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1962

SovietRxiv

Figure 1

Figure 1: Figure 1

Abstract

Full Text

PHYSICAL CHEMISTRY

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A STATIONARY ELECTROCHEMICAL PROCESS IN THE IRRADIATED SYSTEM Pt | SULFURIC ACID SOLUTION | Au

(Presented by Academician A. I. Frumkin, 9 V 1962)

In work (1), using the example of a Pt electrode in a sulfuric acid solution, the conditions for stationarity of the electrode potential in an irradiated solution were considered. This solution was regarded as a corresponding solution of products capable of being electrochemically reduced (oxidizing radiolysis products, conventionally denoted Ox) and oxidized (reducing products–Red) on a platinum electrode. The potential of the electrode in such a solution is determined by the rates of the processes occurring on it, and the condition for stationarity of its value is equality of the rates of the anodic and cathodic processes on the electrode. On a platinum electrode, equalization of these rates occurs at a potential close to the potential of the hydrogen electrode, which leads to the establishment of such a potential on the Pt electrode in the irradiated solution. Analogous questions were also considered in works (2–5).

The condition of equality of the rates of the processes occurring on the electrode may be written as:

$$I = I_{\mathrm{Red}} - I_{\mathrm{Ox}} = k_{\mathrm{Red}}[\mathrm{Red}]\exp(\varphi_{\mathrm{st}}\alpha_{\mathrm{Red}}F/RT) -$$

$$- k_{\mathrm{Ox}}[\mathrm{Ox}]\exp(\varphi_{\mathrm{st}}\alpha_{\mathrm{Ox}}F/RT) = 0,$$

where I_{Red} and I_{Ox} are the corresponding rates of oxidation of reducing radiolysis products and reduction of oxidizing radiolysis products, k_{Ox} and k_{Red} are the corresponding rate constants, and φ_{st} is the stationary value of the electrode potential.

Fig. 1. Dependence of the depolarization currents of a platinum electrode at a potential of 0.4 V on time. Point A–cessation of irradiation

Fig. 2. Electrochemical cell

Figure 2: Fig. 2. Electrochemical cell

When a directed electrochemical process is carried out on such an electrode, I must not be equal to zero; consequently, the electrode potential cannot be equal to φ_{st}. A shift of the potential from the stationary value, for example in the case of a Pt electrode toward more positive values, will lead, on the one hand, to an increase in the rate of oxidation of Red and, on the other, to a decrease in the rate of reduction of Ox, i.e., to the accumulation of oxidizing products near the electrode. As the latter accumulate, evidently, the rate of their reduction will increase, and after some time equality $I_{\mathrm{Red}} = I_{\mathrm{Ox}}$ will again occur, and the external current, equal to the rate of the total electrode process, will be equal to zero.

Figure 1 shows a curve of the dependence of the depolarization currents (total current) on irradiation time in the system Pt/0.8 N H_2SO_4 at a potential of 0.4 V, which well illustrates this point. The experimental procedure

when recording the curve was analogous to that used earlier ([6]). The difference from the previously described experiments was that in the present case there was no gas phase above the solution. The electrode was a tightly rolled Pt mesh, whose geometrical surface area was 50 cm^2. The volume of solution was 0.5 ml. With this ratio between the surface area of the electrode and the volume of the solution, the products of water radiolysis are used more completely in the electrode process, which reduces the possibility that the concentrations of oxidizing and reducing products near the electrode will be equalized by diffusion from other parts of the solution. The electrode potential was kept constant with the aid of an original potentiostat developed by V. A. Vorotyntsev. The change of current with irradiation time was recorded on an EPP-09 potentiometer. The radiation source was Co^{60}. The dose rate of irradiation was $4 \cdot 10^{16}$ eV/ml $\cdot$ s.

Fig. 2. Electrochemical cell

At the initial moment of irradiation, when the composition of the radiolysis products is close to stoichiometric, an increase in current is observed (the ascending branch of the curve), caused by preferential ionization of the reducing products at the Pt electrode. At the same time, there occurs an excess accumulation of oxidizing products and an increase in the rate of their reduction with irradiation time. Therefore the total current, after passing through a maximum, falls practically to zero. The accumulation of oxidants is also indicated by the appearance, after irradiation, of a branch of the curve corresponding to negative currents. The areas of the positive and negative branches of the curve are very close. The decrease in current on the negative branch is associated with depolarization of radiolysis products from a thin layer of solution ($\simeq 10^{-2}$ cm).

Thus, a stationary electrochemical process at one electrode, even one selective with respect to radiolysis products, cannot be carried out, since after a certain time, even at $\varphi \neq \varphi_{st}$, $I_{Red} = I_{Ox}$, i.e., the total rate of the electrode process is equal to zero. A necessary condition for carrying out a directed electrochemical process with $I \neq 0$ is preservation of the stoichiometry of the products of water radiolysis near the electrode. To realize this condition it is necessary that a second electrode be present in the same solution, on which the process of reduction of oxidizing radiolysis products will proceed.

The results of investigations (^{7,8}) show that a suitably treated Au electrode can serve as such an electrode. Owing to the potential difference between Pt and Au in the irradiated solution, when the electrodes are short-circuited to one another in an external circuit, a certain stationary current will flow—

$$I_{st} = (I_{Red} - I_{Ox})_{Pt} = (I_{Ox} - I_{Red})_{Au}.$$

Figure 2 shows a cell permitting such a stationary electrochemical process to be carried out. The electrodes (Pt and Au), made of foil 20 μ thick and insulated from one another by a glass mesh, were rolled, with the aid of special glass manipulators, into a tight roll 1 and sealed into a glass ampoule 2. The ampoule was then evacuated through the side arm 4, filled under vacuum with a degassed solution of 0.8 N H_2SO_4, and sealed. Before use the glass mesh was subjected to thorough cleaning. The preliminary treatment of the electrodes was analogous to that used in work (^{7}).

By varying the value of the resistance R across which the electrodes were short-circuited during irradiation, we were able to record the polarization characteristics of the syste-

we did. In this procedure the potential of each electrode was monitored with the aid of two platinum wires sealed into the ampoule. Their potential had a steady value close to the potential of a hydrogen electrode (^{1}). In some experiments a current equal to 5 μA was passed through the wires, and the wire that served as the cathode was used as the reference electrode. Both methods of potential monitoring gave coincident results.

Figure 3 shows the dependence of the current flowing between Pt and Au under irradiation on the potential difference between them (curve 1). The same figure shows the changes in the potentials of Pt (curve 3) and Au (curve 2) with change in current. As is seen from Fig. 3, up to the maximum current values the platinum potential changes by only 20-30 mV, whereas the gold electrode undergoes considerable polarization. Consequently, the polarizability of the entire system is practically entirely due to the polarizability of the gold electrode. Two regions can be distinguished on curve 1. In the first region, where a dependence of current on potential is observed, the total current is determined by the kinetics of the electrochemical reactions at both electrodes. In the second region the current does not depend on the potential. This region corresponds to maximum utilization of the products of radiolysis. The magnitude of the current in it, over the dose-rate interval from $2 \cdot 10^{15}$ to $4 \cdot 10^{16}$ eV/ml · sec, depends

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

linearly on the dose rate; consequently, it is limited by the rate of formation of the products of radiolysis.

Fig. 3. Dependence of the current on the potential difference between the Pt and Au electrodes (1). Dependence of the potentials of the Au (2) and Pt (3) electrodes on the magnitude of the polarizing current

Fig. 4. Dependence of the current between the Pt and Au electrodes on irradiation time: **1** –electrodes insulated with a glass mesh 200 μ thick, **2** – thickness of the glass mesh 60 μ

Figure 4 gives the dependences of the current on irradiation time at a constant potential difference between the electrodes for two cells. As is seen from the figure, within a short time the current assumes a stationary value and remains so indefinitely long; this confirms the above statements regarding the stationarity conditions of electrochemical processes in a radiation-electrochemical system.

For estimating the efficiency of the electrochemical process occurring in such a system, an essential characteristic is the characteristic of the system defined by us as the separation coefficient of the products of radiolysis

$$k = \frac{I}{I_0} = \frac{(I_{\mathrm{Red}} - I_{\mathrm{Ox}})_{\mathrm{Pt}}}{I_0} = \frac{(I_{\mathrm{Ox}} - I_{\mathrm{Red}})_{\mathrm{Au}}}{I_0}, \tag{1}$$

where I is the measured external current between the electrodes, and I_0 is the rate of formation of radiolysis products in units of current.

$$I_0 = \frac{\mathrm{F}}{\mathrm{N}} \frac{JGv}{100}, \tag{2}$$

where F is the Faraday number, N is Avogadro' s number, J is the dose rate of irradiation, G is the radiation-chemical yield of water decomposition, and v is the volume of the irradiated solution between the electrodes. At a given dose rate I_0 is a constant quantity and characterizes the maximum current value in the given system. Consequently, k depends only on those factors on which the total current I in the system depends. Its change upon shifting the po-

of the potential by a certain amount will, obviously, depend on the selectivity of the electrodes* S_{Pt} and S_{Au}. Therefore $k = f(\varphi, S_{\mathrm{Pt}}, S_{\mathrm{Au}})$. With sufficient displacement of the potential from the stationary value, it may be assumed that on Pt the oxidation process of Red proceeds predominantly, while on Au the reduction process of Ox proceeds, i.e. $(I_{\text{Red}})_{\text{Pt}} \gg (I_{\text{Ox}})_{\text{Pt}}$ and $(I_{\text{Ox}})_{\text{Au}} \gg (I_{\text{Red}})_{\text{Au}}$; then the second terms in the numerator of expression (1) may be neglected and $k = 1$.

Table 1

Electrode surface area, cm^2	Distance between electrodes*, mm	Volume of solution between electrodes, cm^3	I_0, μA	I, μA	$k = I/I_0$	J, eV/ml · sec
20	0.06	0.12	34	40	1.2	$3.8 \cdot 10^{16}$
110	0.20	2.20	640	640	1.0	$4 \cdot 10^{16}$

* The distance between the electrodes was taken to be equal to the thickness of the glass mesh.

Table 1 gives the values of k, calculated from the experimental data, for two cells with different electrode surface areas and distances between them. To calculate k, current values in the region of independence from the potential were used. The values of I_0 were calculated by formula (2) with $G_{(-\text{H}_2\text{O})} = 4.5$. The obtained values $k \simeq 1$ indicate a fairly complete separation of the radiolysis components by involving them in an electrochemical reaction at two selectively operating electrodes. It should be noted, however, that in calculating the value of I_0, only the energy absorbed by the solution itself was taken into account, which could have led to an underestimated value of I_0, and consequently to overestimated values of k.

The independence of k from the distance between the electrodes, which follows from comparison of the data in Table 1, rather indicates the complex character of this dependence, since moving the electrodes away from one another should lead to a violation of stoichiometry in the near-electrode space. Determining this dependence is of undoubted interest. The reported distances between the electrodes are not sufficiently reliable, because they depend on how tightly the electrodes are rolled into a spiral.

In summary, it may be said that in the system Pt | irradiated sulfuric acid solution | Au, it is possible to carry out a stationary electrochemical process due to the products of water radiolysis. The coefficient of utilization of the energy absorbed by the solution is $\sim 3\%$.

In conclusion, we note that the linear dependence of the current on the radiation dose rate can be used for dosimetry of γ-radiation. Such an electrochemical dosimeter, shown in Fig. 2, is very simple and requires no special power-supply devices. Testing of such a dosimeter over the course of a year showed the reliability of its use.

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Received
23 IV 1962

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[*] In paper (1) it was shown that the ratio of the rate constants of the corresponding electrode reactions, $S = k_{\text{Red}}/k_{\text{Ox}}$, may serve as a measure of the selectivity of electrodes.

Note: Figure translations are in progress. See original paper for figures.

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