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ELECTRODE REACTION OF HYDROGEN PEROXIDE IN ALKALINE SOLUTION ON MERCURY

By

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Abstract

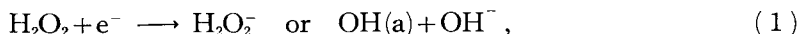
Cathodic and anodic reactions in alkaline H_2O_2 solution were studied on Hg by the galvanostatic and polarographic methods respectively. Experiments were carried out at $[\text{H}_2\text{O}_2] = 2 \sim 30 \text{ mMol/l}$, $\text{pH} = 10 \sim 13.5$ and room temperature.

Results are as follows; (i) Behaviour of the rest potential, V_r , is $\partial V_r / \partial \log [\text{H}_2\text{O}_2] = 0$ and $\partial V_r / \partial \text{pH} = -55 \text{ mv}$. (ii) Cathodic current density, i_c , is expressed as $i_c = \text{const} \cdot [\text{H}_2\text{O}_2] \cdot [\text{OH}^-]^{z(\text{OH}^-)} \exp(-0.2FV/RT)$, where $z(\text{OH}^-)$ is 0 at $\text{pH}'s < 11.6$ and -1.0 at $\text{pH}'s > 11.6$. (iii) Anodic current density, i_a , is expressed as $i_a = \text{const} \cdot [\text{H}_2\text{O}_2][\text{OH}^-]^{z(\text{OH}^-)} \exp(2.0FV/RT)$, where $z(\text{OH}^-)$ is 1.0 at $\text{pH}'s > 12$ and 2.0 at $\text{pH}'s < 12$.

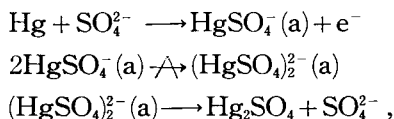
Following conclusions are deduced; (1) Cathodic reaction is the reduction of undissociated H_2O_2 molecule with the same rate-determining step, $\text{H}_2\text{O}_2 + e^- \longrightarrow \text{H}_2\text{O}_2^-$ (or $\text{OH(a)} + \text{OH}^-$), as in acidic solution, where (a) designates the adsorbed state. (2) Anodic reaction is the oxidation of HO_2^- ion with the rate-determining step, $\text{HO}_2^-(a) + \text{OH}^-(a) \longrightarrow \text{O}_2 + \text{H}_2\text{O}$. (3) The rest potential is a mixed potential determined by these two reactions and the result (i) is explained quantitatively from their kinetics, (ii) and (iii).

Introduction

Present authors studied¹⁾ electrochemical processes on Hg in acidic (H_2SO_4) H_2O_2 solution and concluded that (i) the cathodic process is the reduction of H_2O_2 , of which the rate-determining step is



where (a) designates the adsorbed state, (ii) the anodic process is the oxidation of Hg to Hg_2SO_4 and the most probable mechanism is



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where Δ represents the rate-determining step, and (iii) the rest potential is determined by these cathodic and anodic processes.

On the processes in alkaline solution at Hg, on the other hand, only a few works have been reported. The cathodic process on Hg has been studied by IOFA *et al.*²⁾ and BAGOTSKII and YABLAKOVA.³⁾ The latter authors concluded from their polarographic data that the process is the reduction of undissociated H_2O_2 molecule with the rate-determining step (1). The same conclusion was reached by MÜLLER and LANDSBERY⁴⁾ on carbon electrode. Anodic process in alkaline solution, however, seems not to have been studied on Hg. Only, the process on Ag was studied by KRASILSCHCHIKOV *et al.*⁵⁾

Present study aims to determine the mechanism of the anodic process on Hg in alkaline H_2O_2 solution and to interpret quantitatively the behaviour of the rest potential.

Experimental

Experimental apparatus and procedure essentially resembled those reported elsewhere.^{1,6)} Only the outline and supplementary aspects will be described below.

Cell of all glass type⁶⁾ contained the test and counter electrodes in its main compartment and the reference electrode of the reversible hydrogen electrode in another compartment connected *via* a closed tap to the main one. Accessories, such as capillary for dropping mercury, spoon for receiving a drop, and solution inlet, were held in the main compartment as reported earlier.⁶⁾

Electrolyte solutions were prepared from NaOH, Na_2SO_4 and conductivity water, the ionic strength of solutions being always kept at 1.5. Pre-electrolysis of solutions did not affect experimental results and hence was not conducted in most cases. All chemicals used were of guaranteed reagent grade.

After addition of a desired amount of H_2O_2 through the inlet, cathodic process was studied by the galvanostatic pulse method on the hanging mercury electrode under bubbling N_2 . Anodic one, on the other hand, was studied by the polarographic method on the dropping mercury electrode in a static solution saturated with N_2 , since the anodic galvanostatic transient was not displayed accurately on an oscilloscope owing to a small change of potential. Drop time was 3~4 sec/drop and sweep rate of potential was 30 mv/min. The polarogram thus obtained was confirmed to be independent of the sweep rate studied within the range of 10~200 mv/min.

Concentration of H_2O_2 in the electrolyte solution, $[\text{H}_2\text{O}_2]$, changes during measurement, because of its enhanced natural decomposition in alkaline solution (*ca.* 10% decrease within 15 minutes at pH=10.16 in stirred solution by N_2 bubble) and hence the concentration was determined from the diffusion current value of reduction wave of polarogram after each observation of the Tafel relation which needed only a few minutes when measurement conditions are chosen properly. The proportionality of the diffusion current to $[\text{H}_2\text{O}_2]$ was ensured separately to hold within an error of $\pm 3\%$.

Measurements were repeated with additions of H_2O_2 or NaOH solution of known

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concentration. Ranges of cathodic and anodic current densities studied (i_c and i_a), were $3 \times 10^{-4} < i_c < 10^{-1}$ and $5 \times 10^{-6} < i_a < 10^{-2}$ A/cm², respectively. Values of $[\text{H}_2\text{O}_2]$ and pH were varied in the ranges of $2 \times 10^{-3} < [\text{H}_2\text{O}_2] < 3 \times 10^{-2}$ Mol/l and $10 < \text{pH} < 13.5$, respectively.

All experiments were carried out at room temperature. Electrode potential, V , in the text is presented on the normal hydrogen electrode scale.

Results

Rest potential, V_r : The rest potential was found as in acidic solution¹⁾ to shift irregularly by 20 to 50 mv in the negative direction upon stirring of solution with N_2 bubble, whereas in a static solution a steady value was observed. The latter values are shown in Figs. 1 and 2 as a function of

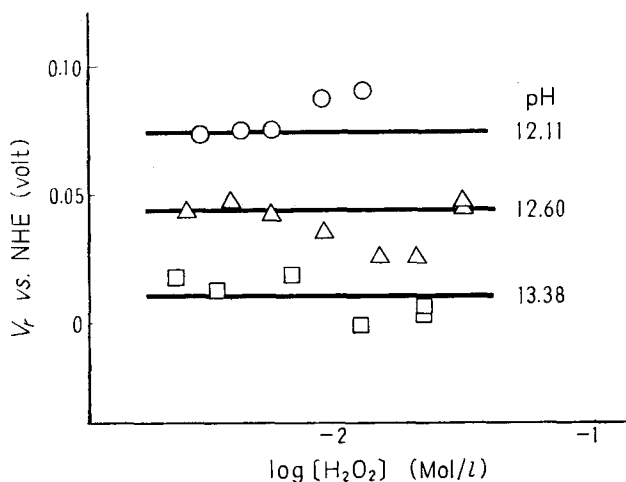


Fig. 1. Dependence of the rest potential, V_r , on $[\text{H}_2\text{O}_2]$.

$[\text{H}_2\text{O}_2]$, and pH (solution was saturated with purified N_2). Figure 1 represents the $[\text{H}_2\text{O}_2]$ dependence of V_r at different pH's. The data fluctuate to some extent but will be taken as being independent of $[\text{H}_2\text{O}_2]$. Figure 2 shows a linear relation between V_r and pH from which we have $\partial V_r / \partial \text{pH} = -55$ mv.

V -log i_c curve for cathodic process: Cathodic galvanostatic transients in alkaline H_2O_2 solution have the same form as in acidic solution.¹⁾ Steady values of potential in each transient are plotted against log i_c in Fig. 3, where i_c represents the cathodic current density. Curve ① in the figure represents the relation obtained in the absence of H_2O_2 (H_2 atmosphere). The other curves, ② to ⑦, are obtained at different $[\text{H}_2\text{O}_2]$ values in N_2 atmosphere. Current densities in the latter cases were limited below a certain value which

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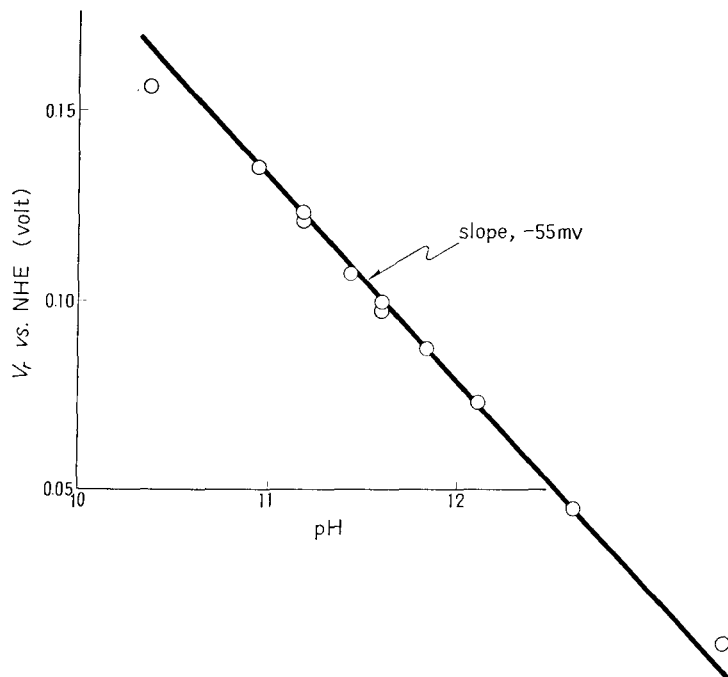


Fig. 2. Dependence of the rest potential, V_r , on pH at $[\text{H}_2\text{O}_2] = 4.0 \times 10^{-3} \text{ Mol/l.}$

corresponds to the limiting diffusion rate of H_2O_2 toward the electrode surface. The diffusion rate in current density, i_d , determined from polarogram, was *ca.* 1 or 10 mA/cm^2 respectively in the solution for ② or ⑦ in Fig. 3. Transients with higher current densities clearly revealed the concentration polarization and it was difficult to estimate the steady potential value of the cathodic reaction. The potential in these cases finally reaches that of curve ① at the same current density. All relations, ② to ⑦ are straight lines with the same slope of 0.30 v.

In Fig. 4, $\log i_c$ at $V = -1.0$ or -0.5 v is plotted against $\log [\text{H}_2\text{O}_2]$ for different pH's. Straight lines are found with the same slope of 1.0. Thus, the reaction rate is proportional to $[\text{H}_2\text{O}_2]$.

The pH dependence of i_c at constant V and $[\text{H}_2\text{O}_2]$ is given in Fig. 5. Different symbols represent the results of different series of measurement. It is seen from the figure that $\log i_c$ is independent of pH at pH's < 11.6, while changes almost linearly with pH at pH's > 11.6, the slope being minus one.

The above results are summarized by the following equation,

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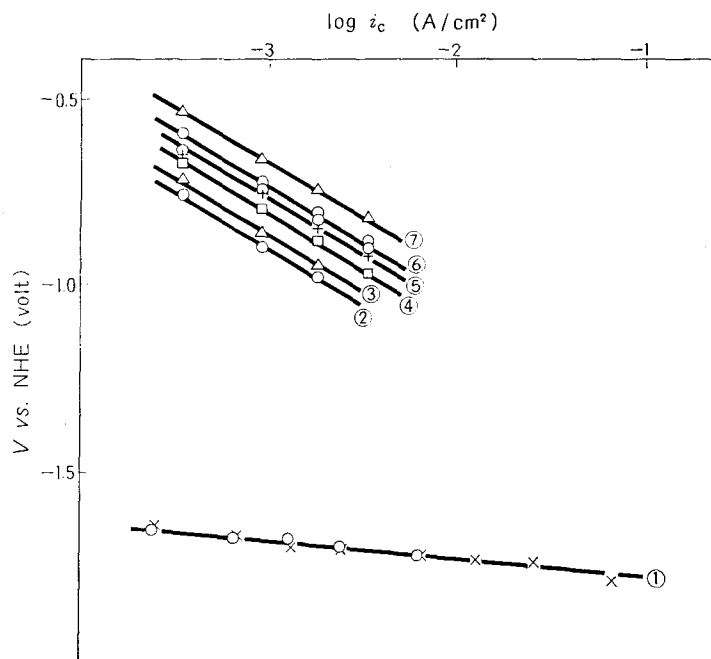


Fig. 3. $V-\log i_c$ curve as a function of $[\text{H}_2\text{O}_2]$.

Value of pH is 12.60 except for \circ and \times of ① where it is 12.38 and 13.78 respectively. Values of $[\text{H}_2\text{O}_2]$ (Mol/l) are; ① 0, ② 3.5×10^{-3} , ③ 5.3×10^{-3} , ④ 8.4×10^{-3} , ⑤ 1.4×10^{-2} , ⑥ 2.0×10^{-2} , ⑦ 2.9×10^{-2} , respectively.

$$V(\text{NHE, volt}) = -0.80 - 0.30 \log i_c + 0.30 \{ \log [\text{H}_2\text{O}_2] + z(\text{OH}^-)(\text{pH} - 11.6) \}, \quad (2a)$$

where the reaction order with respect to OH^- , $z(\text{OH}^-)$, is

$$z(\text{OH}^-) = 0 \quad (\text{pH} < 11.6) \quad \text{or} \quad -1 \quad (\text{pH} > 11.6). \quad (2b)$$

Present value of 0.30 v for the slope is slightly larger than that of BAGOTSKII and YABLAKOVA, $0.24 \sim 0.26 \text{ v}^3$, while slightly smaller than that in acidic solution, 0.33 v^1 . The constant term, -0.80 , is slightly smaller than the value, -0.71 , in acidic solution.¹⁾

Polarogram: Figure 6 shows the dependences of the half wave potential, $V_{\frac{1}{2}}$, of polarogram for cathodic process on $[\text{H}_2\text{O}_2]$ and pH. Different symbols represent the data of different series of measurement. The half wave potential does not depend on $[\text{H}_2\text{O}_2]$ in the whole range studied and also on pH at pH's < 11.5 . At pH's larger than 11.5, however, it decreases linearly

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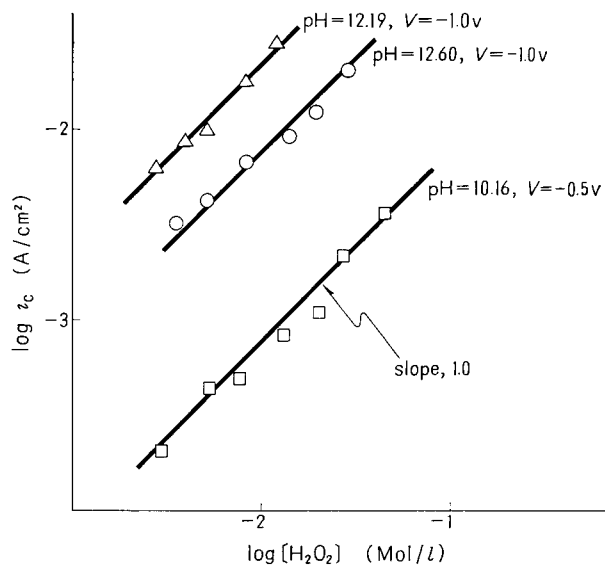


Fig. 4. Relationship between cathodic current density and $[\text{H}_2\text{O}_2]$ at different pH's and a constant potential of -1.0 or -0.5 v .

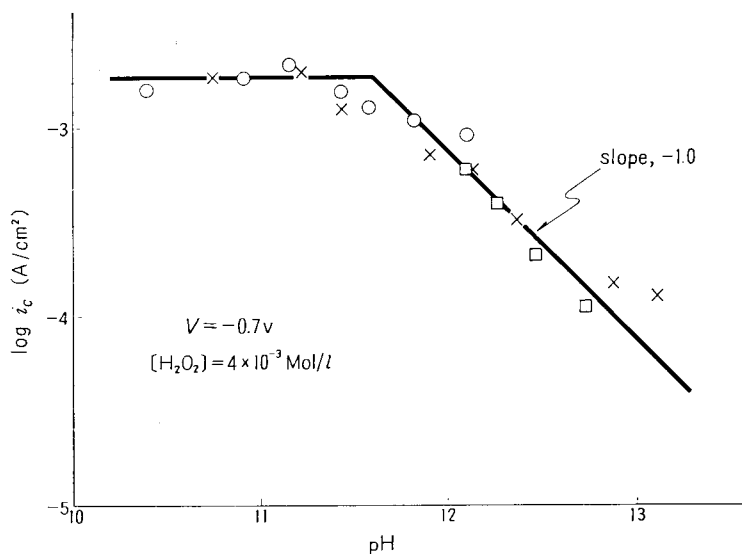


Fig. 5. Relationship between cathodic current density and pH at constant potential and $[\text{H}_2\text{O}_2]$.

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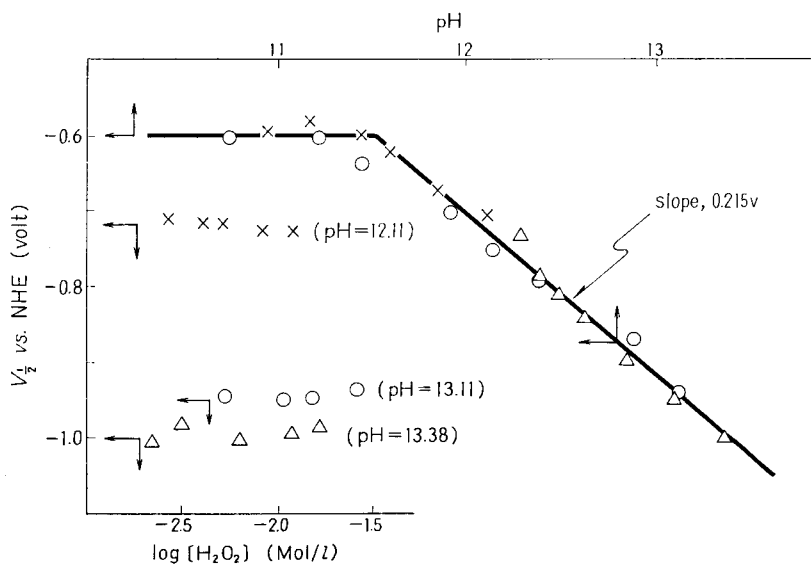


Fig. 6. Dependences of the half wave potential of cathodic polarogram, $V_{1/2}$, on pH and $[H_2O_2]$.

with increase of pH with the slope of 0.215 v. The critical value of pH, 11.5, is in agreement with that observed in Fig. 5. Figure 7 shows a series of polarograms each being taken successively with additions of NaOH solution. Dotted line in the figure is obtained in the absence of H_2O_2 . The figure shows that (1) the diffusion current of the reduction wave, $I_{a,c}$, decreases from curve ① to ⑥ owing to the natural decomposition of H_2O_2 , (2) the diffusion current of oxidation wave, $I_{a,a}$, behaves in entirely different manner from that of $I_{a,c}$; namely, $I_{a,a}$ is much smaller than the value expected from $I_{a,c}$ at low pH's and increases with increase of pH and (3) $I_{a,a}$ becomes finally almost the same with $I_{a,c}$ at pH's above 11.5 (curves, ⑤ and ⑥).

V-log i_a curve for anodic process: The TAFEL relation for anodic process, $V-\log i_a$ curve, was determined from the oxidation wave of polarogram. Here, only the initial part of the wave was used to avoid the concentration polarization effect of H_2O_2 . The initial part used always satisfied the condition that anodic current, I_a , is smaller than one tenth of $I_{a,a}$. As shown in the inset of Fig. 7, I_a was counted from the tangent at the top of the wave.

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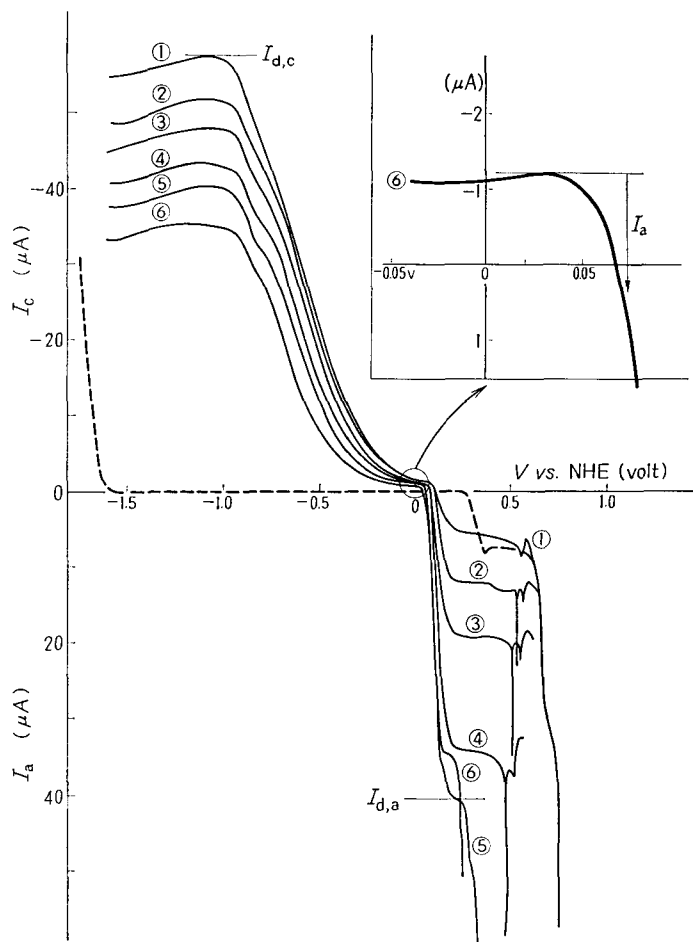


Fig. 7. Polarograms in alkaline H_2O_2 solutions.

Surface area of dropping mercury is 0.0272 cm^2 at 0.1 v . Dotted line is obtained in the absence of H_2O_2 at $\text{pH}=10.40$. Respective values of pH and $[\text{H}_2\text{O}_2]$ (Mol/ℓ) are; ① $10.40, 4.4 \times 10^{-3}$, ② $10.95, 4.2 \times 10^{-3}$, ③ $11.18, 3.9 \times 10^{-3}$, ④ $11.44, 3.5 \times 10^{-3}$, ⑤ $11.60, 3.3 \times 10^{-3}$, ⑥ $11.84, 2.9 \times 10^{-3}$, respectively.

Figure 8 shows $V-\log i_a$ curve thus obtained at various $[\text{H}_2\text{O}_2]$ values. They are linear with a common slope of 0.030 v . In the absence of H_2O_2 in solution, i_a was *ca.* 2×10^{-6} and $2 \times 10^{-5} \text{ A/cm}^2$ at 0.10 and 0.15 v respectively. These values are very much smaller than the values in the presence

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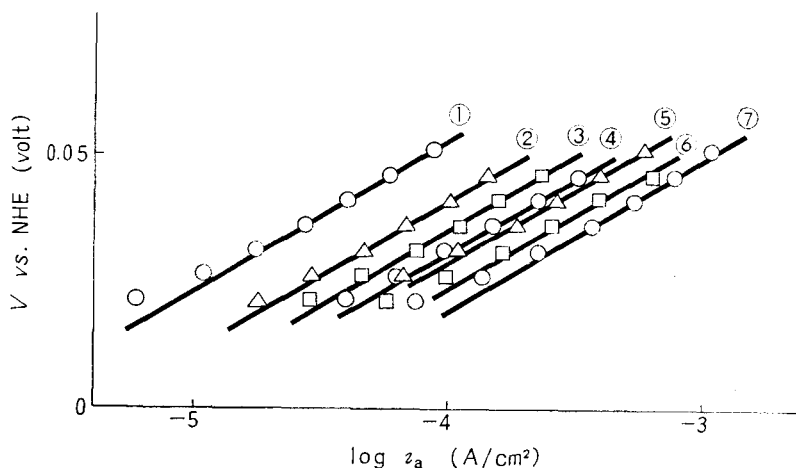


Fig. 8. V - $\log i_a$ curve as a function of $[\text{H}_2\text{O}_2]$ at $\text{pH}=12.60$.

Values of $[\text{H}_2\text{O}_2]$ (Mol/l) are; ① 2.0×10^{-3} , ② 3.5×10^{-3} , ③ 5.3×10^{-3} , ④ 8.4×10^{-3} , ⑤ 1.4×10^{-2} , ⑥ 2.0×10^{-2} , ⑦ 2.9×10^{-2} , respectively.

of H_2O_2 as seen from Fig. 8 (smaller by more than three orders at the same potential). Anodic process in the absence of H_2O_2 will be the oxidation of Hg to HgO ,^{6,7)} where the shape of oxidation wave (dotted line in Fig. 7) is different from others and indicates the formation of HgO and then oxygen evolution.

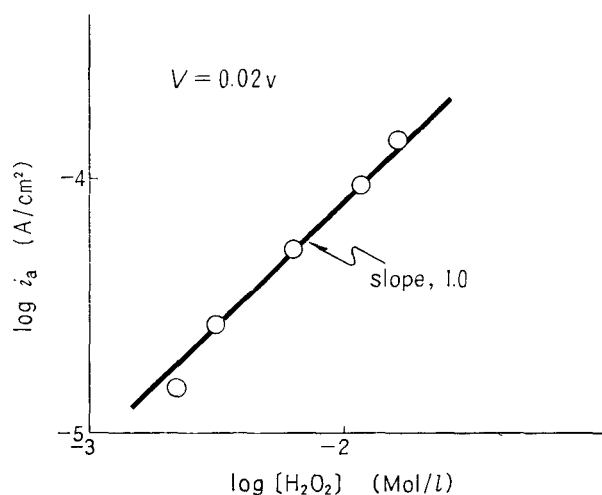


Fig. 9. Relationship between anodic current density and $[\text{H}_2\text{O}_2]$ at constant pH and potential.

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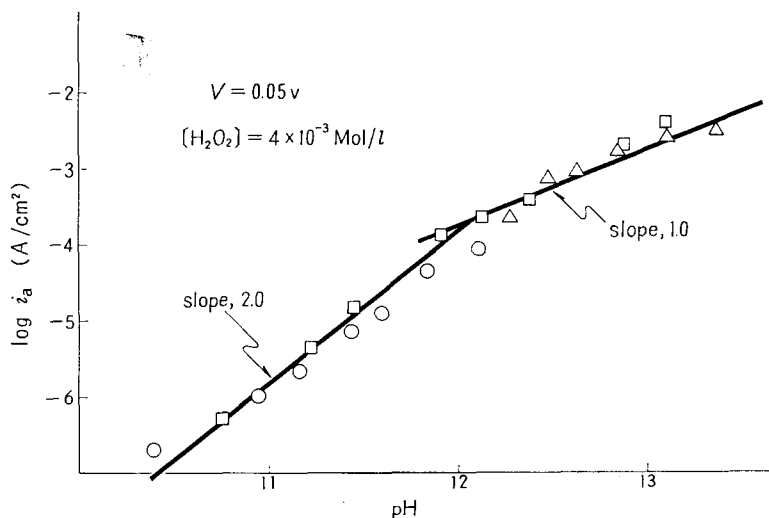


Fig. 10. Relationship between anodic current density and pH at constant potential and $[H_2O_2]$.

Dependence of i_a on $[H_2O_2]$ at a constant potential is illustrated in Fig. 9, where one can see that the reaction is the first order with respect to H_2O_2 . Figure 10 shows the dependence of i_a on pH at constant V and $[H_2O_2]$, from which we have $\partial \log i_a / \partial \text{pH} = 2.0$ at pH's < 12 and 1.0 at pH's > 12 , respectively. Thus, the linear relation of $V - \log i_a$ curve is expressed as

$$V(\text{NHE, volt}) = 0.091 + 0.030 \log i_a - 0.030 \{ \log [H_2O_2] + z(\text{OH}^-)(\text{pH} - 12) \}, \quad (3a)$$

where

$$z(\text{OH}^-) = 1 \quad (\text{pH} > 12) \quad \text{or} \quad 2 \quad (\text{pH} < 12). \quad (3b)$$

KRASILSCHCHIKOV *et al.*⁵⁾ studied the anodic process on Ag. Their rate expression, however, includes no concentration term with respect to H_2O_2 .

Discussion

Experimental results are summarized in Table 1, where the values in parenthesis are those obtained by BAGOTSKII and YABLAKOVA.³⁾

Cathodic reaction: The presence of H_2O_2 in solution reduces the cathodic polarization to a great extent (by more than 0.7 v at a constant i_c , Fig. 3) and the rate of cathodic process is proportional to $[H_2O_2]$. Hence, we conclude that the cathodic process is

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TABLE 1. Kinetic parameters of the cathodic and anodic reactions and dependences of the rest potential on pH and $[H_2O_2]$.

	slope of the TAFEL relation (volt)	Const. term of Eq. (2a) or (3a), (volt)	Reaction order	
			$z(H_2O_2)$	$z(OH^-)$
Cathodic reduction	0.30 [0.24~0.26]	- 0.80	1.0 [1.0]	0, (pH<11.6) [0, (3<pH<11)] -1.0, (pH>11.6) [-1.0, (pH>11)]
Anodic oxidation	0.030	0.091	1.0	2.0, (pH<12) 1.0, (pH>12)
Dependences of V_r		Obs. (mv)	Calc. (mv)	
$\partial V_r / \partial \log [H_2O_2]$		0	0	
$\partial V_r / \partial \text{pH}$		-55	-54	

Values of [] are those of BAGOTSKII and YABLAKOVA³⁾.



The equilibrium potential of the above reaction is given as³⁾

$$V_{\text{eq.c}}(\text{NHE, volt}) = 1.77 + (RT/2F) \ln [H_2O_2][H^+]^2$$

and estimated at *ca* 1.0 v under the present experimental conditions ($V_{\text{eq.c}}$ is 0.96 v at pH=12 and $[H_2O_2]=10^{-3}$ Mol/l). The potential range concerned in the present study is from 0 to -1.0v (Fig. 3) and far apart from the above value of $V_{\text{eq.c}}$. We thus assume that the rate expression of Eqs. (2a) and (2b) represents that of unidirectional rate and is rewritten as follows;

$$\vec{i}_c = \vec{k}_c [H_2O_2][OH^-]^{\bar{z}(OH^-)} \exp(-0.2 FV/RT), \quad (5a)$$

where

$$\bar{z}(OH^-) = 0 \text{ (pH<11.6) or } -1.0 \text{ (pH>11.6)} \quad (5b)$$

and \vec{k}_c is constant and other symbols have their usual meaning.

BAGOTSKII and YABLAKOVA³⁾ studied the cathodic reaction by polarographic method and explained their results by the discharge of undissociated H_2O_2 molecule. Characteristic behaviour of $\bar{z}(OH^-)$ of Eq. (5b) will be explained below in accord with BAGOTSKII and YABLAKOVA³⁾ assuming that

the rate of the cathodic reaction (4) is determined by the step,^{*)}



Concentration of the undissociated H_2O_2 molecule is dependent of solution pH because of the dissociation reaction,



and its value, $[\text{un} \cdot \text{H}_2\text{O}_2]$, is given as

$$[\text{un} \cdot \text{H}_2\text{O}_2] = [\text{H}_2\text{O}_2] / (1 + K_a[\text{OH}^-]/K_w), \quad (8)$$

where K_a and K_w are the dissociation constant of H_2O_2 and the ion product of water respectively and $[\text{H}_2\text{O}_2]$ is the analytical concentration of H_2O_2 .

The rate expression for Eq. (6) is given assuming the mass action law as,

$$\dot{i}_c = \tilde{k}_c [\text{un} \cdot \text{H}_2\text{O}_2] \exp(-\tilde{\alpha}_c FV/RT), \quad (9)$$

where $\tilde{\alpha}_c$ is the TAFEL constant and is found at 0.2 in the present case. From Eqs. (8) and (9), we have at $1 \gg K_a[\text{OH}^-]/K_w$

$$\dot{i}_c = \tilde{k}_c [\text{H}_2\text{O}_2] \exp(-0.2 FV/RT) \quad (10a)$$

or at $1 \ll K_a[\text{OH}^-]/K_w$

$$\dot{i}_c = (\tilde{k}_c K_w / K_a) [\text{H}_2\text{O}_2] [\text{OH}^-]^{-1} \exp(-0.2 FV/RT) \quad (10b)$$

respectively. The condition, $1 = K_a[\text{OH}^-]/K_w$, is rewritten as $1 = K_a/[\text{H}^+]$ or $\text{p}K_a = \text{pH}$. Value of $\text{p}K_a$ is reported as 11.62¹¹⁾ and hence this value is the critical pH value, above or below which the reaction kinetics is different as shown by Eqs. (10a) and (10b). Reaction order with respect to H_2O_2 in these two equations and the critical pH value reproduce the experimental results.

Anodic reaction: Anodic process in alkaline H_2O_2 solution on Hg seems not to have been studied.

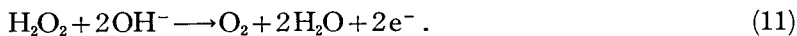
*) The value of reaction order does not necessarily equal the number of a reactant which participates in the rate-determining step.⁹⁾ According to the generalized theory of reaction rate by HORIUTI¹⁰⁾, the unidirectional rate, \tilde{v} , of overall reaction is given as

$$\tilde{v} = (kT/\nu h) \exp[(\sum_j z_j \mu_j - \mu^*)/RT],$$

where ν is the stoichiometric number, z_j the number of the reactant j , μ_j or μ^* the chemical potential of j or the critical complex, respectively of the rate-determining step and other symbols are of their usual meaning. Now, the reaction order with respect to j is defined as $\partial \ln \tilde{v} / \partial \ln a_j$ and only equal to z_j as discussed by ENYO and YOKOYAMA⁹⁾ at the condition, $\partial \mu^* / \partial \ln a_j = 0$, where a_j is the activity of the reactant j . Present integer value of $z(\text{OH}^-)$ will suggest that $\partial \mu^* / \partial \ln a_j = 0$; otherwise, a fractional value will be expected. Hence, in the present case, the value of reaction order equated z_j .

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Present results are essentially different from those in acidic solution.¹⁾ Reaction rate is proportional to $[\text{H}_2\text{O}_2]$ and hence the process will be taken as the oxidation of H_2O_2 , *i. e.*,



The equilibrium potential of the above reaction is given as⁸⁾

$$V_{\text{eq. a}}(\text{NHE, volt}) = 0.682 + (RT/2F) \ln [\text{O}_2][\text{H}^+]^2/[\text{H}_2\text{O}_2] \quad (11, \text{V})$$

and estimated at $0.00 \sim -0.03$ v under the conditions, $\text{pH} = 12.6$, $[\text{H}_2\text{O}_2] = 2 \times 10^{-3} \sim 2.9 \times 10^{-2}$ Mol/l, and 1 atm. O_2 . Since the hydrogen peroxide undergoes the natural decomposition, oxygen will exist in solution, though the experiments were carried out in N_2 saturated solution. The possible maximum O_2 concentration was estimated at *ca.* one tenth of its saturation value by comparison of the residual current with the diffusion current of O_2 reduction wave in O_2 saturated solution. Hence, the value of $V_{\text{eq. a}}$ will be $-0.03 \sim -0.06$ v. The potential range studied (Fig. 8) is apart by at least $0.05 \sim 0.08$ v from the above $V_{\text{eq. a}}$ value. The rate expression of Eqs. (3a) and (3b) is thus taken to represent that of unidirectional rate of the reaction (11), *i. e.*,

$$\dot{i}_a = \tilde{k}_a [\text{H}_2\text{O}_2][\text{OH}^-]^{z(\text{OH}^-)} \exp(2.0FV/RT), \quad (12a)$$

where

$$\tilde{z}(\text{OH}^-) = 2.0 \text{ (pH} < 12) \quad \text{or} \quad 1.0 \text{ (pH} > 12). \quad (12b)$$

The change of $\tilde{z}(\text{OH}^-)$ from 2 to 1 at around $\text{pH} = 12$ will be understood by taking into account the dissociation (7) of H_2O_2 as in the case of cathodic reaction. Concentration of HO_2^- , $[\text{HO}_2^-]$, is expressed as

$$[\text{HO}_2^-] = [\text{H}_2\text{O}_2] / (1 + K_w/K_a[\text{OH}^-]). \quad (13)$$

At $1 \gg K_w/K_a[\text{OH}^-]$, *i. e.*, $\text{pH} > \text{p}K_a$, we have

$$[\text{HO}_2^-] = [\text{H}_2\text{O}_2] \quad (14)$$

and at $1 \ll K_w/K_a[\text{OH}^-]$, *i. e.*, $\text{pH} < \text{p}K_a$,

$$[\text{HO}_2^-] = (K_w/K_a)[\text{H}_2\text{O}_2][\text{OH}^-], \quad (15)$$

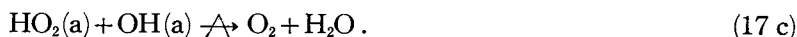
respectively.

It will be reasonably accepted that HO_2^- ion is more easily oxidizable than neutral H_2O_2 molecule owing to its negative charge. Elimination of the term, $[\text{H}_2\text{O}_2]$, from Eq. (12a) and Eq. (14) or (15), yields

$$\dot{i}_a = \text{const} \cdot [\text{HO}_2^-][\text{OH}^-] \exp(2.0FV/RT). \quad (16)$$

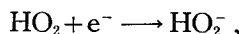
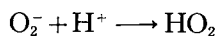
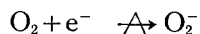
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Hence, the experimental results indicate that the reaction rate is first order with respect to HO_2^- and OH^- respectively. Present TAFEL constant, 2.0, on the other hand, shows that all of two electrons which participate in the oxidation reaction (11), are released in advance of the rate-determining step of the reaction. Consequently, the above implications of the experimental results lead us to conclude the following reaction mechanism,



The reaction kinetics of Eq. (16) is easily deduced from the above mechanism by applying the mass action law to the step (17c) and the equilibrium condition to the steps, (17), (17a) and (17b). The observed value of the critical pH, above and below which $\bar{z}(\text{OH}^-)$ differs, is in agreement with the $\text{p}K_a$ value within an experimental error.

Several works have been reported on the reduction of O_2 to H_2O_2 *i. e.*, backward reaction of (11) in alkaline solution.^{2,3,12,13} BAGOTSKII and YABLA-KOVA³⁾ proposed the following mechanism on Hg,



which is different from the present one. Different mechanisms for the forward and backward direction of a reaction might appear unexpected but such a case has been proposed on chlorine electrode reaction on Pt and Ir by YOKOYAMA and ENYO.¹⁴⁾

Rest potential: Dependences of V_r on pH and $[\text{H}_2\text{O}_2]$ are entirely different from those in acidic (H_2SO_4) solution. In the latter case¹⁾, $\partial V_r / \partial \log [\text{H}_2\text{O}_2]$, $\partial V_r / \partial \text{pH}$ and $\partial V_r / \partial \log [\text{SO}_4^{2-}]$ were 27 ± 1 mv, 0 and -58 ± 1 mv respectively. These dependences were explained from the kinetics observed for the cathodic and anodic reactions, *i. e.*, the reduction of H_2O_2 and oxidation of Hg to Hg_2SO_4 .

Present results in alkaline solution, $\partial V_r / \partial \log [\text{H}_2\text{O}_2] = 0$ and $\partial V_r / \partial \text{pH} = -55$ mv, will be discussed below in terms of the kinetics for the cathodic and anodic reactions of H_2O_2 , *i. e.*, the reactions, (4) and (11).

The rest potential is defined by the condition that no net current is passing through the electrode, *i. e.*,

Electrode Reaction of Hydrogen Peroxide in Alkaline Solution on Hg

$$i_o = i_a \quad (18)$$

and expressed in the present case from Eqs. (18), (5) and (12) as,^{*)1)}

$$V_r = -(RT/1.1 F) \ln [\text{OH}^-] + \text{const.} \quad (19)$$

Dependences of V_r on $[\text{H}_2\text{O}_2]$ and pH are derived by the partial differentiation of the above equation as,

$$\partial V_r / \partial \log [\text{H}_2\text{O}_2] = 0$$

$$\partial V_r / \partial \log [\text{OH}^-] = \partial V_r / \partial \text{pH} = -54 \text{ mv (25}^\circ\text{C)},$$

which reproduce the observed results as seen in Table 1.

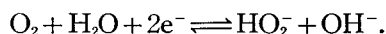
In Table 2, the rest potential observed in a static solution is compared with that calculated from Eq. (5), *i. e.*, from the intersection of the extrapolated cathodic and anodic TAFEL lines (Figs. 3 and 8). Observed values

TABLE 2. Observed and calculated rest potentials at various pH's.

pH	V_r (mv)		Difference (mv)
	obs.	cal.	
10.75	141	88	53
11.22	110	60	50
11.44	84	33	51
11.91	54	5	49
12.13	56	2	54
12.38	40	-16	56
12.88	12	-49	61
13.11	11	-57	68

are always more positive by 55 mv on an average than the calculated ones. The similar discrepancy was observed in acidic solution and discussed by stirring effect of solution on potential of the anodic reaction.¹⁾

BAGOTSKII *et al.*^{3,15)} reported that the rest potential was in agreement with the equilibrium potential of the reaction,



Present results on pH and $[\text{H}_2\text{O}_2]$ dependences of V_r , however, differ from those expected from the above reaction, *i. e.*, $\partial V_r / \partial \text{pH} = \partial V_r / \partial \log [\text{H}_2\text{O}_2] =$

*) The rate expressions, (5) and (12) are assumed here to hold in the potential range to the rest potential.

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—30 mv. Hence, their way of explanation might not be applicable in the present case.

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