Fundamental Research on Anodic Reaction. II.* Activation Energy of Anodic Oxygen-producing Reaction on Some Electrode Materials in Aqueous Solution of N/10 Sodium Hydroxide.

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(Received July 23, 1949.)

Introduction. The activation energy of electrode reaction can be measured without the knowledge of true area of electrode surface, therefore it is important for the determination of the mechanism of the electrode reaction. Activation energy of anodic exygen-producing reaction in aqueous solution of N/5 H_2SO_4 on platinum was determined by F. P. Bowden(1) to be 13–14 kcals./mole after being corrected by the present author on equilibrium oxygen potential, which will be stated in the present paper. H. P. Stout(2) and nearly at the same time René Audubert(3) published the values of activation energy in alkaline solution, but the values calculated were 25.3 and 8.3 kcals. respectively, different from each other. These results are tabulated in the section of "Discussions".

The influence of time on the overvoltage of oxygen anode is remarkable, as Hickling and Hill(4) has stated. Therefore it is important to define the time at which overvoltage is measured. Four different definitions of time are possible as follows:

(a) The time when the maximum curvature on the buit-up curve of potential is obtained.

(b) The time when the potential reaches to stationary state.

(c) The time when the increase of overvoltage per unit time becomes smaller than a certain value.

(d) The fixed time after the closing of electric circuit.

(a) and (b) have some concrete meaning, but (c) and (d) are conventional methods and have rather obscure meaning.

Recently J. N. Agar(5) published his consideration on the theoretical standpoint of activation energy, and classified it into two categories, that is, E_I and E_{II}. E_I is calculated from $\left(\frac{\partial \log i}{\partial(1/T)}\right)_\eta$, taking the temperature coefficient of equilibrium potential into consideration, and E_{II},

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* The first paper, *J. Chem. Soc. Japan*, in press.

(1) F. P. Bowden, *Proc. Roy. Soc. London*, A **126** (1929), 107.

(2) H. P. Stout, *Discussions, Faraday Soc.*, No. 1 (1947), 246.

(3) René Audubert, *ibid*, 72.

(4) A. Hickling and S. Hill, *ibid.*, 236.

(5) J. N. Agar, *ibid.*, 81.

from $\left(\frac{\partial \log i}{\partial(1/T)}\right)_V$, neglecting the temperature coefficient, where V, η and i mean the electrode potential, overvoltage and the current density respectively. From the definition of activation energy, E_I is more precise, but it depends upon the value of η. As E_I is equal to $\Delta H^{\ddagger}-\alpha\eta F$, according to Eyring's notation,(6) the present author adopts,

$$\Delta H^{\ddagger}=-2.303\,R\left(\frac{\partial \log i}{\partial\ 1/T)}\right)_{\eta}+\alpha\eta F, \quad \ldots\ldots\ldots(1)$$

as true activation energy which should be independent of η, where F is Faraday constant, α is a constant, and T is absolute temperature.

Experimental Procedures. Anode materials used were platinum, magnetite, or natural graphite. Platinum was brightly polished and its apparent area was 5 sq. cm. Magnetite had been shaped from a large artificial magnetite anode of practical size, and its area was 5 sq. cm. As natural graphite, positive plate of dry cell was used, and its area was 5 sq. cm., too. It consisted of natural graphite sintered with organic binder, and was treated with xylene to extract soluble matter.

Electrolyte was the aqueous solution of N/10 NaOH, which was prepared not to be contaminated with carbonate or chloride. As reference electrode, mercuric oxide electrode with N/10 NaOH solution as electrolyte was employed, therefore liquid potential was always negligible. A fine tip from reference electrode was slightly pressed upon the surface of electrode. Electrolyte was always stirred by and saturated with the stream of oxygen gas.

Two electric circuits, that is, ordinary and oscillographic methods, for measuring overvoltage were prepared. The ordinary one consisted of a potentiometer and a galvanometer. The oscillographic method means that with electromagnetic oscillograph and vacuum tube amplifier. The sensibility of vibrator (Yokogawa D type) is 1 mm./μA, and the total sensibility, when combined with amplifier and dipped in damping oil, is 0.5 mm./mv.

The potentials by ordinary method both on platinum, (i)*, and on magnetite and natural graphite, (iii)*, were measured. The electrolytic cell was in a thermostat, but the reference electrode was in room temperature. The potential differences caused by this temperature difference were specially measured afterwards and these amounts were corrected for the overvoltage value. In the case of oscillographic method on platinum, (ii)*, both electrolytic cell and reference electrode were in a thermostat. As there was no liquid potential between them in both cases, the equilibrium potential of oxygen electrode against mercuric oxide reference electrode is calculated from the free energy difference of the following reaction,

$$\mathrm{HgO\,(s) = Hg\,(l) + 1/2\ O_2\,(g)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Owing to Lewis and Randall(7), and Shibata and Murata(8), the equilibrium potential of reaction (2) is as follows:

T °C	18	25	35	45	65
$E_T°$ (mv.)	302.7	299.5	293.5	288.0	276.0

The overvoltage is therefore calculated, substracting $E_T°$ from measured potential difference.

Results. Case A. Pt, after 30 minutes from closing of the circuits. (Method (i))*. Overvoltage was measured in the range of temperature of 18° to 65°C, and in the range for current density D_A of 10^{-5}

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(6) H. Eyring, et al., "The Theory of Rate Processes", 587 (1941).

(7) Lewis and Randall, "Thermodynamics", 484 (1923).

(8) E. Shibata and F. Murata, *J. Chem. Soc. Japan*, **52** (1931), 393.

* Refer to "Summary".

to 10^{-2} A./cm.^{2} To obtain reproducible results, electrode had been cathodically polarized previously for 2 to 3 minutes at a current density which was the same as that of anodic polarization of former run. The length of time of the cathodic polarization was almost uneffective.

The relation of the increase of potential with time to D_A was contrary to the Hickling and Hill's observation,⁽⁹⁾ that is, the potential increase per unit time was the greater in the present case, the higher was the D_A. The mean potential increase per 10 minutes (between 20 minutes to 30 minutes from closing of circuit) were zero and 65 mv. for D_A's of 10^{-5} and 10^{-2} A./cm.^{2}, respectively. Two to ten runs, according to the reproducibility, were carried out in the same condition. Mean values of overvoltage ($\bar{x}$), and their unbiased estimates of variance ($\widehat{\sigma^2_{\bar{x}}}$) of $\bar{x}$ are compiled in Table 1.

Table 1.

Temp. (°C)	A./cm.^{2}	10^{-5}	10^{-4}	10^{-3}	10^{-2}
18	$\bar{x}$ (mv.)	491	668	816	1253*
	u.e.v. (mv.^{2})	446	57	100	157
35	$\bar{x}$	430	620	764	968
	u.e.v.	42	51	36	154
45	$\bar{x}$	361	552	737	904
	u.e.v.	189	194	232	58
65	$\bar{x}$	303	435	670	825
	u.e.v.	836	100	62	0

u.e.v. = Unbiased estimate of variance.

Except the figure with asterisk, they hold the linearity in overvoltage vs. log D_A curves, Fig. 1. Making u. e. v. as weight, the coefficient of the Tafel's equation,

$$\text{overvoltage (mv.)} = a + b \log_{10} D_A \text{ (A./cm.}^2\text{)},$$

is calculated for each case of the above measurements through the method of least square, as Table 2, where the error represents the mean square deviation.

Table 2.

Temp. (°C)	a	b	α
18	1308±50	162.5±14.1	0.356±0.031
35	1292±14	172.2± 3.7	0.355±0.008
45	1271±22	179.4± 2.1	0.352±0.004
65	1223±18	192.1± 5.7	0.349±0.010
			mean.......0.353±0.017

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(9) A. Hickling and S. Hill, *Discussions Faraday Soc.*, No. 1 (1947), 237.

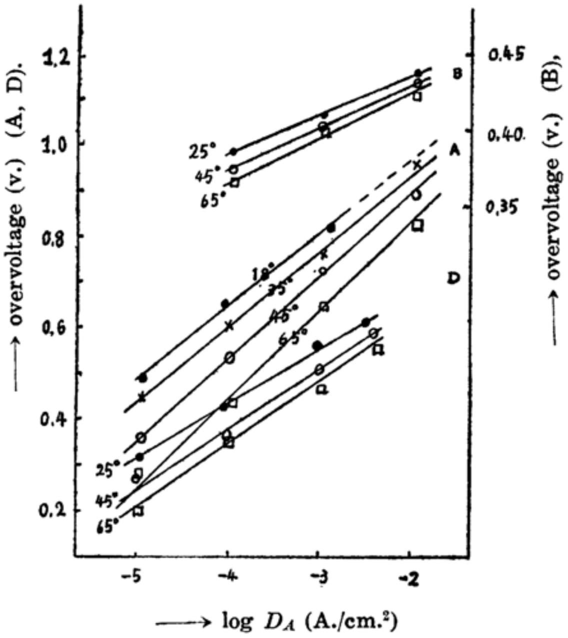

Fig. 1. Overvoltage vs. log D_A.

A: Pt, 30 minutes after closing of the circuit.
B: Magnetite, at the stationary state.
D: Pt, by oscillographic method.

From Fig. 1 and Table 2, we have the following relation at overvoltage of 500 mv., as in Fig. 2,

$$\log D_A = 3.88 - (2.58 \pm 0.41) \times 10^3/T. \qquad \ldots\ldots\ldots\ldots(3)$$

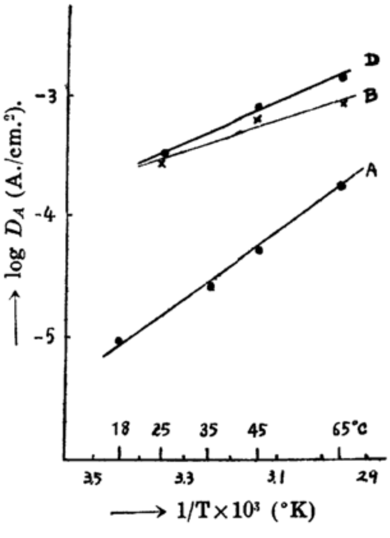

Fig. 2. log D_A vs. 1/T.

From Eq. (1), and taking errors into consideration, activation energy has been found to be 15.9±2.0 kcals. This value is independent of overvoltage.

Case B. Magnetite, at stationary state. (Method (iii)). Temperature range was from 25 to 65°C, and range for D_A was from 10^{-4} to 10^{-2} A./cm.^{2} Stationary potential was obtained after several minutes from closing of circuit and no previous cathodic polarization was carried out. At D_A smaller than 10^{-5} A./cm.^{2}, overvoltage was much lower than that expected. Mean values of two to four runs were plotted in Fig. 1. The unbiased estimate of variance, zero to 42 mv.^{2}, was much smaller in this case than in Case A, and through the above mentioned procedures, coefficients were calculated as in Table 3.

Table 3.

Temp. (°C)	a	b	α
25	492.5± 6.3	26.0±2.5	2.26±0.22
45	491.4± 3.1	28.6±1.3	2.21±0.17
65	491.3±10.0	29.8±4.0	2.25±0.30
			mean……2.24±0.23

Therefrom we have the following relation at overvoltage of 400 mv., as in Fig. 2,

$$\log D_A = 0.524 - (1.207 \pm 0.086) \times 10^3/T. \quad \ldots\ldots\ldots (4)$$

Thus, activation energy on magnetite was calculated from Eq. (1) as 26.2±3.2 kcals.

Case C. Natural graphite, at stationary state. (Method (iii)). Experiments on graphite were carried out in almost the same method as on magnetite, but the range in which the linear relation of Tafel's equation held was so narrow that the activation energy could not be calculated.

Case D. Pt, by oscillographic method. (Method (ii)). Temperature range was from 25° to 65°C, and range for D_A was from about 10^{-5} to 4.6×10^{-3} A./cm.^{2} As for current density of previous cathodic polarization, one tenth of D_A was most preferable, and variation of its duration, 1 to 3 minutes, were not effective on the potential. After the cathodic polarization, the current was reversed, and the built-up curves of anodic potential were recorded. That point which had the maximum curvature on this curve was determined by eye-measurement. Assuming that the adsorption monolayer of oxygen atoms had been completed at this point, overvoltage was calculated substracting the equilibrium potential, Eq. (2), from the potential of this point. Period of rotation of drum, which was 2 to 6 minutes in these case, was not effective in determining this point. Mean values of about six runs are plotted in Fig. 1. The unbiased estimates of variance are smaller than 50 mv.^{2}, except a very few anomalous points. Coefficient of Tafel's equation was calculated as in Table 4.

Table 4.

Temp. (°C)	*a*	*b*	α
25	925.6± 9.3	120.5±2.8	0.492±0.007
45	902.0±15.3	131.9±4.6	0.479±0.007
65	804.7± 9.2	136.3±2.6	0.492±0.009
			0.448±0.008

From Table 4, we have the following relation at overvoltage of 500 mv., as in Fig. 2,

$$\log D_A = 1.76 - (1.57 \pm 0.11) \times 10^3/T. \quad \ldots\ldots\ldots\ldots (5)$$

Activation energy is therefore, 13.8±0.6 kcals.

Discussions. Values of activation energy of anodic oxygen-producing reaction reported hitherto and those determined newly by the present author are summarized in Table 5. As only $E_{,,}$ was to be calculated from the Bowden's experiments, true activation energy defined in Eq. (1) was re-calculated. After estimating the temperature coefficient of standard single electrode potential of oxygen, $dE_T^0(O_2)/dT$, to be −1 mv./°C, from entropies of hydroxyl ion and so on, and as for that of dissociation constant of water, neglecting the liquid potential between both cells at different temperatures, more correct value of 14.3 kcals. was obtained. Taking the fact into consideration that in acid solution potential of the higher temperature side of liquid contact is less noble than of lower side, more correct value, 13–14 kcals., was obtained.

Table 5.

Researcher	Electrode	Electrolyte	Method	Calculation	$\Delta H^{\ddagger}$ (kcals.)	α	Temp. (°C)
Bowden (1)	Pt	N/5 H_2SO_4	Oscillograph	I*	14.3* 13∼14**	0.5	0−81
Yoneda	Pt	N/10 NaOH	,,	I	13.8±0.6	0.49	25−65
	,,	,,	(i)	,,	15.9±2.0	0.39	18−65
	Magnetite	,,	(iii)	,,	26.2±3.2	2.24	25 - 65
Stout (2)	Pt	,,	?	?	25.3	1.0	18−31
Audubert (3)	Pt	N NaOH	?	?	8.3	0.12	?
	,,	0.001 N NaOH	?	?	3.1	0.12	?

* Corrected by the present author.

** Estimated value after taking the liquid potential in consideration.

The Stout's value is too large. The source of this error seems to be that the temperature range in which his experiments were performed was too narrow, and moreover he neglected the influence of time on determining the potential, and it might make α too large, as was pointed out by Bockris.(10)

On the contrary, the Audubert's value of α is too small, and his small value of the activation energy may be led herefrom.

The activation energy on platinum measured by the ordinary method and by osccillographic method agreed with each other. This fact means that there is scarcely any difference between the reaction on so-called monolayer of oxygen atom and that on oxide film which is assumed to be deposited on platinum surface after a certain period of anodic polarization. On the other hand, the discrepancy of value of activation energies and α's between of platinum and of magnetite suggests a discontinuous property between metal and oxide anodes.

Now let us compare the results of the present author in alkaline solution to that of Bowden in acid solution. Method for measurement and calculation are common in both cases. Activation energies and α's are almost the same. Absolute value of overvoltage measured by Bowden, however, is about 250 mv. higher than that by the author, though, according to the former experiment of the author,(11) the overvoltage in aqueous solution of N/10 H_2SO_4 measured by the same method as in Case A was, on the contrary, 100 mv. lower than in alkaline solution. Hoar(12) made an experiment in acid solution by a similiar method to Case A, and his values of 10^{-5} and 10^{-4} A./cm.^{2} are almost the same as the one in alkaline solution above mentioned.

Putting these facts together, the present author suggests the following hypothesis:

In ordinary solution, either acid or alkaline, oxygen is evolved on platinum anode through the same rate-determining step from the same reactant.

Summary.

Activation energies of anodic oxygen-producing reaction on electrode of platinum, magnetite, or natural graphite were measured in aqueous solution of N/10 NaOH under stirring by the stream of oxygen gas, at temperature from about 25° to 65°C. On platinum anode, overvoltage was measured by two methods, (i) by the ordinary method just after 30 minutes from the time of closing the electric circuit, and (ii) by the oscillographic method. The activation energy calculated herefrom was

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(10) J. O'M. Bockris, *Discussions Faraday Soc.*, No. 1 (1947), 252.

(11) Y. Yoneda, *J. Chem. Soc. Japan*, in press.

(12) T. P. Hoar, *Proc. Roy. Soc. London*, **A 142** (1933), 628.

found 15.9 ± 2.0 kcals. by (i) method, and 13.8 ± 0.6 kcals. by (ii) method. On magnetite and natural graphite, overvoltage was measured by (iii) ordinary method at the stationary state which was obtained after a few minutes. Activation energy of the former was found to be 26.2 ± 3.2 kcals., and that of the latter is not obtained. The activation energy on platinum by oscillographic method is consistent with that measured by F. P. Bowden in the aqueous solution of N/5 H_2SO_4, which is 13–14 kcals. after being corrected about the temperature coefficient of oxygen equilibrium potential. These facts suggest that the anodic oxygen-producing reaction on platinum proceeds through the same rate-determining step both in acid and alkaline solutions, and the mechanism is rather different on platinum from the one on magnetite.

The author wishes to express his grateful thanks to Professor N. Kameyama and Assistant Professor T. Mukaidou for their kind guidance in this work, and for their kindness in reading the original manuscript.

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