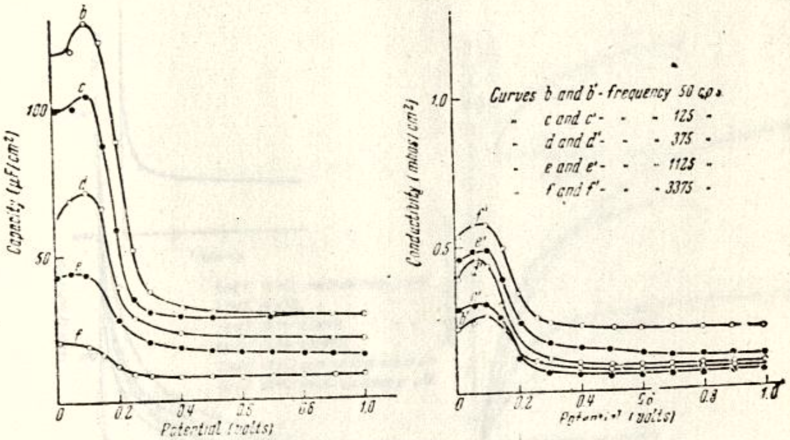

Fig. 8. Capacity and ohmic conductivity curves for N HCl (poisoned electrode).

b. The dependence of the capacity and of the ohmic component of the electrode conductivity on the frequency. Fig. 9 represents the curves showing the relation of the capacity and of the ohmic component of the electrode conductivity to the frequency in acid solutions at a potential of 0.1 V.

From Fig. 9 it may be seen that with increase of frequency the capacity decreases rapidly and the ohmic component of the electrode conductivity rapidly increases, both approaching at high frequencies certain limiting values. In $N\,HCl$ and $0.2\,N\,HCl + N\,KBr$ solutions, in the frequency interval in which the measurements were carried out, the limiting values of the capacity and of the ohmic component of con-

[8] The poisoning of the electrode was carried out in the following way: the electrode was dipped into a vessel containing a 5×10^{-3} molar solution of Na_3AsO_4 and cathodically polarized by a current of 1.5×10^{-3} A/cm.^{2} for 1 sec.

ductivity were, apparently, not reached. But we could not carry out the measurements at higher frequencies, because in this case the resistance of the solution would make the experimental error too large. In solutions of $N\,H_2SO_4$ and N NaOH the ohmic component of the

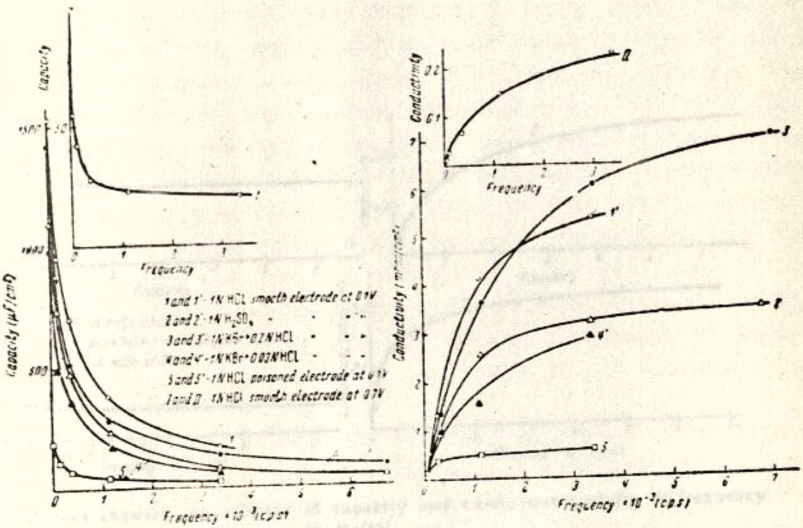

Fig. 9. Curves showing the relation of capacity and ohmic conductivity to frequency.

electrode conductivity is considerably smaller than in the N HCl solution; it was accordingly possible in this case to carry out the measurements at higher frequencies (up to 6750 c. p. s.).

Comparison of the curves representing the relation of the ohmic component of conductivity to the frequency in different solutions shows that the limiting value of the ohmic component in $0.2\,N$ HCl + N KBr is reached at higher frequencies than in N HCl, and in $N\,H_2SO_4$ at considerably lower frequencies than in N HCl.

The horizontal part of the curve obtained with a poisoned electrode in N HCl is situated at a height which is nearly 10 times as small as that of the corresponding part of the curve for a non-poisoned smooth electrode in the same solution.

From Fig. 10 it can be seen that the curves showing the relation of the capacity and ohmic conductivity of the electrode to the frequency, obtained in alkali solutions, lie considerable lower than the corresponding curves in the solutions of acids. The limiting values of the capa-

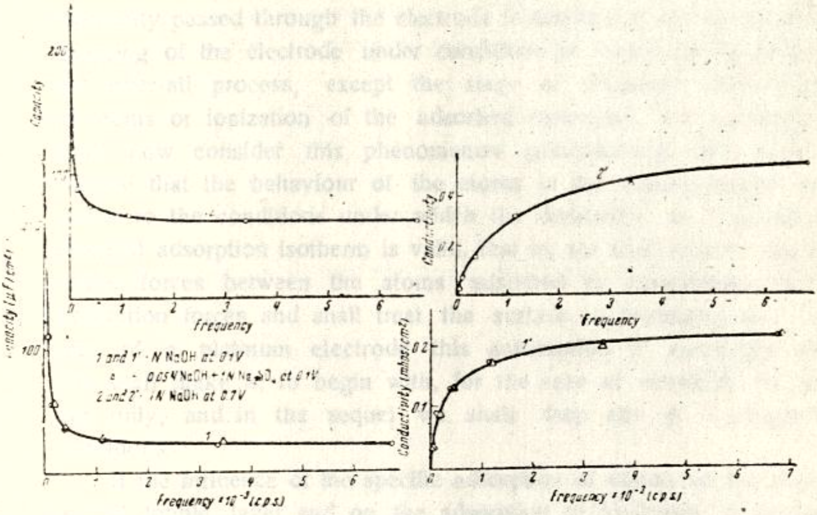

Fig. 10. Curves showing the relation of capacity and ohmic conductivity to frequency in NaOH.

city and of the ohmic conductivity in alkali are reached at considerably lower frequencies than in acids. From Fig. 10 it can moreover be seen that the curves obtained in N NaOH and $0.05\,N$ NaOH + $N\,Na_2SO_4$ coincide nearly completely.

The dependence of the capacity and of the ohmic conductivity of the electrode on the frequency was also observed in the region of the double layer. Fig. 9 represents the curves (*I* and *II*) showing this dependence in N HCl at a potential of 0.7 V. Nearly the same relation is observed in $N\,H_2SO_4$.

In $0.2\,N$ HCl + N KBr the capacity and the ohmic conductivity of the electrode at a potential of 0.7 V. are nearly independent of the frequency. In N NaOH, as is seen from Fig. 10, the effect of frequency on the ohmic component of conductivity at a potential of 0.7 V. is stronger than at a potential of 0.1 V.

III. Discussion of experimental results

1. The physical nature of the capacity and of the ohmic conductivity of the platinum electrode

It has previously been shown qualitatively how the quantity of electricity passed through the electrode is distributed on non-equilibrium charging of the electrode under conditions in which all the stages of the over-all process, except the stage of discharge with formation of atoms or ionization of the adsorbed hydrogen, are excluded. We shall now consider this phenomenon quantitatively. We shall first assume that the behaviour of the atoms in the adsorbed layer corresponds to the conditions under which the derivation of Langmuir's classical adsorption isotherm is valid, that is, we shall neglect the interaction forces between the atoms adsorbed in comparison with the adsorption forces and shall treat the surface as homogeneous. In the case of a platinum electrode this assumption is obviously wrong. We shall make it, to begin with, for the sake of simplicity of derivation only, and in the sequel we shall drop one of Langmuir's conditions.

If the influence of the specific adsorption of anions on the structure of the double layer and on the adsorption of hydrogen is neglected, then, following the assumption made by Volmer in his derivation of the equations for the velocity of discharge and ionization of hydrogen according to the theory of slow discharge, we can represent the distribution of the quantity of electricity passed through the electrode in the following way:

$$dQ = C_1 d\Delta\varphi - \Gamma_m F d\Delta\theta = C_1 d\Delta\varphi + \\ + \left\{K_r \theta e^{\frac{\beta\Delta\varphi F}{RT}} - K_d [\mathrm{H}^{\cdot}](1-\theta) e^{-\frac{\alpha\Delta\varphi F}{RT}}\right\} dt, \tag{2}$$

where C_1 denotes the capacity of the double layer, $\Delta\varphi$ — the potential of the electrode reckoned from a certain equilibrium value φ_r, Γ_m — the number of gram-atoms in a monolayer per unit area, K_r and K_d — the velocity constants of hydrogen ionization and hydrogen ion discharge, respectively, at a given potential φ_r, θ — the fraction of the surface covered by the adsorbed atoms, α and β — constants satisfying the condition $\alpha + \beta = 1$.

In the case of equilibrium, when $dQ=0$ and $\Delta\varphi=0$,

$$K_i\,\theta_r = K_d\,[\mathrm{H}^\cdot]\,(1-\theta_r),$$

where θ_r is the fraction of the occupied surface at the equilibrium potential φ_r. Replacing θ in equation (2) by $\theta_r+\Delta\theta$, expanding the exponential terms in power series and limiting ourselves to the first two terms ($\Delta\varphi$, as will be shown below, is small) we obtain the fol-owing expression:

$$\frac{dQ}{dt}=i=C_1\frac{d\Delta\varphi}{dt}+K_i\,(\theta_r+\Delta\theta)\left(1+\frac{\beta\Delta\varphi F}{RT}\right)-$$

$$-K_d\,[\mathrm{H}^\cdot]\,(1-\theta_r-\Delta\theta)\left(1-\frac{\alpha\Delta\varphi F}{RT}\right). \tag{2a}$$

After cancelling and neglecting the terms containing the product $\Delta\theta\Delta\varphi$ we obtain:

$$\frac{dQ}{dt}=i=C_1\frac{d\Delta\varphi}{dt}+\frac{\Delta\varphi}{N}+M\Delta\theta=C_1\frac{d\Delta\varphi}{dt}+\frac{\Delta\varphi+NM\Delta\theta}{N}, \tag{3}$$

where $N=\dfrac{1}{K_i\,\theta_r\,\dfrac{F}{RT}}$ and $M=K_i+K_d\,[\mathrm{H}^\cdot]$.

Equation (3) corresponds to circuit I represented in Fig. 11. This can easily be seen if one writes the equation corresponding to this circuit:

$$dQ=C_1\,d\psi+dA=C_1\,d\psi+\frac{\psi-A/C_2}{r}\,dt, \tag{4}$$

where ψ denotes the potential on the plates of condenser C_1, and A is the charge of the condenser.

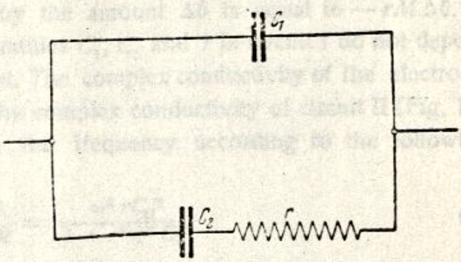

Fig. 11. Circuit I.

If it is now taken into account that C_1 in equation (4) corresponds to C_1 in equation (3) and ψ corresponds to $\Delta\varphi$, we obtain by comparing equations (2), (3) and (4) the following relations:

$$N=r;\quad -A=\Delta\theta\Gamma_m F;\quad \frac{1}{C_2}=\frac{NM}{\Gamma_m F}\ \text{or}\ C_2=\frac{\Gamma_m F}{NM}.$$

Reverting to the former expression for N, we find:

$$N = r = \frac{RT}{F}\frac{1}{K_i\theta_r} = \frac{RT}{F}\frac{1}{K_d[\mathrm{H}^\cdot](1-\theta_r)}$$

or

$$\frac{1}{r} = \frac{F}{RT}K_i\theta_r = \frac{F}{RT}K_d[\mathrm{H}^\cdot](1-\theta_r), \tag{5}$$

that is, the reciprocal of the resistance r in circuit I divided by the quantity $\frac{F}{RT}$ is equal to the velocity of discharge and of ionization at a certain potential φ_r.

If we denote by $\Delta\theta$ the increase of the fraction of the surface covered with hydrogen corresponding to an equilibrium of the hydrogen layer with the ionic layer at a potential $\varphi_r + \Delta\varphi$, then, according to formula (3), $i = 0$ and $C_1\frac{d\Delta\varphi}{dt} = 0$; consequently:

$$\frac{\Gamma_m F}{rM} = C_2 = -\frac{\Delta\theta\Gamma_m F}{\Delta\varphi}. \tag{6}$$

The quantity $\frac{\Gamma_m F}{rM} = C_2$ is thus equal to the capacity of the hydrogen layer on equilibrium charging of the electrode.

We shall now introduce the notion of the potential of the hydrogen layer φ_{H}. By the potential of the hydrogen layer for a given degree of covering we shall denote the potential of the electrode corresponding to an equilibrium between the hydrogen atoms adsorbed on the electrode and the ions in the double layer. According to (6) the shift of the potential of the hydrogen layer $\Delta\varphi_{\mathrm{H}}$ corresponding to a variation of the degree of covering by the amount $\Delta\theta$ is equal to $-rM\Delta\theta$.

It is clear that the quantities C_1, C_2 and r in circuit I do not depend on the frequency of the current. The complex conductivity of the electrode, measured experimentally as the complex conductivity of circuit II (Fig. 12) must, however, depend on the frequency according to the following expressions:

$$\frac{1}{R} = \frac{\omega^2 r C_2^2}{1 + r^2\omega^2 C_2^2} \tag{7}$$

and

$$C = \frac{C_2}{1 + r^2\omega^2 C_2^2} + C_1, \tag{8}$$

where ω is the cyclic frequency of the alternating current.

From equations (7) and (8) it follows that with increase of frequency the quantity R tends to a constant value r, while C tends to the constant value C_1.

The velocity of the reaction of discharge and ionization is therefore proportional to that limiting value of the ohmic component of the electrode conductivity, which is found in measuring the capacity of the electrode with a current of sufficiently high frequency. In order to find the absolute rate of discharge and ionization at a given equilibrium potential, that is, the so-called "exchange current", the value of the limiting ohmic component of the electrode conductivity found at this potential must be divided by $\frac{F}{RT}$.

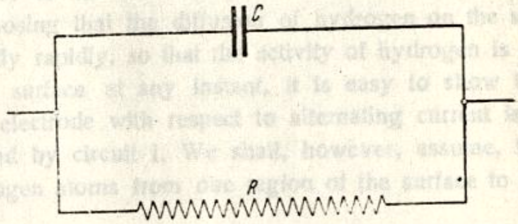

Fig. 12. Circuit II.

Using equation (3) it is easy to calculate the overvoltage of hydrogen arising as a result of the passage of a constant current i through the electrode if it is due to a slow discharge. We shall also assume that the deviations of the potential $\Delta\varphi$ from the equilibrium value are small. When the double layer is charged to the new value of the potential corresponding to the overvoltage, the total current will be used for the discharge of hydrogen ions only. Since we have assumed that the removal of hydrogen atoms from the surface (*i. e.*, the recombination) proceeds more rapidly than the discharge of the ions, the quantity $M\Delta\theta$ in equation (3) can be neglected, because the degree of covering of the surface must correspond to the concentration of molecular hydrogen in the solution, that is, must be equal to θ_r, so that $\Delta\theta$ is near to 0. Hence we obtain from equation (3)

$$\frac{dQ}{dt} = i = \frac{\Delta\varphi}{r} \quad \text{or} \quad \Delta\varphi = ir.$$

The limiting value of the ohmic component of the electrode resistance must thus be equal to the coefficient R_d in the equation expressing the relation between the overvoltage η and the current density i,

$$\eta = R_d i, \tag{9}$$

which describes correctly this relation in the region of small polarizations[9].

At the beginning assumptions have been made which underly the derivation of Langmuir's adsorption isotherm for a homogeneous surface. We shall now drop one of these assumptions: we shall assume, namely, that the surface of the electrode consists of n different homogeneous regions. Supposing that the diffusion of hydrogen on the surface proceeds sufficiently rapidly, so that the activity of hydrogen is the same throughout the surface at any instant, it is easy to show that the behaviour of the electrode with respect to alternating current is in this case also described by circuit I. We shall, however, assume, that the transition of hydrogen atoms from one region of the surface to the other is hindered.

In this case one must write instead of equation (3), the following equation:

$$\frac{dQ}{dt}=i=C_1\cdot\frac{d\Delta\varphi}{dt}+\Delta\varphi\sum_1^n\frac{1}{r_e}+\sum_1^n M_e\,\Delta\theta_e=C_1\frac{d\Delta\varphi}{dt}+$$

$$+\left(\Delta\varphi+\frac{\sum\limits_1^n M_e\,\Delta'_e}{\sum\limits_1^n\frac{1}{r_e}}\right)\sum_1^n\frac{1}{r_e}. \tag{3a}$$

The electric circuit corresponding to this equation consists of n resistances r_e, n capacities C_e and a capacity C_1 (capacity of the double layer) connected as shown in Fig. 13 (circuit III).

Since in the experiment the complex resistance of the electrode is compensated by the complex resistance of circuit II (Fig. 12), it is clear that at sufficiently high frequencies the ohmic component of the electrode conductivity $\frac{1}{r}$ will be equal to the quantity

$$\frac{1}{r}=\sum_1^n\frac{1}{r_e}=\frac{F}{RT}\sum_1^n(K_i)_e(\theta_r)_e=\frac{F}{RT}[\mathrm{H}^{\cdot}]\sum_1^n(K_d)_e(1-\theta_r)_e. \tag{5a}$$

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[9] The quantity R_d has the dimensions of resistance and will in the sequel be referred to as the resistance found from the overvoltage.

In this case too the limiting value of the ohmic component of the electrode conductivity, found at a given potential and divided by the quantity $\frac{F}{RT}$ is thus equal to the rate of discharge and ionization of hydrogen.

From the course of the curves representing the relation between the ohmic component of the conductivity and the frequency (Figs. 9

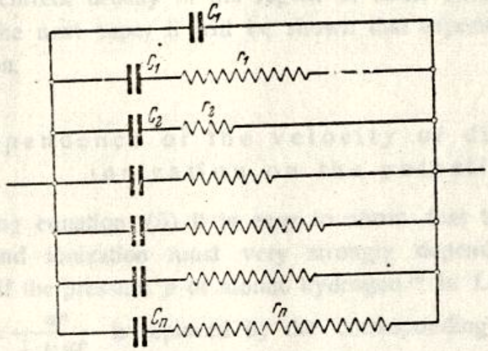

Fig. 13. Circuit III.

and 10) it follows that, with rise of frequency, the ohmic component of conductivity actually tends to a constant value. In N HCl and 0.2 N HCl + N KBr solutions, at the highest frequencies which were used in our measurements, the ohmic component of the conductivity does not reach its limiting value, but apparently lies close to it. In N H_2SO_4 and N NaOH the limiting value of the ohmic component of the electrode conductivity is reached already at a frequency of about 3000 c. p. s.

These measurements thus showed that the process $H_3O^{\cdot} + (Pt) + e \rightleftarrows (Pt)H + H_2O$ actually proceeds with a finite velocity and enables the absolute value of this velocity to be determined.

If it is assumed that in the case of a heterogeneous surface the overvoltage is also determined by the rate of the discharge of $H^{\cdot}$-ions, then in equation (3a) the quantity $\sum_{1}^{n} M_e \Delta\theta_e \simeq 0$ because each $\Delta\theta_e \simeq 0$.

Consequently, when the double layer is charged to the potential at which the overvoltage is measured, we obtain from equation (3a)

$$i = \Delta\varphi \sum_1^n \frac{1}{r_e} \quad \text{or} \quad \Delta\varphi = i \frac{1}{\sum_1^n \frac{1}{r_e}},$$

that is, in this case the limiting value of the ohmic component of the electrode resistance must be equal to the resistance R_d [see equation (9)] which is obtained from the observed relation between the overvoltage and the current density in the region of small polarizations.

In the next paper it will be shown that experiment contradicts this conclusion.

2. Dependence of the velocity of discharge and ionization on the potential

Using equation (5) it is easy to show that the velocity of discharge and ionization must very strongly depend on the potential In fact, if the pressure p of atomic hydrogen[10] in Langmuir's equation $\theta = \frac{ap}{1+ap}$ is replaced by the corresponding potential φ, and θ substituted into equation (5), we obtain:

$$\frac{1}{r}\frac{F}{RT} K_i \theta_r = \frac{F}{RT}(K_i)_0 e^{\frac{\varphi F}{2RT}} \frac{ae^{-\frac{\varphi F}{RT}}}{1+ae^{-\frac{\varphi F}{RT}}},$$

since

$$K_i = (K_i)_0 e^{\frac{\varphi F}{2RT}}.$$

When $\theta = \frac{1}{2}$, with a change of φ by the amount ± 0.058 V., the velocity of charging and ionization must decrease nearly twice and with a change of ± 0.116 V., 10-fold.

The equilibrium capacity C_2 must also strongly depend on the potential according to (5) and (6):

$$C_2 = -\frac{\Delta\theta}{\Delta\varphi}\Gamma_m F,$$

[10] The pressure of atomic hydrogen p is proportional to the activity of the adsorbed hydrogen at a given degree of covering.

since, if the pressure p is replaced by the potential φ and the expression obtained is differentiated, the relation between C_2 and φ will have the following form:

$$C_2 = \frac{\frac{F}{RT}\Gamma_m Fae^{-\frac{\varphi F}{RT}}}{1 + 2ae^{-\frac{\varphi F}{RT}} + a^2 e^{-\frac{2\varphi F}{RT}}}.$$

However, as has been shown above, in the hydrogen region the ohmic component of conductivity and the capacity of the electrode vary but insignificantly at all frequencies. The equilibrium capacity obtained from Šlygin's charging curve also remains constant, because the relation between φ and Q in the hydrogen region is linear. If φ is replaced by the corresponding pressure p, and Q by the fraction of the surface occupied by adsorbed atoms, the linear relation of φ to Q leads to a logarithmic relation between the adsorbed quantity and the pressure. The logarithmic adsorption isotherm has been theoretically obtained by Temkin[11]. In his derivation he dropped the assumption that the surface of the adsorbent is homogeneous and assumed that the heterogeneity of the surface is characterized by a linear relation of the differential heat of adsorption to the degree of covering. A similar relation between adsorption heat and degree of covering is also obtained if the surface is assumed to be homogeneous, but if the repulsive forces between the adsorbed atoms are accounted for. The conclusions arrived at below and based on the conception of a heterogeneous surface are thus to a certain extent equivalent to those which we should obtain taking into account the repulsive forces. A theory of hydrogen overvoltage on nickel, which takes into account the repulsive forces in the adsorbed layer, has been developed in the papers of Horiuti[12, 13] and his co-workers.

The equations of the velocity of discharge and ionization on a heterogeneous surface, characterized by a linear relation between the

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11 M. Temkin and V. Pyzhev, Acta Physicochimica URSS, **12**, 327 (1940); J. Phys. Chem. (Russ.), **13**, 851 (1939).

12 J. Horiuti and G. Okamoto, Sci. Pap. Inst. Phys. Chem. Res., **28**, 231 (1936).

13 Okamoto, Horiuti and Hirota, Sci. Pap. Inst. Phys. Chem. Res., **29**, 213 (1936).

adsorption heat and the degree of covering have been derived by Temkin[11]. He made use of Polanyi's principle that the change in the activation energy on transition, for example, from one surface element to another is equal to a fraction of the change of adsorption heat:

$$\Delta A = -\alpha \Delta \varepsilon.$$

This derivation is moreover based on the assumption of a complete surface mobility of the adsorbed atoms.

With the help of these assumptions Temkin arrived at the following equations for the rate of adsorption and desorption in the region of medium surface covering. The adsorption velocity is equal to

$$v = K_a \frac{P}{p^{\alpha}}, \tag{10}$$

and the desorption velocity to[14]

$$w = K_d p^{\beta}, \tag{11}$$

where P denotes the pressure of atomic hydrogen and p — the equilibrium pressure of atomic hydrogen corresponding to the given degree of covering of the surface.

It is now assumed that a change in the field of adsorbing forces, just as in the case of an electric field, does not change the shape of the potential curve of an atom, but only shifts it parallel to itself; then α and β, both for the influence of an electric field and for the influence of the field of adsorption forces, must have the same value. This assumption is obviously correct only for not too large changes of the field, and holds apparently in the region of medium degrees of surface covering.

If we now take into account the influence of the electric field on the process of the discharge and ionization, the following equations for the velocity are obtained:

$$i_d = K_d [\mathrm{H}^{\cdot}]\, e^{-\frac{\alpha \varphi F}{RT}} \frac{1}{p^{\alpha}}, \tag{12}$$

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[14] These equations are given in a somewhat different form in the paper by Temkin and Pyzhev[11] "Kinetics of the synthesis of ammonia on a promoted iron catalyst". In these equations the pressure p is replaced by the degree of covering according to the logarithmic isotherm $\theta = \frac{1}{f} \ln a_0 p$, where f and a_0 are constants.

$$i_i = K_i e^{-\frac{\Delta\varphi F}{RT}} p^{\beta}. \qquad (13)$$

We shall now use these equations along with the equation describing the distribution of the current similar to equation (2):

$$i = C_1 \frac{d\varphi}{dt} + K_i e^{\frac{\beta\varphi F}{RT}} p^{\beta} - K_d[\mathrm{H}^{\cdot}] e^{-\frac{\alpha\varphi F}{RT}} \frac{1}{p^{\alpha}} =$$

$$= C_1 \frac{d\varphi}{dt} + K_i e^{\frac{\beta\varphi_0 F}{RT}} e^{\frac{\beta\Delta\varphi F}{RT}} p^{\beta} - K_d[\mathrm{H}^{\cdot}] e^{-\frac{\alpha\varphi_0 F}{RT}} e^{-\frac{\alpha\Delta\varphi F}{RT}} \frac{1}{p^{\alpha}}, \qquad (14)$$

where φ is replaced by $\varphi_0 + \Delta\varphi$.

At equilibrium, that is, with $i = 0$,

$$p_0 = \frac{K_d[\mathrm{H}^{\cdot}]}{K_i} e^{-\frac{\varphi_0 F}{RT}}.$$

The pressure p corresponding to a given degree of surface covering can be expressed in terms of p_0 and the shift of potential of the hydrogen layer in the following way:

$$p = p_0 e^{-\frac{\Delta\varphi_{\mathrm{H}} F}{RT}} = \frac{K_d[\mathrm{H}^{\cdot}]}{K_i} e^{-\frac{\varphi_0 F}{RT}} e^{-\frac{\Delta\varphi_{\mathrm{H}} F}{RT}}.$$

After substituting p in equation (14) and cancelling we obtain:

$$i = C_1 \frac{d\Delta\varphi}{dt} + K_d^{\beta}[\mathrm{H}^{\cdot}]^{\beta} K_i^{\alpha} \left\{ e^{\frac{\beta(\Delta\varphi - \Delta\varphi_{\mathrm{H}})}{RT}} - e^{-\frac{\alpha(\Delta\varphi - \Delta\varphi_{\mathrm{H}})}{RT}} \right\}. \qquad (14a)$$

Since $\Delta\varphi$ is very small and $(\Delta\varphi - \Delta\varphi_{\mathrm{H}}) < \Delta\varphi$, the exponential expressions in equation (14a) can be expanded in power series; limiting ourselves to the first two terms we thus get

$$i = C_1 \frac{d\Delta\varphi}{dt} + K_d^{\beta}[\mathrm{H}^{\cdot}]^{\beta} K_i^{\alpha} \frac{F}{RT} (\Delta\varphi - \Delta\varphi_{\mathrm{H}}) =$$

$$= C_1 \frac{d\Delta\varphi}{dt} + \frac{\Delta\varphi - \Delta\varphi_{\mathrm{H}}}{K}, \text{ where } \frac{1}{K} = K_d^{\beta}[\mathrm{H}^{\cdot}]^{\beta} K_i^{\alpha} \frac{F}{RT}. \qquad (15)$$

Equation (15) is quite similar to equation (3) because the quantity $NM\Delta\theta$, as has been shown above, is equal to the shift of the potential of the hydrogen layer, $\Delta\varphi_{\mathrm{H}}$. We thus come back to the same

Table 1

The ohmic component of the electrode conductivity (in reciprocal ohms)

Solutions	Frequencies c. p. s.	0.0 V.	0.05 V.	0.1 V.	0.15 V.	0.2 V.
N HCl . . .	3375	4.8	5.0	5.4	5.3	4.8
N H_2SO_4 . .	6750	3.4	3.6	3.5	3.2	
0.2 N HBr .	6750	7.9	7.0	7.2	7.1	
N NaOH . .	6750	0.2	0.22	0.22	0.23	0.24

electric scheme of the electrode as in the case of a homogeneous surface [15] with the difference that the constant $\frac{1}{K}$, equal to the limiting value of the ohmic component of the electrode conductivity, $\frac{1}{r}$, as can be seen from equation (15) is now independent of the potential. This means that in the region of potentials corresponding to medium degrees of covering of the surface (hydrogen region) the velocity of the reaction of discharge and ionization must not depend on the potential.

As is seen from Table 1, in the potential interval between 0.0 and 0.2 V. the limiting value of the ohmic component of electrode conductivity varies by an amount of 10%. The experimental results are thus in good agreement with the above conclusion.

3. Dispersion of the capacity and ohmic conductivity with the frequency

It is interesting to ascertain whether circuit I actually corresponds to the platinum electrode, that is, to check thereby the correctness

[15] If one makes the assumption of a complete surface mobility of the atoms, then, for any type of heterogeneity of the surface, the electric scheme of the electrode will be expressed by circuit I. In fact the assumption of a complete surface mobility implies that the shift of the potential of the hydrogen layer, $\Delta\varphi_{II} = r_e M_e \Delta\varphi_e$, is the same for all the surface elements. In this case equation (3a) will have the following form:

$$i = C\frac{d\Delta\varphi}{dt} + \frac{\Delta\varphi - \Delta\varphi_{II}}{1\Big/\sum\frac{1}{r_e}},$$

that is, the same as in the case of equation (3).

of the assumption as to the complete mobility of the atoms, since on this assumption circuit I must be correct for any surface. This can be done in the following way: using circuit I we calculate from the experimental data the equilibrium capacity of the hydrogen layer C_2 and its ohmic conductivity $\frac{1}{r}$ corresponding to the velocity of the discharge of hydrogen according to circuit I, and see whether these quantities remain independent of the frequency. The capacity C_2 and the conductivity $\frac{1}{r}$ are expressed in terms of the experimental values of the capacity C, the resistance R and the capacity of the double layer C_1, according to the following formulae:

$$\frac{1}{r}=\frac{1+\omega^2 C_3^2 R^2}{R}, \tag{16}$$

$$C_2=\frac{1}{\omega^2 C_3 R^2}+C_3, \tag{17}$$

where $C_3=C-C_1$.

In the calculations given below the value of the capacity C and of the resistance R measured experimentally have been corrected for the resistance of the electrolyte situated between the test-electrode a and the polarization electrode b. As has been shown earlier, this resistance can be calculated according to formula (1). For HCl and HBr it is equal to 0.048 Ω, for H_2SO_4 to 0.077 Ω, and for NaOH to 0.080 Ω [16]. The value of the capacity of the double layer C_1 in the hydrogen region can be found in the following way. Frumkin and Šlygin [17] have found from adsorption measurements that the capacity of the double layer for a surface covered with adsorbed hydrogen is 3.7 times smaller than the capacity of the double layer in the case of a positively charged surface. In the latter case the capacity of the double layer is found from the slope of the charging curves in the region of the double layer. If one now finds the actual surface of the platinized electrode

[16] The correction for the resistance of the electrolyte was taken into account in the following way: from the complex resistance of the test-electrode, measured experimentally in the form of ohmic and capacity components, the resistance of the electrolyte was subtracted with the help of a vector diagram. The remaining resistance was again resolved into two components — capacity C and resistance R. This calculation can conveniently be carried out graphically.

[17] A. Frumkin u. A. Šlygin, Acta Physicochimica URSS, 5, 819 (1936).

by comparing the quantity of adsorbed hydrogen on platinized and on smooth platinum according to the data of Šlygin[5] and Ershler[18], the capacity of the double layer C_1 in the hydrogen layer region can be easily calculated. It is equal, in N HCl, to 19 $\mu F/cm.^2$.

In our calculations we take it, for all the solutions, as equal to 20 $\mu F/cm.^2$. The error involved, which may reach $\pm 30\%$ and even more, is easily seen to be of no importance for the calculation of the quantities $\frac{1}{r}$ and C_2 in HCl and HBr solutions, because C is much larger than C_1. This refers also to H_2SO_4 solutions at frequencies up to 3775 c. p. s. At a frequency of 6750 c. p. s. the error in the determination of the quantity C_1 may give a considerable deviation of the value of C_2 from the calculated one. In alkaline solution an error in the value of C_1 can be of importance already beginning from a frequency of 375 c. p. s.

The values calculated in this way for various frequencies at a potential of 0.06 V. are plotted in Fig. 14, and the values of C_2 are given in Table 2.

As is seen from Fig. 14, in N HCl, 0.2 N HBr and N H_2SO_4 the constancy of the values of $\frac{1}{r}$ is only observed beginning from frequencies of 3000—3500 c. p. s. At lower frequencies $\frac{1}{r}$ depends strongly

Table 2

Frequencies in c. p. s.	Equilibrium capacity of hydrogen layer, C_2, calculated according to circuit I			
	0.2 N HBr	N HCl	N H_2SO_4	N NaOH
10	1870	1860	1200	990
50	1320	1290	880	1100
125	1520	1270	860	1340
375	1130	1050	800	402
1125	1120	1100	690	145
3375	665	507	600	35
6750	520	—	725	32

[18] B. Ershler, Acta Physicochimica URSS, 7, 327 (1937).

on the frequency. In N NaOH this quantity practically does not vary starting from a frequency of 375 c. p. s.

One can see from Table 2 that the equilibrium capacity of the hydrogen layer too does not remain constant with the variation of the

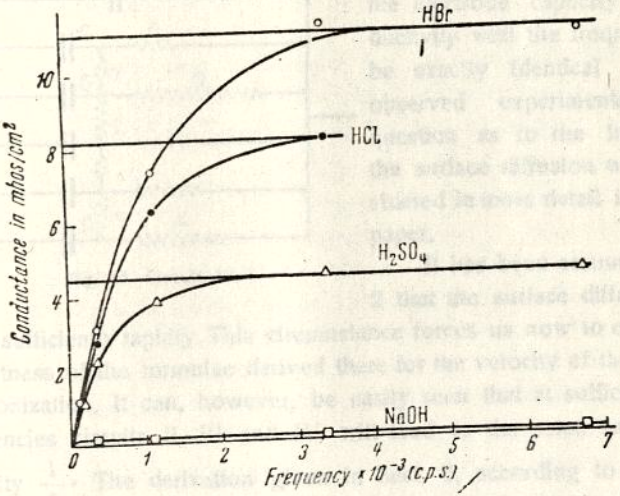

Fig. 14. Relation between the value, $\frac{1}{r}$, calculated for circuit I and the frequency.

frequency, but varies several-fold within the range mentioned. As has been shown above, this variation, at least in the case of solutions of HCl and HBr, cannot be explained by an error in the determination of the double layer capacity in the hydrogen region.

On increasing the frequency, the capacity of the hydrogen layer calculated according to circuit I will thus be considerably smaller than the equilibrium one, while $\frac{1}{r}$ calculated according to the same circuit tends to a certain limiting value; with a decrease in the frequency the capacity of the hydrogen layer tends to the equilibrium value, while $\frac{1}{r}$ decreases markedly. This character of variation of the capacity and of the value $\frac{1}{r}$ calculated according to circuit I shows that the latter does not fully correspond to the platinum electrode.

It must be noted that according to circuit IV (Fig. 15) for the platinum electrode, based on the supposition of slow surface diffusion, the character of the variation of the electrode capacity and conductivity with the frequency must be exactly identical with that observed experimentally. The question as to the influence of the surface diffusion will be considered in more detail in a special paper.

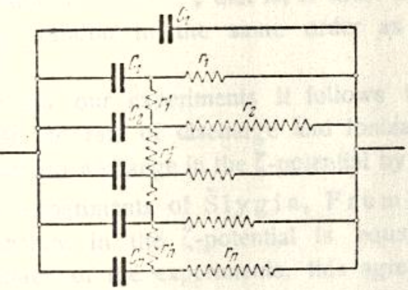

Fig. 15. Circuit IV.

It has been assumed in Sect. 2 that the surface diffusion proceeds sufficiently rapidly. This circumstance forces us now to question the correctness of the formulae derived there for the velocity of the discharge and ionization. It can, however, be easily seen that at sufficiently high frequencies circuits II, III and IV will lead to the same value of the quantity $\frac{1}{r}$. The derivation given in Sect. 2, according to which the rate of discharge and ionization does not depend on the potential over a wide range, remains therefore valid.

4. Dependence of the rate of discharge and ionization on the nature of the solution

From the curves showing the relation between the ohmic component of the electrode conductivity and the frequency (Figs. 9 and 10) it follows that the rate of the reaction of discharge and ionization increases, as a function of the nature of the solution, in the following order:

$$NaOH < H_2SO_4 < HCl < HBr.$$

With respect to the acids this order has been predicted by **Frumkin**[5] on the basis of the influence of the ζ-potential, depending on the specific adsorption of anions, on the rate of discharge and ionization.

It is well known that on metallic surfaces the specific adsorption of anions increases in the following order: $SO_4'' < Cl' < Br'$. The ζ-potential must increase in the same order. According to Frumkin's theory of the slow discharge, the rate of ionization is proportional to the expression $e^{-\frac{\beta(\varphi-\zeta)F}{RT}}$, that is, it must increase according to the nature of the solution in the same order as the specific adsorption of the anions.

From our experiments it follows that on transition from H_2SO_4 to HBr the rate of discharge and ionization increases twice. This corresponds to a change in the ζ-potential by the amount 0.048 V. According to the experiments of Šlygin, Frumkin and Medwedowsky[19] the change in the ζ-potential is equal to 0.090 V. In view of the inaccuracy of the experiments, this agreement can be considered satisfactory. The sharp difference in the kinetics of removal and formation of a hydrogen layer in alkali can be explained, apparently, by the fact that in this case we have to do with another reaction, different from that in acids. In the work of Lukowzew, Lewina and Frumkin[20] it has been shown that in the case of nickel in alkali solutions the process of removal and formation of the hydrogen layer involves mostly not $H^{\cdot}$-ions but water molecules. Such a mechanism of this process in alkali also applies to the case of the platinum electrode.

5. Dependence of the rate of discharge and ionization of hydrogen on the concentration

From equation (15) it follows that the rate of discharge and ionization in solutions of acids must depend on the concentration of hydrogen ions according to the following expression:

$$\frac{1}{r} = \frac{1}{K} = K^{\beta}_{d} K_{i}^{\alpha} [H^{\cdot}]^{\beta} \frac{F}{RT}.$$

If one assumes that $\alpha = \beta = \frac{1}{2}$, the change in the velocity of discharge and ionization observed experimentally on decreasing the concentration of the HBr solution from $0.2\,N$ to $0.03\,N$ nearly coincides with the

[19] A. Šlygin, A. Frumkin u. W. Medwedowsky, Acta Physicochimica URSS, **4**, 911 (1936).
[20] P. Lukowzew, S. Lewina and A. Frumkin, Acta Physicochimica URSS, **11**, 21 (1939).

theoretical value 2.2. We assume that in the process of removal and formation of the hydrogen layer in alkali, water molecules mainly participate. In this case, as can easily be seen, the rate of discharge and ionization depends on the concentration of OH′-ions, according to the equation:

$$\frac{1}{r}=K_d^{\beta}K_i^{\alpha}\,[\mathrm{OH}']^{\alpha}\,\frac{F}{RT}\cdot$$

Experiment shows, however, that with a 20-fold variation of the alkali concentration the rate of discharge and ionization remains practically constant. This is perhaps due to the fact that we have hitherto neglected the influence of the ionic double layer on the adsorption of hydrogen, that is, we have assumed, for example, that the hydrogen layer is not altered when the concentration of the solution varies at constant potential. This, of course, is not the case; in acids, however, this is apparently less essential than in alkalies. Besides, the circumstance that in alkalies, in contradistinction to acids, a different reaction takes place, for which α and β are, parhaps, not equal to $^1/_2$, may be of importance.

6. Variation of the capacity and ohmic conductivity with the frequency in the region of the double layer

The variation of the capacity and of the ohmic component of conductivity with the frequency is observed also in the double-layer region (Figs. 9 and 10, curves *I* and *II*). With increase of frequency, the capacity decreases in this region of potentials till a certain limiting value is reached. At a potential of 0.7 V. in HCl this limiting value is equal to 20 μF/cm.^{2}; in HBr — 19 μF/cm.^{2}; in H_2SO_4 — 15 μF/cm.^{2} and in NaOH 55—60 μF/cm.^{2}.

Such a low value of the capacity in the double-layer region at high frequencies is in contradiction with the equilibrium value of the capacity found by Šlygin[5] and Ershler[18]. In fact, if the real surface of the platinized electrode is found by comparing the amounts of hydrogen adsorbed on platinized and smooth platinum, the capacity of this electrode in the region of the double layer in HCl is equal to 71 μF/cm.^{2}, in HBr to 47 μF/cm.^{2}, and in H_2SO_4 to 65 μF/cm.^{2}. The adsorption measurements of Šlygin, Frumkin and Medwedowsky[19] have shown, on the other hand, that the charging current is used in this region mostly for charging the double layer. Besides, it has been found by Borissowa and Proskurnin[21] that the capacity of Hg at potentials for which the outer part of the double layer, just as in the case of platinum in the region mentioned, consists of anions, is equal to 40—50 $\mu F/cm.^2$. At present it is difficult to explain this contradiction; in any case such a large variation of the capacity and ohmic conductivity with the frequency in this region shows that part of the process of the adsorption of the electrolyte on a platinum electrode proceeds with a finite velocity. The absence of any rise in the capacity and ohmic conductivity curves in the anodic region for all frequencies, beginning from 50 c. p. s. in acid solutions, shows that in these solutions the process of the electrode oxidation proceeds very slowly. It is scarcely perceptible when a 50 c. p. s. current is used. In alkali, the dispersion of capacity and ohmic conductivity in this region of potentials is observed up to a frequency of 6750 c. p. s. The limiting value of the ohmic component of the electrode conductivity is in this case nearly equal to 0.37 Ω^{-1}. This means that in alkalies the process of platinum oxidation at these potentials proceeds many times faster than in acids.

Summary

1. The kinetics of the reaction of the discharge and ionization on a smooth platinum electrode in solutions of N HCl, N H_2SO_4, N NaOH, 0.2 N HCl + N KBr, 0.05 N NaOH + N $NaSO_4$ and on a poisoned electrode in N HCl was studied by measuring the capacity and the ohmic component of the electrode conductivity with a current of variable frequency in the frequency interval between 10 and 6750 c. p. s.

2. It is shown that the ohmic component of the electrode conductivity, measured with the help of an alternating current of sufficiently high frequency, is equal to the absolute rate of discharge and ionization multiplied by $\frac{F}{RT}$. These measurements thus made it possible

[21] Borissowa and M. Proskurnin, Acta Physicochimica URSS, **4**, 819 (1936).

for the first time to determine directly the velocity of a separate stag of the reaction $H_3O^{\cdot} + (Pt) + e \rightleftarrows (Pt)H + H_2O$ and to show that thi stage proceeds with a finite velocity.

3. It was established that the rate of discharge and ionization does not depend on the potential in the region corresponding to a medium degree of covering of the surface (hydrogen region). This fact can be fully accounted for if it is assumed that the surface is heterogeneous and if the heterogeneity of the surface is characterized by a linear relation between the differential heat of adsorption and the degree of covering.

4. It has been found that the rate of discharge and ionization as a function of the nature of the solution increases in the order:

$$NaOH < H_2SO_4 < HCl < HBr.$$

This order, in the part referring to acids, is explained by the influence of the specific adsorption of the ions.

5. It has been established that the oxidation of platinum proceeds very slowly in acid solutions and considerably faster in alkalies.

In conclusion we feel it our pleasant duty to express our gratitude to Prof. A. Frumkin, who proposed us this work, for his help in discussing the experimental results, and to M. Temkin for his assistance in the discussion of the influence of surface heterogeneity.

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