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ELECTRODE REACTION OF HYDROGEN PEROXIDE IN ACIDIC SOLUTION ON MERCURY

By

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Abstract

Electrochemical reactions in acidic H_2O_2 solution were studied on Hg by a galvanostatic and a polarographic method, respectively for cathodic and anodic measurements.

Results are as follows: (i) The dependence of the rest potential, V_r , on pH, $[\text{H}_2\text{O}_2]$ and $[\text{SO}_4^{2-}]$ is $\partial V_r/\partial \text{pH}=0$, $\partial V_r/\partial \log [\text{H}_2\text{O}_2]=27 \pm 1.5 \text{ mv}$ and $\partial V_r/\partial \log [\text{SO}_4^{2-}]=-58 \pm 1 \text{ mv}$, where [] indicates the concentration. (ii) Rate equation for the cathodic reduction is $i_c = \text{const.} \cdot [\text{H}_2\text{O}_2] \cdot \exp(-0.18 FV/RT)$, being independent of pH and $[\text{SO}_4^{2-}]$, where i_c , and V are the cathodic current density and the electrode potential (N.H.E. scale), respectively. (iii) Rate equation for the anodic process is $i_a = \text{const.} \cdot [\text{SO}_4^{2-}]^{2.2} \exp(1.9 FV/RT)$, being independent of $[\text{H}_2\text{O}_2]$ and pH.

These results lead to the following conclusions; (i) the rate-determining step of the cathodic reduction is $\text{H}_2\text{O}_2 + e \rightarrow \text{OH(a)} + \text{OH}^-$ (or H_2O_2^-), where (a) designates the adsorbed state, (ii) the anodic process is not the oxidation of H_2O_2 but of Hg electrode by $2\text{Hg} + \text{SO}_4^{2-} = \text{Hg}_2\text{SO}_4 + 2e$ with the rate-determining step, $2\text{HgSO}_4^- \rightarrow (\text{HgSO}_4)_2^{2-} \text{(a)}$, and (iii) the rest potential is explained quantitatively as a mixed potential determined with the reduction of H_2O_2 to water and the oxidation of Hg to Hg_2SO_4 .

Introduction

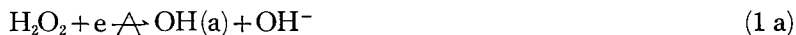
The formation of hydrogen peroxide has been discussed by many authors^{1~3)} as an intermediate of electroreduction of oxygen on various electrodes. Thus, it is of interest to study the electrochemical behaviour of hydrogen peroxide itself, as it will provide a useful information on the mechanism of oxygen electrode reaction.

Cathodic reduction of hydrogen peroxide to water has been studied by several authors on different electrodes.^{4~7)} The following mechanism for the reaction is proposed by WINKELMAN⁴⁾ and R. and H. GERISHER⁵⁾ on Pt, and also by BAGOTSKII and YABLAKOVA⁶⁾ on Hg,

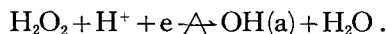
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where \nrightarrow designates the rate-determining step and (a) the adsorbed state, respectively. ANUROVA *et al.*⁷⁾ gave the following rate-determining step on carbon electrode,



BAGOTSKII and YABLAKOVA⁶⁾ arrived at the mechanism, (1a) and (1b), on Hg from the dependence of half wave potential of polarograms on pH and on hydrogen peroxide concentration.

On the other hand, the anodic oxidation of hydrogen peroxide may be superposed by other anodic process(es), *e.g.* oxidation of electrode metal, oxygen evolution, and seems not to have been studied in detail on Hg, though several works on Pt^{4,5)} and Ni⁸⁾ have been reported.

The open circuit potential on Hg, *i.e.*, its rest potential thus has not been studied in detail, especially in connection with its dependence on the solution composition.

In this paper it is the object to confirm the mechanism of the cathodic reduction on Hg by the different experimental technique, that is, the galvanostatic method and to clarify the anodic process on Hg in acidic hydrogen peroxide solution. It was then attempted on the basis of the results for the cathodic and anodic processes to interpret quantitatively the behaviour of the rest potential of the system as a function of the solution composition.

Experimental

Experiments were mainly concerned with the determination of dependence of the rest potential and the cathodic and anodic kinetics upon pH, [H₂O₂] and [SO₄²⁻], where [H₂O₂], *etc.* are the concentrations of H₂O₂, *etc.*

Cell: Cell used was the same as reported elsewhere⁹⁾. It was cleaned overnight with a mixture of 1:1 conc. sulfuric and nitric acids and then washed thoroughly by triply distilled water.

Electrodes: Test electrodes were prepared from purified Hg (spectroscopically pure) and used in the form of a hanging drop (surface area, 0.03~0.05 cm²) for studies of the cathodic reduction, or of a dropping Hg for studies of the anodic process. Counter electrode was a Hg pool (surface area, 12 cm²). Reference electrode was the reversible hydrogen electrode of platinized Pt in the solution with no H₂O₂ but of otherwise the same composition as that in the main compartment, and was isolated from the main compartment with a closed stopcock. Its potential was not affected by closing the stopcock. Reversible potential of the reference electrode was occasionally checked against the calomel electrode.

Solutions: Electrolyte solutions were sulfuric acid solutions (0.01~1N) of which ionic

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strength was in most cases controlled at 1.5 by addition of Na_2SO_4 , and was purified by pre-electrolysis for half to three days at about 3 mA. The pre-electrolysis was carried out under bubbling of purified H_2 or N_2 , by using a platinized Pt wire as an auxiliary cathode, an auxiliary anode of platinized Pt foil being placed in another compartment separated from the main one via a closed stopcock.

Materials: Hydrogen from cylinder was purified by filtering through a Pd-Ag membrane (Hydrogen purifier, LW-063, Japan Pure Hydrogen Co.). N_2 was purified by a purification train composed of a liquid N_2 cooled trap, three tubes (length, 40 cm) containing Cu net heated at 350°C , and a liquid N_2 cooled trap. Chemicals of g. r. grade, H_2O_2 (EDOGAWA Chem. Co., Tokyo), Na_2SO_4 and H_2SO_4 , were used without further purification.

Procedure: The rest potential was first measured in a static N_2 saturated solution with an electrometer (KAWAGUCHI Electric Works, NA-12E) and/or a potentiostat (YANAGIMOTO Co. V8-2010), having the input impedance of 10^{10} and more than 5×10^8 ohm, respectively. Bubbling of gas affected the rest potential value, shifting it in the negative direction. Current-potential curves for the cathodic reduction were then obtained by a galvanostatic pulse method in the range of current density from 10^{-4} to 3×10^{-1} A/cm² under the bubbling of N_2 . No effect of bubbling was observed. Anodic process was studied by a polarographic method with the potentiostat in a static solution.

A series of measurements was repeated at different concentration of H_2O_2 and H_2SO_4 with the successive additions of the respective solutions of known concentration.

The $[\text{H}_2\text{O}_2]$ in the main compartment was determined from the total volume of the solution and the added volume of H_2O_2 solution. The latter concentration was determined separately by titrations with KMnO_4 and $\text{Na}_2\text{S}_2\text{O}_3$, both giving the same results within the experimental error. The ranges of concentration studied were $10^{-3}\text{M} < [\text{H}_2\text{O}_2] < 3 \times 10^{-2}\text{M}$, $0.5\text{M} < [\text{SO}_4^{2-}] < 1.2\text{M}$ and $0.01\text{N} < [\text{H}^+] < 1.0\text{N}$ respectively. Preliminary experiments showed that the concentration change of H_2O_2 due to its spontaneous decomposition during the measurements is negligible in acidic solution. Determination of $[\text{SO}_4^{2-}]$ and pH was made similarly with the case of $[\text{H}_2\text{O}_2]$.

Experiments were carried out mainly in an atmosphere of the purified N_2 at room temperature ($22 \pm 2^\circ\text{C}$). Supplementary experiments were conducted in an atmosphere of the purified H_2 .

Potential values in this paper are expressed on the normal hydrogen electrode scale (NHE).

Results

Rest potential: Values of the rest potential, V_r , are shown in Figs. 1 and 2 as a function of $[\text{H}_2\text{O}_2]$ and $[\text{SO}_4^{2-}]$. We obtain from these Figures the following relations; $\partial V_r / \partial \log [\text{SO}_4^{2-}] = -58 \pm 1$ mv and $\partial V_r / \partial \log [\text{H}_2\text{O}_2] = 27 \pm 1.5$ mv. V_r was, however, independent of pH, *i. e.*, $\partial V_r / \partial \text{pH} = 0$. These results differ from those on Pt and Au observed by BOCKRIS and OLDFIELD,¹⁰⁾ *i. e.*, $\partial V_r / \partial \log [\text{H}_2\text{O}_2] = 0$, and $\partial V_r / \partial \text{pH} = -59$ mv.

Transient: Figures 3a and 3b show typical galvanostatic transients for the cathodic reduction of hydrogen peroxide. At relatively high current

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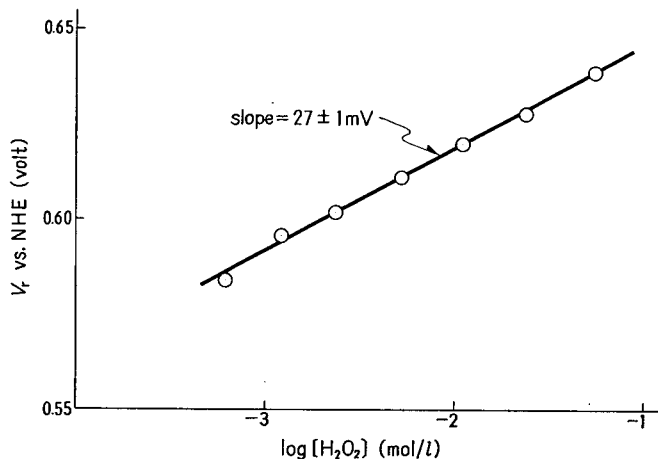


Fig. 1. Dependence of the rest potential on the concentration of H_2O_2 in 1 N H_2SO_4 solution.

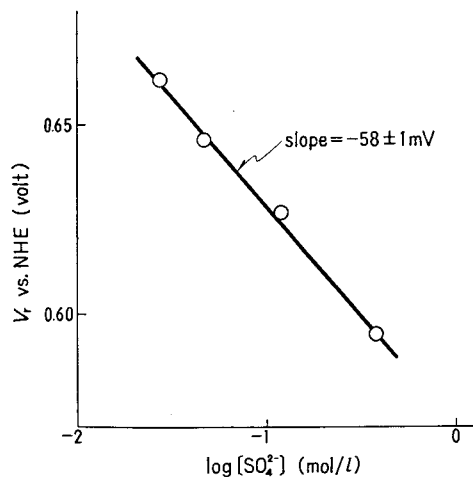


Fig. 2. Dependence of the rest potential on the concentration of SO_4^{2-} at $[H_2O_2] = 6.3 \cdot 10^{-2}$ Mol/l.

densities (Fig. 3b), the potential first changes very rapidly to a certain value and then slowly reaches a steady one. Such a slow potential change was observed at current densities larger than the limiting diffusion current of hydrogen peroxide estimated from polarograms in the same solution. When we plot the final steady value of potential in Fig. 3b as a function of current density, we obtain the Tafel line (see Fig. 5 Curve 1) which is in good agreement with that^{9,11)} of the hydrogen evolution reaction. Accordingly, in

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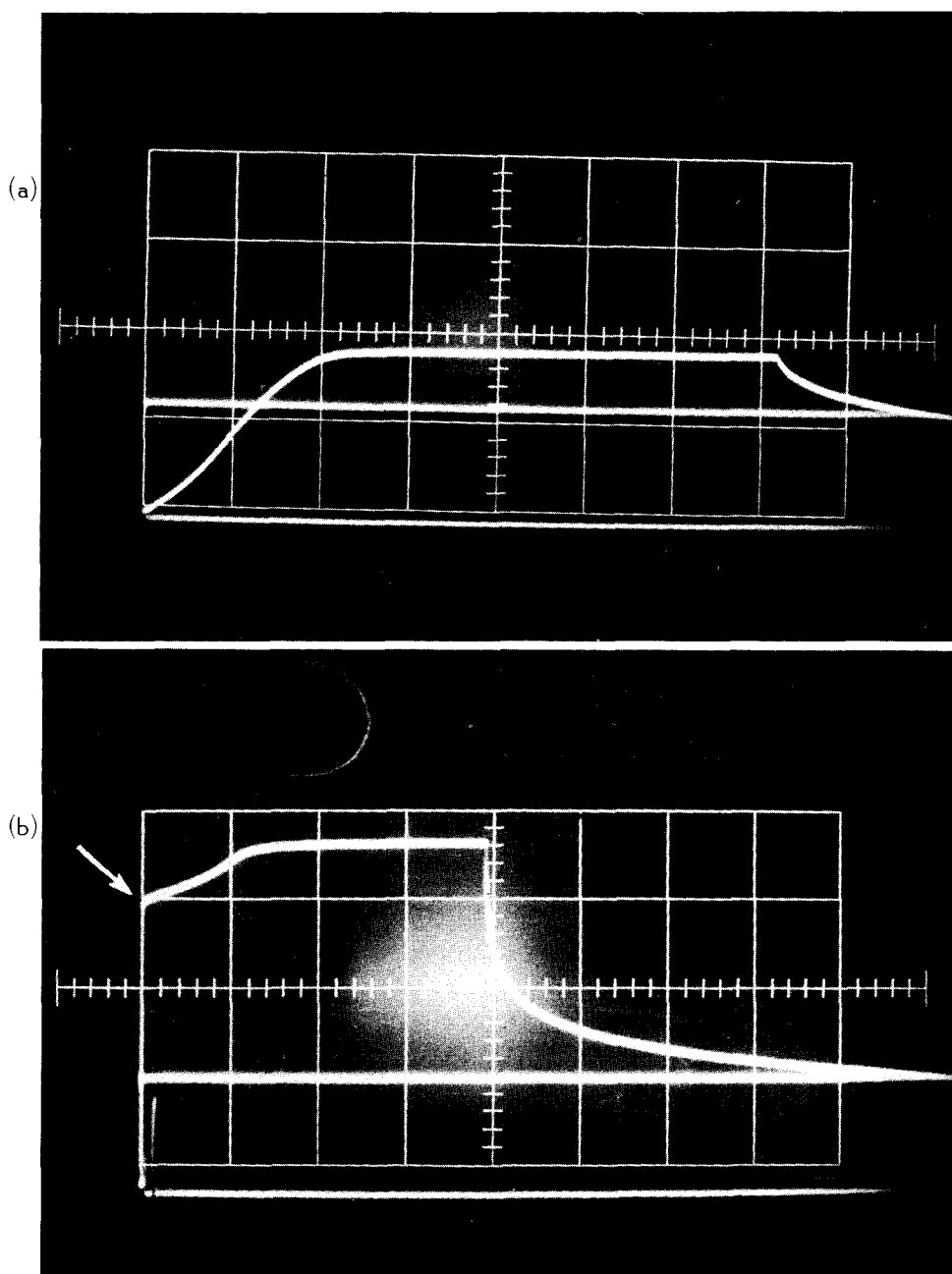


Fig. 3. Galvanostatic transient in the solution of 1 N H_2SO_4 , $[\text{H}_2\text{O}_2] = 2.2 \cdot 10^{-2} \text{ Mol/l}$. Ordinate, 0.5 v/div; (a) $i = 2.0 \cdot 10^{-3} \text{ A/cm}^2$; Abscissa, 10 msec/div. (b) $i = 2.0 \cdot 10^{-1} \text{ A/cm}^2$; Abscissa, 5 msec/div. The upper horizontal trace indicates the reference potential (-56 mV vs NHE). The lower one indicates the rest potential.

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such cases, we took the potential value at the break, shown by the arrow in Fig. 3b, as the steady potential relevant to the reduction of hydrogen peroxide.

Figure 4 shows a typical polarogram for the anodic process, where the smooth curve was obtained by connecting the current densities at the end of

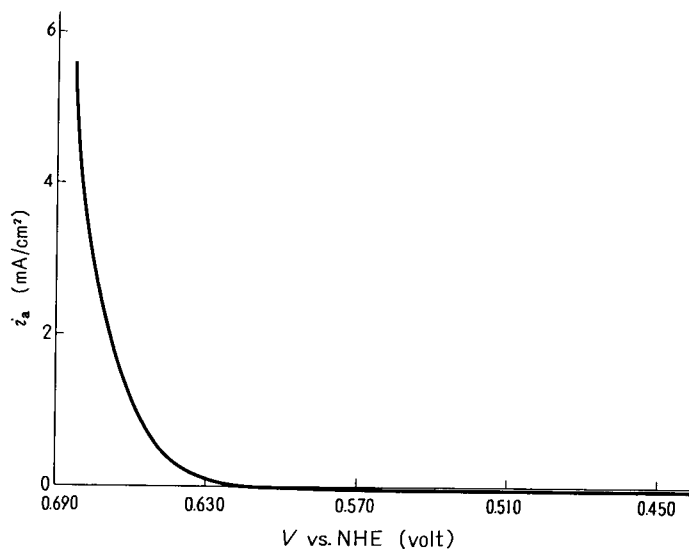


Fig. 4. Typical polarogram for anodic process in the solution of 1N H_2SO_4 , $[\text{H}_2\text{O}_2] = 2.2 \cdot 10^{-2}$ Mol/l. Sweep rate, 30 mv/min.

life of each drop. The polarogram in Fig. 4 was used to obtain the following potential-current curve for the anodic process.

V- log i_c curve for cathodic reduction: Figure 5 shows $V- \log i_c$ and $V- \log i_a$ curves for the cathodic reduction and anodic process in the presence of hydrogen peroxide in solution in an N_2 atmosphere, where V , and i_c or i_a represent the electrode potential and the cathodic or anodic current density respectively. Figure 5 includes also the $V- \log i_c$ curve for the cathodic reduction in the absence of hydrogen peroxide in H_2 atmosphere, *i.e.*, hydrogen evolution reaction. The current densities at a constant value of V , *e.g.* -0.74 v, are presented in Fig. 6 as a function of $[\text{H}_2\text{O}_2]$ at various electrolyte composition; the rate of the reduction is proportional to $[\text{H}_2\text{O}_2]$, but independent of pH and $[\text{SO}_4^{2-}]$. The latter results are in agreement with those obtained by BAGOTSKII and YABLAKOVA⁽⁶⁾ using the polarographic method, whereas their value of the Tafel slope, $0.24 \sim 0.26$ v, is smaller than the present one.

The linear part in $V- \log i_c$ curve is expressed in the present case as

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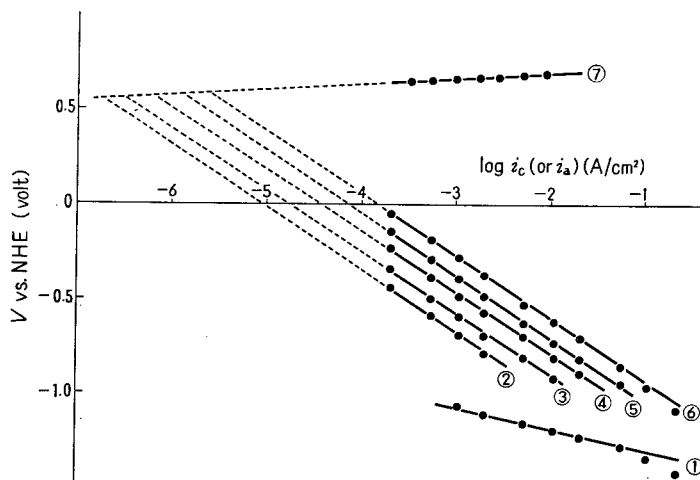


Fig. 5. $V - \log i_c$ (or i_a) curves in 1N H_2SO_4 solution as a function of $[\text{H}_2\text{O}_2]$. $[\text{H}_2\text{O}_2]$; ① 0, ② $1.3 \cdot 10^{-3}$, ③ $2.5 \cdot 10^{-3}$, ④ $5.5 \cdot 10^{-3}$, ⑤ $1.1 \cdot 10^{-2}$ and ⑥ $2.2 \cdot 10^{-2}$ Mol/l. The anodic curve ⑦ is independent of $[\text{H}_2\text{O}_2]$.

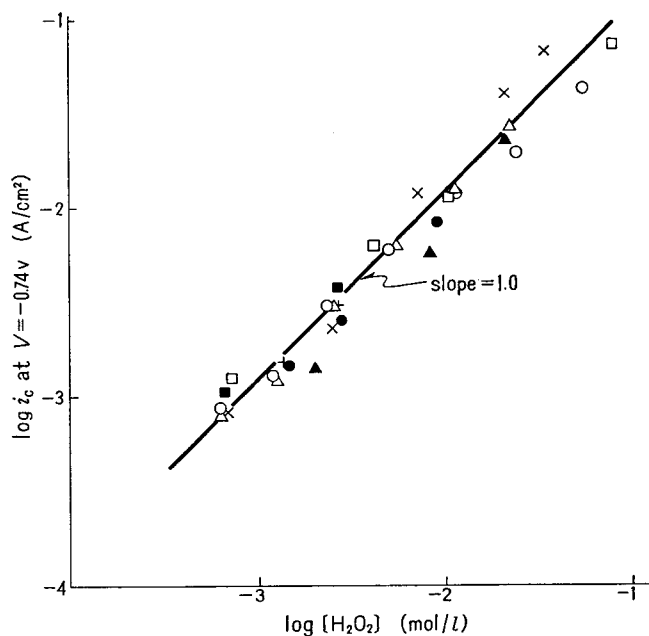


Fig. 6. Relationship between cathodic current density at $V = -0.74$ volt and $\log [\text{H}_2\text{O}_2]$.

Open symbols, in 1N H_2SO_4 ; Other symbols, in 0.1N H_2SO_4 (\times and \blacksquare , ionic strength=1.5). Different symbols correspond to the different experiments.

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$$V = -0.71 - 0.33 \log i_c + 0.33 \log [\text{H}_2\text{O}_2]. \quad (2)$$

Iofa *et al.*¹²⁾ reported the following relation,

$$V = -0.70 - 0.300 \log i_c + 0.300 \log [\text{H}_2\text{O}_2] + 0.116 \text{ pH}$$

in the solution of 0.5N $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$. This result is in agreement with the present one except for the pH dependence.

V-log i_a curve for anodic process: Anodic V -log i_a curves at different $[\text{H}_2\text{O}_2]$ and electrolyte concentrations are shown in Fig. 7. Straight V -log i_a lines are obtained with the slope of 31 mv, being independent of $[\text{H}_2\text{O}_2]$

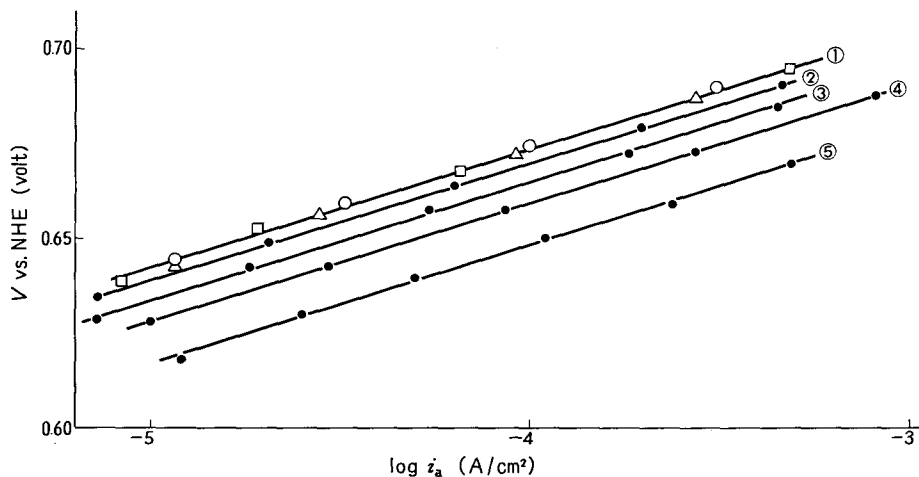


Fig. 7. V -log i_a curves as a function of $[\text{H}_2\text{O}_2]$ or $[\text{SO}_4^{2-}]$.

The curve ① is obtained at $[\text{SO}_4^{2-}] = 0.50 \text{ Mol/l}$ with various values of $[\text{H}_2\text{O}_2]$; \square 0, \triangle $6.6 \cdot 10^{-4}$ and \circ $2.6 \cdot 10^{-3}$ (in Mol/l).

The other curves are obtained at $[\text{H}_2\text{O}_2] = 0.26 \cdot 10^{-3}$ with different values of $[\text{SO}_4^{2-}]$; ② 0.58, ③ 0.66, ④ 0.81 and ⑤ 1.2 (in Mol/l).

(curve ①). The log-log plot of the current density at constant value of V , e.g. 0.65 v, against $[\text{SO}_4^{2-}]$ (Fig. 8) gives a straight line with the slope of 2.2; that is, the reaction order with respect to $[\text{SO}_4^{2-}]$ is 2.2.

In the experiments of Fig. 8, the solution composition was initially $[\text{H}_2\text{O}_2] = 2.6 \cdot 10^{-3} \text{ M}$, $\text{pH} = 2$ and ionic strength = 1.5 ($\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$), and was changed later by the successive additions of the desired amount of 18N H_2SO_4 . Thus, the pH value was not parallel with $\log [\text{SO}_4^{2-}]$. Consequently, if the rate is a function of pH, the log-log plot of Fig. 8 is expected to deviate from the linear relation. The presence of the linear relation, therefore, in-

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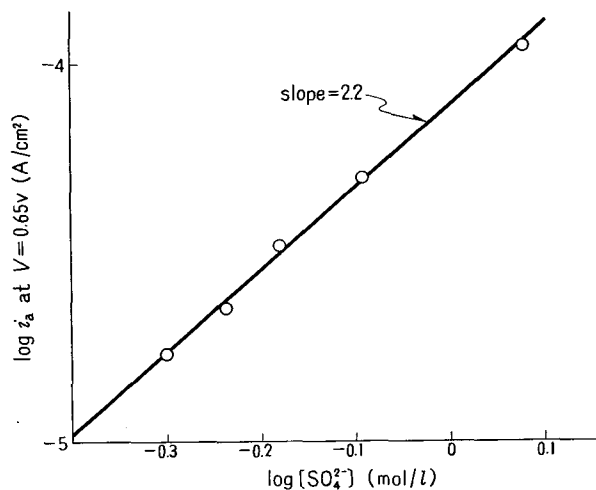


Fig. 8. Relationship between $\log i_a$ at $V=0.65$ volt and $\log [\text{SO}_4^{2-}]$ at constant value of $[\text{H}_2\text{O}_2]$, $2.6 \cdot 10^{-3}$ Mol/l.

dicates no dependency of the rate on pH.

The linear part of V - $\log i_a$ curve is thus expressed as

$$V = 0.78 + 0.031 \log i_a - 0.068 \log [\text{SO}_4^{2-}]. \quad (3)$$

Discussion

The observed kinetic parameters and the dependences of the rest potential are summarized in Table 1.

TABLE 1. Mean values of kinetic parameters and dependences of the rest potential on experimental variables

	Tafel const. α , (volt)	Constant term of Eq. (2) or (3), (volt)	Reaction order, z		
			$z(\text{H}_2\text{O}_2)$	$z(\text{H}^+)$	$z(\text{SO}_4^{2-})$
Cathodic reduction	0.18	- 0.71	1.0	0	0
Anodic process	1.9	0.78	0	0	2.2
			Obs.	Calc.	
$\partial V_r / \partial \log [\text{H}_2\text{O}_2]$			27 ± 1.5 mv	28 mv	
$\partial V_r / \partial \text{pH}$			0	0	
$\partial V_r / \partial \log [\text{SO}_4^{2-}]$			-58 ± 1 mv	-56 mv	

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Cathodic reduction: The rate of the cathodic reduction is given from Eq. (2) or Table 1 as

$$i_e = k_e [\text{H}_2\text{O}_2]^{z(\text{H}_2\text{O}_2)} \exp(-\alpha_e FV/RT) \quad (4a)$$

$$\alpha_e = 0.18, \quad z(\text{H}_2\text{O}_2) = 1, \quad (4b), (4c)$$

where k_e is the constant and F , R and T have their usual meaning. The above expression, (4a), represents the uni-directional rate of the cathodic reduction, since the equilibrium potential, V_{eq} , of the overall reaction,



is estimated at 1.56~1.71 v under present experimental conditions according to the relation¹³⁾

$$V_{eq}(\text{volt}) = 1.77 + (RT/2F) \ln [\text{H}_2\text{O}_2][\text{H}^+]^2, \quad (6)$$

whereas the potential range studied in the cathodic reduction is far more negative than the above equilibrium potential. Thus, the contribution of the backward reaction of (5) to i_e is negligible. Therefore, the i_e and the kinetic parameters in Eqs. (4) are designated as \tilde{i}_e , \tilde{k}_e , $\tilde{z}(\text{H}_2\text{O}_2)$ and $\tilde{\alpha}_e$ in what follows.

The possible mechanism in harmony with Eqs. (4) will be



where the rate-determining step is the first electron transfer to the hydrogen peroxide molecule, *i.e.*, step (7a). This mechanism is the same as that concluded by BAGOTSKII and YABLAKOVA⁶⁾ on Hg. It is to be mentioned here that the product of step (7a) is not necessarily $\text{OH(a)} + \text{OH}^-$; the intermediate, H_2O_2^- , may also be possible without conflicting with the observed kinetics.

The value of $\tilde{\alpha}_e$ (Eq. (4b)) is extraordinarily small in comparison with the value observed on the hydrogen electrode reaction¹⁴⁾. Such a small value of $\tilde{\alpha}_e$ might be attributed to an asymmetry of potential energy curves of the initial and final states of step (7a) at their intersection point (*cf.* ref. 15).

Further studies are supplemented to see whether the hydrogen in gas phase partially participates in the cathodic reaction of hydrogen peroxide. There might be a possibility that hydrogen peroxide is reduced by the adsorbed hydrogen atom, H(a) , formed from the hydrogen molecule by the step



Thus, experiments were carried out in an atmosphere of hydrogen instead

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of nitrogen, but no noticeable effect of hydrogen gas was observed on the kinetics of Eq. (2) or (4) at current densities lower than the limiting diffusion current of hydrogen molecule. Thus, the possibility of the partial participation of hydrogen gas is eliminated.

Anodic process: The experimental result that the rate is independent of the H_2O_2 concentration (Eq. (3) or Table 1) leads to the conclusion that the oxidation of hydrogen peroxide,



is not the anodic process working on Hg. This conclusion is also supported by the fact that the limiting diffusion current of the polarogram was not affected by the introduction of hydrogen peroxide into the solution. The polarographic wave of the oxidation always appears from the potential of *ca* 0.66 v, which is close to the equilibrium potential¹³⁾

$$V_{\text{eq}}(\text{volt}) = 0.615 - (RT/2F) \ln [\text{SO}_4^{2-}] \quad (10)$$

of the reaction



Thus, the most possible reaction is the oxidation of mercury itself. The formation of mercurous sulfate film during the anodic oxidation of mercury has been reported^{9,16,17).}

The rate of the anodic oxidation is expressed from Eq. (3) or Table 1 as

$$\vec{i}_a = \vec{k}_a [\text{SO}_4^{2-}]^{\vec{z}(\text{SO}_4^{2-})} \exp(\vec{\alpha}_a FV/RT), \quad (12 \text{ a})$$

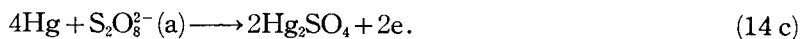
$$\vec{\alpha}_a = 1.9, \quad \vec{z}(\text{SO}_4^{2-}) = 2.2, \quad (12 \text{ b}), (12 \text{ c})$$

where kinetic parameters were taken as those of the uni-directional rate, since the potential range, in which Eq. (12a) holds, is sufficiently more positive than V_{eq} of Eq. (10) for the backward reaction of (11) to be neglected.

Possible mechanisms which satisfy Eqs. (12) are



and



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The first mechanism, (13), is taken more reasonable on the basis of the following two considerations. First, let us assume that the rate of the backward reaction of Eq. (11) in the anodic potential range is given as

$$\tilde{i}_a = \tilde{k}_a [\text{SO}_4^{2-}]^{\tilde{z}} \exp(-\tilde{\alpha}_a FV/RT), \quad (15)$$

where \tilde{k}_a , \tilde{z} and $\tilde{\alpha}_a$ are constants. At equilibrium ($V = V_{\text{eq}}$), we have $\tilde{i}_a = \tilde{i}_c$ and hence from Eqs. (12) and (15),

$$\tilde{k}_a/\tilde{k}_c = [\text{SO}_4^{2-}]^{\tilde{z}-2.2} \exp[-(1.9 + \tilde{\alpha}_a)FV_{\text{eq}}/RT] \quad (16)$$

under the assumption that the kinetic equations (12) and (15) are extensible to V_{eq} from the range of anodic potentials studied. The ratio, \tilde{k}_a/\tilde{k}_c , is related in general to the equilibrium constant, K , of Eq. (11) as⁽¹⁸⁾

$$\tilde{k}_a/\tilde{k}_c = K^{1/\nu}, \quad (17)$$

where ν is the stoichiometric number of the rate-determining step, *i.e.*, 1 and 1/2 for the step (13b) and (14b) in reference to the reaction (11). Thus, from Eqs. (16), (17) and the following relation^{(19)*}

$$\tilde{\alpha}_a + \tilde{\alpha}_c = n/\nu, \quad (18)$$

we have

$$V_{\text{eq}} = -(RT/2F) \ln K + (RT/2F) \ln [\text{SO}_4^{2-}]^{\nu(\tilde{z}-2.2)},$$

where $n=2$ according to Eq. (11). Comparison of the above equation with the Nernst equation (10) leads to

$$\nu(\tilde{z}-2.2) = -1. \quad (19)$$

Applying the values of $\tilde{\alpha}_a$ [Eq. (12 b)], and of ν 's for the respective rate-determining steps, to Eqs. (18) and (19), one obtains

$$\tilde{z} = 1.2, \quad \tilde{\alpha}_a = 0.1 \quad \text{for the first mechanism, (13)}$$

$$\tilde{z} = 0.2, \quad \tilde{\alpha}_a = 2.1 \quad \text{for the second mechanism, (14).}$$

WEIR and ENKE⁽²¹⁾ reported $\tilde{\alpha}_a = 0.3$ for the reaction, $\text{Hg}_2^{2+} + 2e \longrightarrow 2\text{Hg}$, in acidic perchlorate solution. This value is favourable for the first mechanism.

Secondly, the reaction consisting of the steps (14a) and (14b) of the second mechanism, *i.e.*,

*) PARSONS⁽²⁰⁾ has derived similar equation, $\alpha_a + \alpha_c = n/\nu$, where α_a and α_c are the Tafel constants to be observed in the anodic and cathodic branches of polarization curve for a given electrode reaction. However the $\tilde{\alpha}_a$ and $\tilde{\alpha}_c$ in Eq. (18) should correctly be the Tafel constants for the respective uni-directional rates at one and the same potential. His equation is valid only in the case that the value of α_c (or α_a) remains unchanged even in the potential range where α_a (or α_c) is observed.

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has the standard equilibrium potential of $+2.01 \text{ v}^{13)}$, which is far more positive than the potential range studied in the present case, *viz.*, $0.62 \sim 0.70 \text{ v}$. Hence, the reaction (20) will hardly occur in the present potential range.

Rest potential: It is now clear that the rest potential is determined by the cathodic reduction of hydrogen peroxide and the anodic oxidation of mercury; that is, it is a mixed potential. Dependence of the rest potential on the concentrations of reaction components is derived as follows.

Let us assume that the net cathodic and net anodic current densities are represented by the uni-directional rates respectively, *i. e.*, \vec{i}_c and \vec{i}_a , and that they are of the forms*),

$$\vec{i}_c = \vec{k}_c [\text{C}]^{\vec{z}(\text{C})} \exp(-\vec{\alpha}_c FV/RT) \quad (21 \text{ a})$$

$$\vec{i}_a = \vec{k}_a [\text{A}]^{\vec{z}(\text{A})} \exp(\vec{\alpha}_a FV/RT), \quad (21 \text{ b})$$

where C and A signify the reaction components, $\vec{z}(\text{C})$ and $\vec{z}(\text{A})$ the reaction orders, $\vec{\alpha}_c$ and $\vec{\alpha}_a$ the Tafel constants for the cathodic and anodic reactions, respectively. At the rest potential, V_r , $\vec{i}_c = \vec{i}_a$ and hence from Eqs. (21)

$$V_r = [RT/(\vec{\alpha}_c + \vec{\alpha}_a)F] \left\{ \ln(\vec{k}_c/\vec{k}_a) + \vec{z}(\text{C}) \ln[\text{C}] - \vec{z}(\text{A}) \ln[\text{A}] \right\}.$$

Thus, we obtain upon differentiation of the above equation,

$$\partial V_r / \partial \ln[\text{C}] = (RT/F) \left[\vec{z}(\text{C}) / (\vec{\alpha}_c + \vec{\alpha}_a) \right] \quad (22 \text{ a})$$

and

$$\partial V_r / \partial \ln[\text{A}] = -(RT/F) \left[\vec{z}(\text{A}) / (\vec{\alpha}_c + \vec{\alpha}_a) \right]. \quad (22 \text{ b})$$

We apply the above equations to the present system, where C and A equal H_2O_2 and SO_4^{2-} , respectively. Thus, Eqs. (22) give the values "calc" in Table 1 using the observed values of $\vec{\alpha}$'s and \vec{z} 's in Eqs. (4) and (12). Agreement between the calc. and obs. values is excellent.

Different value of $\partial V_r / \partial \text{pH} = -59 \text{ mv}$ reported by BOCKRIS and OLD-FIELD¹⁰⁾ on Pt and Au might be due to the difference of anodic process from the present one.

Table 2 shows values of V_r observed at different concentrations of hydrogen peroxide and those calculated from Eqs. (2) and (3). The latter is more negative by about 45 mv on an average than the former. This dis-

*) The rates, \vec{i}_c and \vec{i}_a in the present system, were independent of $[\text{H}^+]$ and hence we took into account only one component for the respective reactions. A general case including more than one components will be treated in a similar way²²⁾.

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TABLE 2. Calculated and observed values of the rest potential

[H ₂ O ₂] (Mol/l)	V _r (volt)		Difference (volt)
	Obs.	Calc.	
1.3·10 ⁻³	0.586	0.540	0.046
2.5·10 ⁻³	0.595	0.550	0.045
5.5·10 ⁻³	0.603	0.558	0.045
1.1·10 ⁻²	0.613	0.570	0.043
2.2·10 ⁻²	0.622	0.575	0.047

crepancy can be explained as follows. When the solution is stirred with bubbling of N₂ or H₂ gas, the rest potential shifts by about 20 mv towards negative direction. Since the potential-current curves for the cathodic reduction were independent of the bubbling, the above stirring dependence of the mixed potential leads to the conclusion that the potential-current curve of the anodic oxidation should depend on the stirring and should move to the more negative side. The anodic oxidation was studied on dropping mercury electrode of which surface is expanding continuously, resulting in the stirring of the solution near the surface. Consequently, the rest potential calculated from the kinetics of the anodic oxidation, *i.e.*, Eq. (3), and Eq. (2), will be more negative than the values observed in a static solution.

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