The Anodic Behavior of Cathodically Prepolarized Bright Platinum Electrode in Sulfuric Acid Solution

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Numerous accounts[1-19] have been published on the charging curve which is a variation of potential with quantity of electricity passed when a platinum electrode is forced from the equilibrium potential of hydrogen to the oxygen evolution potential with a steady direct current. The curve was distinguished principally into three stages: an initial slow rise of potential which is generally considered to correspond to ionization of hydrogen atoms which have been adsorbed on the electrode surface, rapid linear rise for charging a double layer, and finally a slow linear change to deposition of oxygen which forms an adsorbed or an oxide layer prior to the evolution of gas. In addition, Pearson and Butler[5] and also Hickling[10] found that, when the electrode was first cathodically polarized and anodic current was passed, a new stage, which consists of a horizontal portion of steady potential, which we call stage α', appeared prior to the above-mentioned three stages. Pearson and Butler considered this stage to be attributable to the ionization of free hydrogen in the solution, but Hickling explained that it may be more complex than this simple view. As to the behavior of the stage α', Breiter, Knorr and Völkl[16] found that it is considerably lengthened when the electrode was cathodically prepolarized with high current density (c. d.). They have considered that this phenomenon was ascribed to bubbles which evolved on the surface of the electrode by cathodic prepolarization. Experimental or theoretical studies on the stage α' have been done by these authors, nevertheless the results of those studies are not satisfactory, because they are only qualitative and imperfect. The present investigation was undertaken to throw some light on this problem.

Experimental

In order to establish a suitable condition for the observation, a network as shown diagrammatically in Fig. 1, similar in principle to that used by Breiter et al.[16], was used. An electrolysis cell can be fed with a steady current from Circuit I as well as from Circuit II, these currents being opposite to each other in direction, with regulated power supplies P and P′. R and R′ are variable high resistances. When, at first, the switch S_1 is closed, a steady current i_k supplied from Circuit I begins to pass through the cell. At a suitable instant the switch S_2 is closed, the other switch being left as it is, so that a steady current i_a' supplied from Circuit II, which is opposite in direction and larger in magnitude, superposes with the former, resulting in a current with the same direction as that of the latter and the amount of $i_a = i_a' - i_k$.

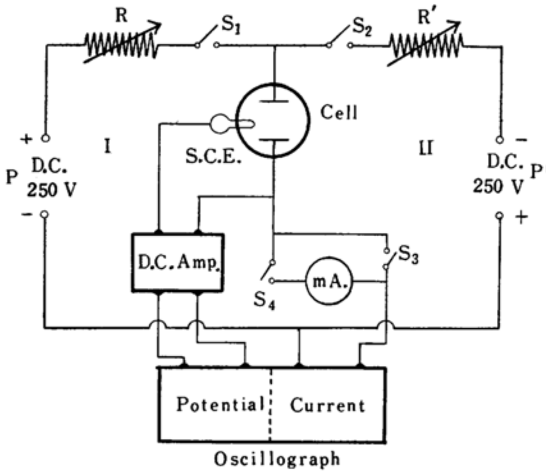

Fig. 1. Circuit diagram.

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[2] J. A. V. Butler and G. Armstrong, ibid., **137A**, 604 (1932).

[3] G. Armstrong, F. R. Himthworth and J. A. V. Butler, ibid., **143A**, 89 (1933).

[4] J. A. V. Butler and G. Drever, *Trans. Faraday Soc.*, **32**, 427 (1936).

[5] J. D. Pearson and J. A. V. Butler, ibid., **34**, 1163 (1938).

[6] B. Ershler and A. Frumkin, ibid., **35**, 464 (1939).

[7] J. A. V. Butler, "Electrocapillarity", Methuen & Co. Ltd., London (1940), p. 174.

[8] J. A. V. Butler and G. Armstrong, *J. Chem. Soc.*, **1943**, 743.

[9] A. L. Ferguson and M. B. Towns, *Trans. Electrochem. Soc.*, **83**, 271, 285 (1943).

[10] A. Hickling, *Trans. Faraday Soc.*, **41**, 333 (1945).

[11] A. Hickling, ibid., **42**, 518 (1946).

[12] G. Armstrong and J. A. V. Butler, *Discussion Faraday Soc.*, **1**, 122 (1947).

[13] B. Ershler, ibid., **1**, 269 (1947).

[14] A. Hickling and D. Taylor, *Trans. Faraday Soc.*, **44**, 262 (1948).

[15] El Wakkad and S. H. Emara, *J. Chem. Soc.*, **1952**, 461.

[16] M. Breiter, C. A. Knorr and W. Völkl, *Z. Electrochem.*, **59**, 681 (1955).

[17] M. Becker and M. Breiter, ibid., **60**, 1080 (1956).

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[19] J. Giner, ibid., **63**, 386 (1959).

The potential changes of the working electrode, measured against a saturated calomel electrode, were recorded by means of a mechanical oscillograph. All potentials referred to are on the hydrogen scale. Switch S_2 was geared with a shutter of the oscillograph. The electrolysis cell used was of H type as previously described[20]. The working electrode of bright platinum plate having an area of one square centimeter per side, the back side of which was covered with a thin layer of molten glass, was placed in one compartment, and an antipodal electrode of platinized platinum plate, having an apparent area of 2 cm², was placed in the other compartment. 1 N sulfuric acid solution made with G. R. sulfuric acid and conductivity water redistilled several times with a silica still was used as the electrolyte. Prior to use, the working electrode was carefully cleaned with hot chromic acid, hot concentrated nitric acid and finally with distilled water, and then activated by anodic polarization with a current of 100 mA./cm² for one hour in 1N sulfuric acid solution, reduced cathodically, and introduced into the cell containing the electrolyte saturated with hydrogen. After passing purified hydrogen through the electrolyte for 10 min., the cell was let stand for 5 min. with or without the passing of a given cathodic current, till it was polarized for the oscillographic observation. All experiments were carried out in a thermostat of 15°C.

Results

It was observed that the horizontal stage α' which is characteristic of the prepolarized electrode could be clearly found also for the nonpolarized electrode in the solution saturated with hydrogen at low anodic polarization c. d. as shown in Fig. 2(A). Fig. 3(A) shows a plot of q_{H_2}, the quantities of electricity required in stage α', against the anodic c. d. As to the relation between the anodic polarization c. d. i_a and the transition time τ_{H_2} of the stage α', Sand's equation is applicable[21]. As seen in

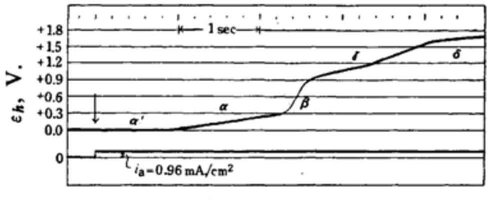

Fig. 2(A). Anodic oscillogram of the nonpolarized electrode in 1 N sulfuric acid solution saturated with hydrogen.

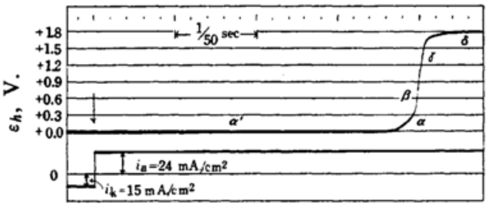

Fig. 2(B). Anodic oscillogram of the prepolarized electrode in 1 N sulfuric acid solution saturated with hydrogen.

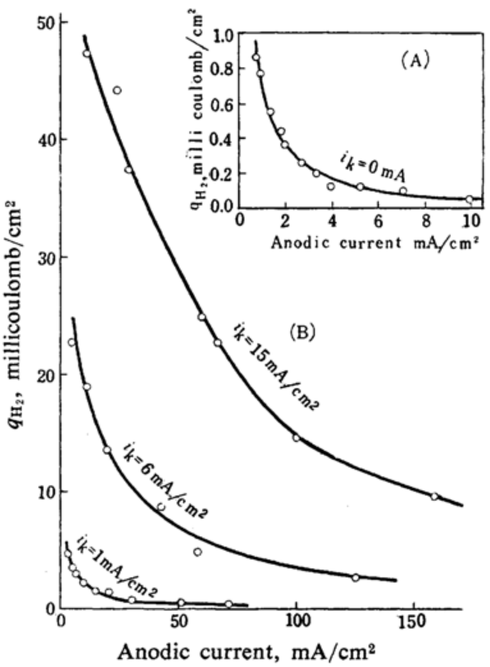

Fig. 3. Variation of q_{H_2} with anodic polarizing c. d.
(A) The nonpolarized electrode
(B) The cathodically prepolarized electrode

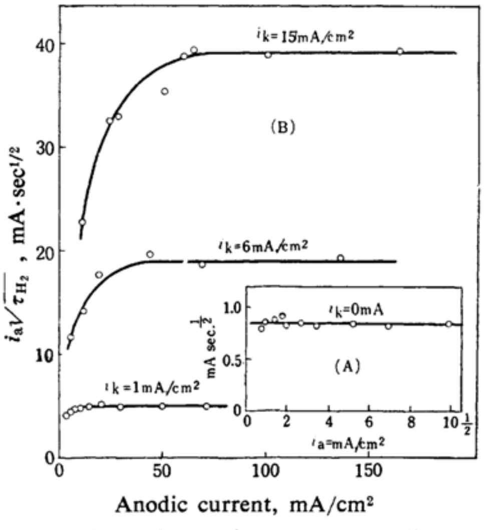

Fig. 4. Dependence of $i_a\sqrt{\tau_{H_2}}$ on anodic polarizing c. d.
(A) The nonpolarized electrode
(B) The prepolarized electrode

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[20] S. Shibata, *J. Chem. Soc. Japan, Pure Chem. Soc.* (*Nippon Kagaku Zasshi*), **79**, 239 (1958).

[21] H. J. S. Sand, *Phil. Mag.*, **1**, 45 (1901).

Fig. 4(A), $i_a\sqrt{\tau_{H_2}}$ is independent of i_a. Taking the diffusion coefficient D as 4.7×10^{-5} cm./sec.[22], we can compute the value of C^0, the result being obtained as 7.67×10^{-4} mol./l., which is in good agreement with the solubility of hydrogen 7.3×10^{-4} mol./l.[23] Consequently, the electrode reaction at the stage α' in this case is ionization of hydrogen molecule in the solution and its reaction rate is controlled by diffusion of the hydrogen.

When the electrode was led from a cathodically polarized state with a given c. d. immediately to an anodically polarized state, the stage α' was lengthened considerably, as shown in Fig. 2(B). In Fig. 3(B), q_{H_2} is traced in relation with the polarization c. d. The value of q_{H_2} decreased with the increase of i_a when i_k is kept unchanged, and increased with the increase of i_k when i_a is kept unchanged. It was found that for a given i_k the function $i_a\sqrt{\tau_{H_2}}$ in Sand's equation increased with the increase of i_a in the range of low i_a, but tended to a definite value when i_a grew sufficiently. This can be seen in Fig. 4(B). The concentration of hydrogen in the vicinity of the electrode polarized cathodically was computed with Sand's equation, taking the constant value of $i_a\sqrt{\tau_{H_2}}$ at large i_a. The results obtained were 4.08, 16.2 and 32.8×10^{-3} mol./l. for the cathodic c. d.'s of 1, 6 and 15 mA/cm², respectively.

The behavior of q_{H_2} under the turbulence of the electrolyte were studied with the rotated electrode at various rates varying up to 1500 r. p. m., i_k and i_a being kept unchanged. The result thus obtained is shown in Fig. 5. It is seen in this figure that q_{H_2} decreases quickly with the increase of the rate of rotation in the range of low rotations. This can be attributed to the removal of the hydrogen accumulated owing to the prepolarization in the solution in the vicinity of the electrode, but as the rotation becomes vigorous, the rate of this decrease diminishes. As the rate exceeds 1000 r. p. m., the value of q_{H_2} tends to a constant value independent of i_a and i_k. This value is coincident to that of the nonpolarized electrode, and suggests the vanishing of the accumulated hydrogen.

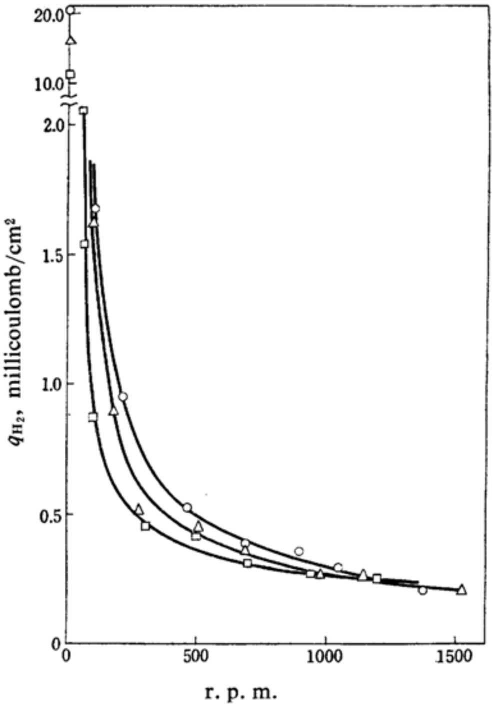

Fig. 5. Variation of q_{H_2} of the prepolarized electrode with number of rotation per min.

	i_k, mA/cm²	i_a, mA/cm²
—○—	8.85	5.0
—△—	3.0	5.0
—□—	8.85	15.3

Discussion

The fact that we have found several phenomena which need to be attributed to accumulation of hydrogen in the vicinity of the electrode leads us to assume the existence of temporary supersaturation of hydrogen. It was reported in the experiment performed by Clamroth and Knorr[24] with an active palladium electrode that the maximum value of the diffusion overpotential of the hydrogen on the cathode was $-30\sim-60$ mV. This corresponds to the fact that the concentration of hydrogen in the solution near the electrode is as $10\sim100$ times large as the saturation value at 1 atm. As such a state of high concentration must be very unstable. At the instant of the shut-off of the cathodic current the concentration should begin to fall irreversibly due to the exclusion from the solution. This process is also confirmed in the present results in the behavior of $i_a\sqrt{\tau_{H_2}}$ in reference to i_a. As seen in Fig. 4(B) the value of $i_a\sqrt{\tau_{H_2}}$ diminished considerably as i_a decreased. This discrepancy can not be understood unless it is attributed to the spontaneous exclusion of hydrogen from the solution due to the supersaturation. In order to study this point in detail, the following observation was performed. After the steady current which had kept the electrode cathodically polarized, was shut off, the electrode was left as it was for a suitable time elapse—say t —till a steady anodic current was switched on,

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[22] "International Critical Tables", Vol. V, McGraw-Hill Book Co. Inc., New York (1929), p. 63.

[23] A. Seidell, "Solubilities of Organic and Inorganic Compounds", Van Nostrand Co., New York (1940), p. 557.

[24] R. Clamroth and C. A. Knorr, *Z. Electrochem.*, 57, 399 (1953).

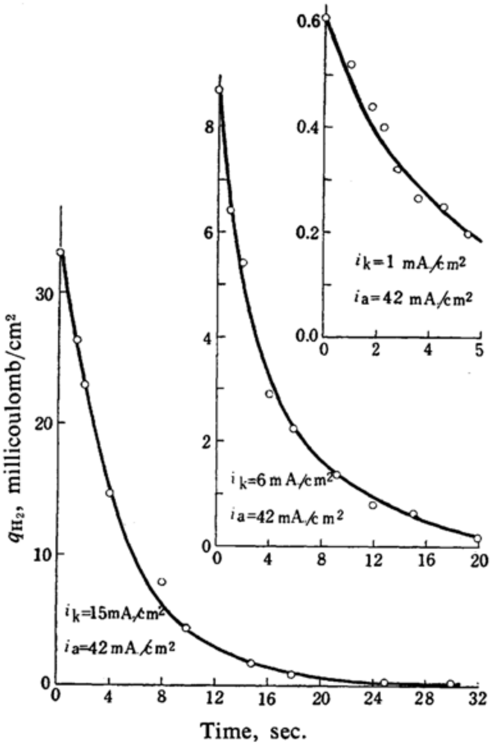

Fig. 6. Decay of q_{H_2} with standing time.

the oscillographic observation taking place simultaneously. Fig. 6 shows the relation between q_{H_2} and t. In this figure, we can see the q_{H_2} decreases with the time t, in a manner closely resembling that of the decrease of reactant in the usual chemical reaction of first order. That is to say, the spontaneous reduction of the concentration of the hydrogen should obey the following equation

$$-\mathrm{d}c/\mathrm{d}t=k({}_tC-C^0) \qquad (1)$$

where ${}_tC$ is the concentration of hydrogen in the vicinity of the electrode at the time elapse t from the instant of the shut-off of the polarizing current and k a proportional constant. Solving this equation, we obtain

$$t=-\frac{1}{k}\ln\frac{{}_tC-C^0}{{}_0C-C^0} \qquad (2)$$

where ${}_0C$ is the concentration in the vicinity of the electrode at $t=0$. As the anodic current is sufficiently large (42 mA/cm² in this experiment) for the spontaneous decrease of the concentration of the hydrogen by exclusion during τ_{H_2} to be disregarded, $\sqrt{\tau_{H_2}}$ is proportional to C as Sand's equation requires. Consequently, the total decrease of q_{H_2} during t can be regarded as corresponding to the decrease of C.

$$t=-\frac{1}{k}\ln\frac{\sqrt{{}_t\tau_{H_2}}-\sqrt{\tau^0{}_{H_2}}}{\sqrt{{}_0\tau_{H_2}}-\sqrt{\tau^0{}_{H_2}}} \qquad (2')$$

where ${}_t\tau_{H_2}$ is the transition time of stage α' consecutive to the unpolarizing time interval t, and ${}_0\tau_{H_2}$ that for $t=0$. When ${}_0C \gg C^0$, also ${}_tC \gg C^0$, Eqs. 2 and 2′ can be simplified as

$$t=-1/k\ln({}_tC/{}_0C) \qquad (3)$$

$$=-1/2k\ln({}_t\tau_{H_2}/{}_0\tau_{H_2}) \qquad (3')$$

It is seen from Fig. 7 that a plot of $\log({}_t\tau_{H_2}/{}_0\tau_{H_2})$ against standing time t is linear. From the slope of this line, the value of the rate constant was evaluated as 0.101 sec.

Now, since we can reasonably say that the rate of decay of hydrogen concentration in the vicinity of the electrode, which led from the cathodically polarized state, consists of the superposition of the decay due to the diffusion and the spontaneous decrease due to the supersaturation, it can be expressed mathematically as follows,

$$\frac{\partial C(x,t)}{\partial t}=D\frac{\partial^2 C(x,t)}{\partial x^2}-k\{C(x,t)-C^0\} \qquad (4)$$

where $C(x,t)$ is the concentration of hydrogen at a point x apart from the electrode surface at time t. While the concentration near the electrode polarizing cathodically should fall from the surface toward the bulk solution in macroscopical range, it would be natural to assume that through the thin layer in the vicinity of the surface, in which the diffusion zone would be formed during τ_{H_2} in the subsequent anodic polarization, the concentration

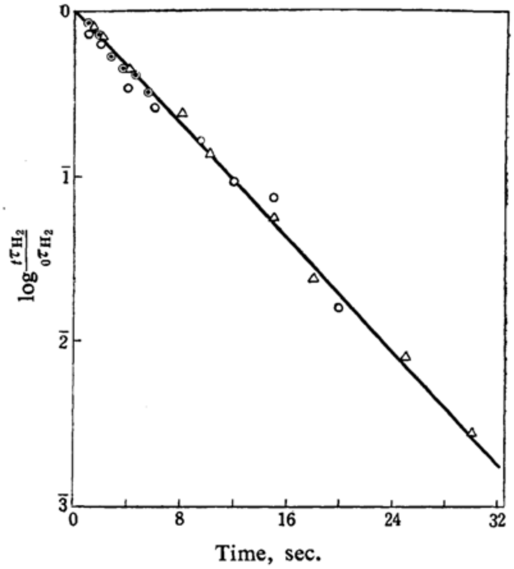

Fig. 7. A plot of $\log\frac{{}_t\tau_{H_2}}{{}_0\tau_{H_2}}$ against standing time.

i_k
—⊙— 1 mA/cm²
—○— 6 mA/cm² } i_a=42 mA/cm²
—△— 15 mA/cm²

is constant. So the initial condition can be taken as

$$C(x,0)={}_0C \tag{5}$$

The boundary condition is

$$D\left(\frac{\partial C(x,t)}{\partial x}\right)_{x=0}=\frac{i_a}{2F} \tag{6}$$

The solution of Eq. 4 which satisfies the conditions 5 and 6 is given by

$$\begin{aligned}C(x,t)={}&{}_0C\exp(-kt)+C^0\{1-\exp(-kt)\}\\&-\frac{i_a}{2F\sqrt{Dk}}\exp\left(-\sqrt{\frac{k}{D}}x\right)\\&+\frac{i_a}{4F\sqrt{Dk}}\left\{\exp\left(-\sqrt{\frac{k}{D}}x\right)\operatorname{erfc}\left(\sqrt{kt}-\frac{x}{2\sqrt{Dt}}\right)\right.\\&\left.+\exp\left(\sqrt{\frac{k}{D}}x\right)\operatorname{erfc}\left(\sqrt{kt}+\frac{x}{2\sqrt{Dt}}\right)\right\}\end{aligned} \tag{7}$$

The variation of the concentration at $x=0$ is

$$\begin{aligned}C(0,t)={}&{}_0C\exp(-kt)+C^0\{1-\exp(-kt)\}\\&+\frac{i_a}{2F\sqrt{Dk}}\operatorname{erfc}(\sqrt{kt})\end{aligned} \tag{8}$$

If we assume that $C(0,\tau_{H_2})\approx 0$, then

$$\begin{aligned}&{}_0C\exp(-k\tau_{H_2})+C^0\{1-\exp(k\tau_{H_2})\}\\&=\frac{i_a}{2F\sqrt{Dk}}\operatorname{erf}(\sqrt{k\tau_{H_2}})\end{aligned} \tag{9}$$

If $k\rightarrow 0$, we obtain Sand's equation. When ${}_0C \gg C^0$ or τ_{H_2} is sufficiently small, the second term on the left side of Eq. 9 can be neglected against other terms; then we have

$${}_0C\exp(-k\tau_{H_2})=\frac{i_a}{2F\sqrt{Dk}}\operatorname{erf}(\sqrt{k\tau_{H_2}}) \tag{10}$$

Taking logarithumus of both sides of the equation, this becomes

$$\begin{aligned}\log i_a&=\log 2F\sqrt{Dk}\,{}_0C-\{k\tau_{H_2}/2.303\\&\qquad+\log\operatorname{erf}(\sqrt{k\tau_{H_2}})\} &&(11)\\&=\log 2F\sqrt{Dk}\,{}_0C-f(\tau_{H_2}) &&(11')\end{aligned}$$

where $f(\tau_{H_2})$ in Eq. 11′ expresses the second term on the right hand side of Eq. 11. Eq. 11 is in favour of the experimental results as shown in Fig. 8. If we write ${}_0i_a$ anodic c. d. at $f(\tau_{H_2})=0$, it is obtained, by using Eq. 11′, that

$${}_0i_a=2F\sqrt{Dk}\,{}_0C \tag{12}$$

By means of Eq. 12 it is possible to calculate the initial concentration ${}_0C$ if ${}_0i_a$ is known. Using the value of ${}_0i_a$ obtained by extrapolating the curve to $f(\tau_{H_2})=0$ in Fig. 8, ${}_0C$ at cathodic c. d.'s of 1, 6 and 15 mA/cm^2 was evaluated as 4.0, 14.3 and 30.0×10^{-3} mol./l., respectively. These were in good agreement with the values obtained by calculation with Sand's equation at large i_a.

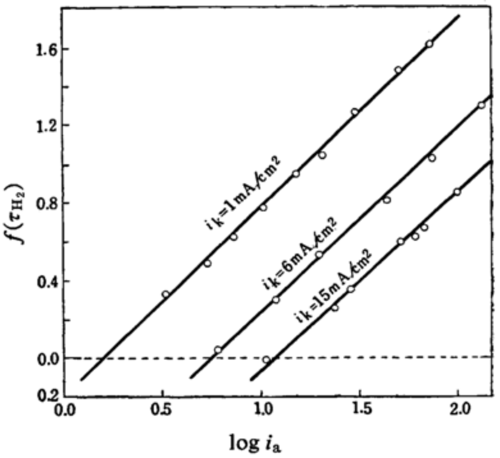

Fig. 8. Relation between $f(\tau_{H_2})$ and log i_a.

Summary

The anodic charging curves of a cathodically prepolarized bright platinum electrode in 1 N sulfuric acid solution saturated with hydrogen have been studied by means of a mechanical oscillograph.

The behavior of stage α' for anodic polarizing c. d. can be explained on the assumption that its stage is due to the molecular hydrogen accumulated in the vicinity of the electrode during the cathodic prepolarization, and that the concentration of the accumulated hydrogen decreases in the same manner as the chemical reaction of first order.

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Appendix

On writing

$$C_1(x,t)=C(x,t)-C^0 \tag{13}$$

Eq. 4 becomes

$$\frac{\partial C_1(x,t)}{\partial t}=D\frac{\partial^2 C_1(x,t)}{\partial x^2}-kC_1(x,t) \tag{14}$$

and the initial condition is given by

$$\begin{aligned}C_1(x,0)&={}_0C-C^0\\&=B\end{aligned} \tag{15}$$

the boundary condition 6 do not change.

We may attempt to find a solution of Eq. 14 by putting

$$C_1(x,t)=\psi(x)+\varphi(x,t) \tag{16}$$

where $\psi(x)$ is a function of x, $\varphi(x,t)$ is of x and t. We have to satisfy

$$\frac{\partial\psi(x)}{\partial t}=D\frac{\partial^2\psi(x)}{\partial x^2}-k\psi(x) \tag{17}$$

and

$$\frac{\partial\varphi(x,t)}{\partial t}=D\frac{\partial^2\varphi(x,t)}{\partial x^2}-k\varphi(x,t) \tag{18}$$

The general solution of Eq. 17 is

$$\psi(x)=Ae^{-\sqrt{(k/D)}x} \tag{19}$$

where A is an integration constant. Substitution by the boundary condition 6, yields

$$D\left(\frac{\partial\psi(x)}{\partial x}\right)_{x=0}=-DA\sqrt{\frac{k}{D}}$$
$$=i_a/2\boldsymbol{F}$$

Thus, we obtain

$$\psi(x)=\frac{i_a}{2\boldsymbol{F}\sqrt{Dk}}e^{-\sqrt{(k/D)x}} \tag{20}$$

If we put

$$\varphi(x,0)=B-\psi(x) \tag{21}$$
$$=\phi(x) \tag{21'}$$

the function $C_1(x,t)$ of Eq. 16 satisfy the initial condition (15), i. e.

$$C_1(x,0)=\psi(x)+\varphi(x,0)$$
$$=B$$

The function $\varphi(x,t)$ must satisfy also the boundary condition

$$D\left(\frac{\partial\varphi(x,t)}{\partial x}\right)_{x=0}=0 \tag{22}$$

The general solution of Eq. 18 is

$$\varphi(x,t)=e^{-(D\alpha^2+k)t}\cos\alpha x \tag{23}$$

According to Fourie's integral theorem we obtain

$$\varphi(x,t)=\frac{2}{\pi}\int_0^\infty \mathrm{d}\alpha\int_0^\infty \phi(\lambda)e^{-(D\alpha^2+k)t}\cos\alpha x\cos\alpha\lambda\,\mathrm{d}\lambda \tag{24}$$

Summing Eq. 19 and the integrated result of Eq. 24, and using Eq. 13 we obtain the solution 7.