Kinetics of Processes on the Platinum Electrode[1,2].

III. The influence of the diffusion of molecular hydrogen on the capacity of the platinum electrode

By *A. Frumkin, P. Dolin* and *B. Ershler*

It has been shown in the preceding paper that by measuring the capacity and the ohmic component of the conductivity of a platinum electrode with an alternating current of variable frequency it is possible to measure the absolute rate of the discharge stage of H-ions:

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

In order that the influence of the evolution and solution of molecular hydrogen on the measurements with an alternating current as well as the effect of the diffusion process connected with it could be neglected, the concentration of the molecular hydrogen in the solution must be insignificant, or the rate of discharge must be much larger than the rate of evolution of molecular hydrogen.

Our measurements were carried out at potentials more anodic than that of a reversible hydrogen electrode. It can easily be shown that even for very small deviations from the hydrogen potential in the anodic direction, the influence of molecular hydrogen vanishes owing to a decrease of its concentration. On the other hand, comparison of the rate of the discharge stage for H-ions with that of the over-all process of the hydrogen evolution has shown that in HCl the rate of the former process is 27 times larger than that of the latter. This means that in the vicinity of the reversible hydrogen electrode potential, where the concentration of molecular hydrogen is considerable,

[1] P. Dolin and B. Ershler, Acta Physicochimica URSS, **13**, 747 (1940).
[2] P. Dolin, B. Ershler and A. Frumkin, Acta Physicochimica URSS, **13**, 779 (1940).

the effect of the formation of molecular hydrogen on our measurements can be avoided if the rate of charging of the electrode is of the same order as that of the stage of discharge of H-ions; it is only in this case that the advantage of the first, more rapid reaction over the second will manifest itself. If, however, the electrode is charged slowly, so that the formation of molecular hydrogen and its diffusion into the solution proceed with a velocity but slightly differing from that of the charging of the electrode, both these processes must cause a depolarizing influence and must accordingly affect the polarization capacity. One must thus expect a marked change in the capacity and in the ohmic component of the conductivity of the platinum electrode at low frequencies and in the neighbourhood of the reversible hydrogen potential.

In fact, as can be seen from Fig. 3 of our first paper and from Table 1, the capacity and ohmic conductivity curves plotted at low frequencies display a sharp rise near the potential of the reversible hydrogen electrode.

Table 1

Frequency in c. p. s.	C in μF/cm.^{2}		$\frac{1}{R}$ in mhos/cm.^{2}	
	0.0 V.	0.06 V.	0.0 V.	0.06 V.
10	2060	1410	0.133	0.036
30	1400	1040	0.23	0.084
125	713	683	1.20	0.51
375	535	560	1.41	1.21
1125	300	310	3.6	3.64
3375	132	141	4.85	5.0

The relations of the polarization capacity to the current frequency, to the concentration of the substance participating in the electrode process, and to the rate of diffusion was determined by W a r b u r g[3] and later by K r ü g e r[4].

W a r b u r g assumed that the whole current which serves to polarize the electrode is spent on changing the concentration of the substance which determines the electrode potential. He neglected the existence of a double layer at the electrode — solution boundary and his conclusions are therefore applicable to certain particular cases only.

K r ü g e r advanced a theory of the polarization capacity which accounts both for the double layer and for the influence of the diffusion of the substance which determines the potential. This theory was based on the assumption that the ions are exchanged between the solution and the metal instantaneously. Hence he found that when a weak alternating current $i = a \sin \omega t$ is passed through the electrode, the concentration c_x of the substance which determines its potential at a certain distance x from it varies with the time according to the following law:

$$c_x = c_0 - B\frac{a}{gF} e^{-\frac{x}{k'}} \cos\left(\omega t - \frac{x}{k'} + \vartheta\right), \tag{1}$$

where c_0 is the concentration of the substance in the bulk of the solution,

$$k' = \sqrt{\frac{2D}{\omega}}, \quad B = \frac{\sin\vartheta}{\sqrt{\frac{D\omega}{2}}}, \tag{2}$$

$$\operatorname{tg}\vartheta = \frac{1}{1 + \frac{C_1}{F}\left(\frac{\partial\varphi}{\partial c}\right)_{c=c_0}\sqrt{\frac{2\omega}{D}}},$$

D — the diffusion coefficient, C_1 — the capacity of the double layer, φ — the potential of the electrode.

The polarization capacity of the electrode is expressed by the following equation:

$$\overline{C} = \frac{F}{\left(\frac{\partial\varphi}{\partial c}\right)_{c=c_0}} \frac{\sqrt{\frac{D}{2\omega}}}{\sin\vartheta}. \tag{3}$$

K r ü g e r's theory was based on the instance of the mercury electrode. The potential was here determined by the concentration of the mercury ions. In our case the concentration of the hydrogen ions is assumed to remain constant, and the equilibrium potential will thus be determined by the concentration of the molecular hydrogen. In

[3] W a r b u r g, Wied. Ann., **67**, 493 (1899).
[4] K r ü g e r, Z. physik. Chem., **45**, 1 (1903).

order to apply formula (2) to our case it is necessary, therefore, to replace the concentration of mercury ions by the concentration of molecular hydrogen; c_0 denotes therefore in our case the concentration of molecular hydrogen in the solution in equilibrium with hydrogen gas at atmospheric pressure and room temperature. Further, as can easily be seen, the capacity of the double layer C_1 must be replaced by the total capacity of the electrode C at the potential at which the influence of diffusion is absent. In all the calculations given below, we assume that this takes place already at a potential which is 0.06 V. more anodic than that of the reversible hydrogen electrode. In order to apply eqs. (1) and (2) we must moreover assume that the establishment of equilibrium between the molecular hydrogen in the solution and the hydrogen adsorbed on the surface occurs instantaneously.

Substituting accordingly the numerical values of the quantities appearing in equations (2) and (3) we obtain for a HCl solution at a frequency of 10 c. p. s.

$$\operatorname{tg}\vartheta = \frac{1}{1 + \frac{1.5 \times 10^{-1}}{1.92 \times 10^{5}} \times 12.6 \times 10^{-3} \times 1.2 \times 10^{6} \sqrt{\frac{126}{4.7 \times 10^{-5}}}} = 0.84$$

and

$$\overline{C} = \frac{1.92 \times 10^{5} \times \sqrt{\frac{4.7 \times 10^{-5}}{126}}}{12.6 \times 10^{-3} \times 1.2 \times 10^{6} \times 0.65} = 12\,000 \ \mu\mathrm{F/cm.}^2.$$

From Table 1 we see, however, that in the case of a frequency of 10 c. p. s. and at the potential of the reversible hydrogen electrode the capacity is equal to 2060 μF/cm.^{2} and the ohmic component to 0.133 mho/cm.^{2}. Complex addition of these quantities gives 2930 μF/cm.^{2} for the polarisation capacity; tg ϑ is in this case equal to 0.98.

According to equations (2) and (3) the effect of diffusion of molecular hydrogen on the capacity varies inversely as the square root of the frequency. Hence this effect sould be still observed at sufficiently high frequencies, but it follows from Table 1 that already at a frequency of 125 c. p. s., no rise of the capacity curve at a potential equal to that of the reversible hydrogen electrode is to be observed.

This shows that our assumption about the instantaneous establishment of equilibrium between the dissolved and the adsorbed hydrogen is too rough an approximation for these calculations. Consequently, a complete theory of the polarization capacity of the platinum electrode must take into account, along with the diffusion velocity, the rate of electrochemical evolution and solution of molecular hydrogen.

In order to derive a formula allowing for the finite velocity of the formation of molecular hydrogen we shall make use of the circumstance that if an alternating sinusoidal current is applied to the electrode, the relation of the concentration of the substance which determines the potential of the electrode to the distance x and the time t must be the same as in Krüger's theory, that is,

$$\overline{c}_x = c_0 - Ae^{-\frac{x}{k'}} \cos\left(\omega t - \frac{x}{k'} + \vartheta\right), \tag{1a}$$

where

$$k' = \sqrt{\frac{2D}{\omega}},$$

and A is a constant.

This formula can be applied to our case because it gives the relation of the concentration of the substance to the time and the distance from a certain surface at which for some reason the concentration varies according to a sinusoidal law. With the help of equation (la) we can determine the current due to the diffusion of molecular hydrogen from the layer directly adjacent to the electrode into the bulk of the solution in the following way:

$$i_{\text{diff.}} = 2FD\left(\frac{\partial c}{\partial x}\right)_{x=0} = 2F\sqrt{D\omega}\, A \sin\left(\omega t + \vartheta + \frac{\pi}{4}\right). \tag{4}$$

This current must at any moment be equal to the current flowing from the electrode into the solution as a result of the evolution of molecular hydrogen, because in the contrary case, in the layer of the solution adjacent to the electrode, infinitely large concentrations would result.

We shall now determine the magnitude of the second current — that due to the process $H_2 \rightleftarrows H + H^{\cdot}$. According to the theory of the hydrogen overvoltage on metals adsorbing hydrogen as developed by

Frumkin[5, 6], the evolution of molecular hydrogen will proceed according to the reaction:

$$H_3O^{\cdot} + (Pt)\,H + e \rightleftarrows H_2 + H_2O + (Pt).$$

It has been shown in the first paper of this series that the kinetics of the reactions proceeding on the platinum electrode follows Temkin's kinetic equations derived for a heterogeneous surface. Hence, for the current flowing from the electrode into the solution, we obtain the following equation:

$$i_{H_2} = 2\left\{K_2\,[H^{\cdot}]\,e^{-\frac{\varphi F}{2RT}}\,p^{1/2} - K_4\,[H_2]\,e^{\frac{\varphi F}{2RT}}\,p^{-1/2}\right\}; \tag{5}$$

where K_2 and K_4 are the constants of the reactions of formation and of ionization of molecular hydrogen; $[H^{\cdot}]$ the concentration of hydrogen ions; $[H_2]$ — the concentration of molecular hydrogen, p — the pressure of the atomic hydrogen in equilibrium with a given amount of the adsorbed substance.

From the equilibrium condition we find:

$$p_0 = \frac{K_4\,[H_2]_0}{K_2\,[H^{\cdot}]}\,e^{\frac{\varphi_0 F}{RT}}.$$

Here it must be noted that in all the preceding conclusions the quantity $[H_2]$ was assumed to be constant. This assumption must now be dropped, because the problem is to allow for the influence of the variation of the concentration $[H_2]$ near the electrode on the polarization capacity. The concentration of the molecular hydrogen in equilibrium with the layer of atomic hydrogen and the ions in the double layer will be denoted with $[H_2]_0$ and the deviation from this concentration, with $\Delta\,[H_2]$.

Above we have introduced the conception of the potential of a hydrogen layer φ_H as an electrode potential at which the ions in the double layer are in equilibrium with the given amount of atomic hydrogen adsorbed on the surface.

In a similar way we shall introduce the conception of a potential φ_{H_2} corresponding to that of a hydrogen electrode in equilibrium with a given concentration of molecular hydrogen and $H^{\cdot}$-ions.

[5] A. Frumkin, Acta Physicochimica URSS, **7**, 485 (1937).
[6] P. Lukowzew, S. Lewina a. A. Frumkin, Acta Physicochimica URSS, **11**, 21 (1939).

Let us now replace $[H_2]$ and p in equation (5) by the corresponding potentials:

$$[H_2] = [H_2]_0 + \Delta\,[H_2] = Ke^{-\frac{2\varphi_0 F}{RT} - \frac{2\Delta\varphi_{H_2} F}{RT}},$$

$$p = p_0 + \Delta p = \frac{K_4\,K}{K_2\,[H^{\cdot}]}\,e^{-\frac{\varphi_0 F}{RT} - \frac{\Delta\varphi_H F}{RT}}$$

and φ by $\varphi_0 + \Delta\varphi$. Supposing that $\Delta\varphi_{H_2}$, $\Delta\varphi_H$ and $\Delta\varphi$ are small we can expand the exponential terms of the equation in power series and confine ourselves to the first two terms; this gives

$$i_{H_2} = \frac{1}{2R_d}\,(2\Delta\varphi_{H_2} - \Delta\varphi_H - \Delta\varphi), \tag{6}$$

where

$$\frac{1}{R_d} = \frac{4F}{RT}\,(K_4\,K_2\,[H^{\cdot}]\,[H_2]_0)^{1/2}$$

denotes the resistance found from the slope of the overvoltage curves at small current densities.

The latter expression is easily obtained from the equation $\frac{1}{R_d} = \frac{4S}{1+L}$ if in the equation unity is neglected in comparison with the quantity L. Such an approximation appears admissible because, according to our measurements, the equilibrium between the hydrogen layer and the ions in the double layer in the neighbourhood of the reversible hydrogen potential in HCl is established at least 27 times more rapidly than the equilibrium between the molecular hydrogen in the solution and the hydrogen adsorbed on the surface of the electrode. We can thus assume here that at low frequencies the hydrogen layer of the electrode has enough time to get into equilibrium with the ions in the double layer, *i. e.*, that $\Delta\varphi_H = \Delta\varphi$.

Hence[7]

$$i_{H_2} = \frac{1}{R_d}\,(\Delta\varphi_{H_2} - \Delta\varphi). \tag{6a}$$

[7] Equation (6a) has been derived here on the basis of eq. (5), but it is obvious that it can be derived on the basis of any overvoltage theory as well in which the current density under non-stationary conditions is unambiguously determined by the electrode potential and concentration of molecular hydrogen, *i. e.*, only one slow stage in the formation of molecular hydrogen is taken into consideration. R_d must be thereby determined from the slope of the experimental overvoltage curves in the vicinity of the equilibrium potential. The

As has been pointed out, the current flowing into the solution must be equal to the "diffusion current":

$$i_{H_2}=i_{diff}=\frac{1}{R_d}(\Delta\varphi_{H_2}-\Delta\varphi)=2F\sqrt{D\omega}\,A\sin\left(\omega t+\vartheta+\frac{\pi}{4}\right). \qquad (7)$$

For small deviations of the potential, we have $\Delta\varphi_{H_2}=-m(\Delta c)_{x=0}$, where

$$m=-\left(\frac{\partial\varphi_{H_2}}{\partial c}\right)_{c=c_0}=\frac{RT}{2Fc_0}.$$

After finding from equation (1a) $(\Delta c)_{x=0}$ and substituting it in equation (7), we obtain

$$\Delta\varphi=A\left[m\cos(\omega t+\vartheta)-n\sin\left(\omega t+\vartheta+\frac{\pi}{4}\right)\right], \qquad (8)$$

where

$$n=2F\sqrt{D\omega}\,R_d.$$

Equation (8) can be transformed as follows:

$$\Delta\varphi=AQ\sin(\omega t+\vartheta+\beta), \qquad (8a)$$

where

$$Q=\sqrt{n^2-\sqrt{2}\,nm+m^2}$$

and

$$\operatorname{tg}\beta=1-\sqrt{2}\,\frac{m}{n}.$$

The current used for charging the electrode only is equal to

$$i_e=C\frac{\partial\varphi}{\partial t}=-CAQ\omega\sin\left(\lambda-\frac{\pi}{2}\right), \qquad (9)$$

where

$$\lambda=\omega t+\vartheta+\beta.$$

We shall now resolve the diffusion current into two components: the ohmic component, which is in phase with the electrode potential, and the capacity component which is in phase with the charging current, *i. e.*, shifted with respect to the former by 90°. We thus obtain

$$i_{diff}=A\frac{n}{R_d}\sin\left(\omega t+\vartheta+\frac{\pi}{4}\right)=A\frac{n}{R_d}\sin\left(\frac{\pi}{4}+\beta\right)\sin\lambda-A\frac{n}{R_d}\times$$
$$\times\sin\left(\frac{\pi}{4}-\beta\right)\sin\left(\lambda-\frac{\pi}{2}\right). \qquad (10)$$

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theoretical meaning of the constant R_d will of course be different in different cases, but this should have no influence on our subsequent calculations, as we used values of R_d found from experimental results.

Comparing the amplitudes of the capacity component of the diffusion current with the amplitude of the charging current, we obtain the following expression for the change of the capacity due to the diffusion of the molecular hydrogen:

$$\Delta C=\frac{n\sin\left(\frac{\pi}{4}-\beta\right)}{R_dQ\omega}. \qquad (11)$$

In the same way we find the expression for the change in the ohmic component of the electrode conductivity

$$\frac{1}{\Delta R}=\frac{n\sin\left(\frac{\pi}{4}+\beta\right)}{R_dQ}. \qquad (12)$$

The quantities ΔC and $\frac{1}{\Delta R}$ calculated in this way are given in Table 2.

The values of the solubility of hydrogen and of its diffusion coefficient in aqueous solutions at room temperature necessary for the estimation of n and m were taken from the International Critical Tables.

Table 2

Frequency in c. p. s.	ΔC in μF/cm.²		C at a potential 0.06 V.	$\frac{1}{\Delta R}$ in mhos/cm.²		$\frac{1}{R}$ at a potential 0.06 V.
	calc.	experim.		calc.	experim.	
10	660	650	1410	0.17	0.10	0.036
50	65	360	1040	0.19	0.15	0.084
125	16	30	683	0.20	0.69	0.51
375	3.5	−25	560	0.19	0.21	1.20
1125	0.5	−10	310	0.18	0.00	3.64
3375	0.1	−9	141	0.18	−0.15	5.0

The coincidence between the calculated and experimental values can be considered satisfactory if it is taken into account that ΔC and $\frac{1}{\Delta R}$ are smallf ractions of the quantities C and $\frac{1}{R}$ beginning from a frequency of 50 c. p. s. in the former case and from 375 in the latter.

The more considerable deviations in the case of ΔC at 50 c. p. s. and of $\frac{1}{\Delta R}$ at 125 c. p. s. are probably due to accidental experimental errors.

From equations (11) and (13) and also from Table 2 it is clear that the quantity ΔC decreases sharply with increase of frequency while the quantity $\frac{1}{\Delta R}$ remains constant. The latter circumstance is not observed in the experimental data at high frequencies only because the quantity $\frac{1}{\Delta R}$ for large frequencies is smaller that the experimental error.

Conclusions

It is shown that Krüger's equation for the polarization capacity cannot be applied directly to the platinum electrode, because the assumption about the instantaneous establishment of equilibrium between the hydrogen ions in the solution and the hydrogen adsorbed on the surface of the electrode proves to be too rough an approximation.

A relation of the capacity and of the ohmic component of the platinum electrode conductivity to the frequency of the current is derived allowing for the finite rate of the reaction of evolution of molecular hydrogen. This relation is confirmed by experimental data.

The Karpov Institute of Physical Chemistry,
Laboratory of Surface Phenomena,
Moscow.

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