

# The Poly-dimensional Problem on Electrode Reaction Process

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## §1. Introduction

The polarization and its phenomena on the electrode surface are among the most important factors for the researches concerning the electrolytic process.

As in an electro-magnetic field, Laplace's equation is also applicable in an electrolytic cell. In this case, however, the boundary conditions at the electrode surface are much more complicated.

Although many investigations have been made since years past as to the relations between polarization and the external factors such as current density and terminal voltage, it is only of latest years that these problems have come to be considered directly through the analysis of the electrolytic field.<sup>1,2,3)</sup>

The view-points of new investigators are, in essence, the same; that is, the polarization,  $\pi_i$ ; may be very much affected by the current density at any point of the electrode surface:

$$\pi_i = \varphi(i). \quad (1)$$

But considering that the current density,  $i$ , is also affected by the coordinate,  $z$ , of the point under consideration:

$$i = f(z), \quad (2)$$

$\pi_i$  is the function of the coordinate as:

$$\pi_i = \varphi\{f(z)\}. \quad (3)$$

As the above explanation shows, current density is affected by polarization, while polarization depends on current density. Thus, cause and effect are complicated, and thereby the concept of the function is confused. Several workers

1) Kasper, Trans. Am. Electrochem. Soc., 77, 353; 365 (1939), *idid.*, 78, 131; 147 (1940).

2) Wagner, J. Electrochem. Soc., 98, 116 (1951).

3) Ishizaka, J. Electrochem. Soc. Japan, 17, 1; 47 (1949), *Kogyo-butsuri-kagaku* (Industrial Physical Chemistry), 2, 78 (1948).

adopted the successive methods for this analysis. Wagner, apart from them, employed the method of the integral equation which, however, has a flaw of being too difficult for generalization.<sup>1)</sup>

But does the difficulty consist only of mathematical ones in the treatment of this problem?

In general, when researches into the polarization phenomena are made the one-dimensional fields in an electrolytic cell is discussed for the sake of convenience. Because only it is necessary that the heterogeneous reaction of the normal direction against the electrode surface should be treated.

When the poly-dimensional field in a cell is to be discussed, however, the polarization itself must also be considered as a poly-dimensional problem.

We may reconsider the polarization phenomena from this point of view in the followings.

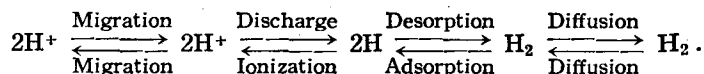
## §2. A Model of the Mechanism of the Activation Overpotential

The reactions in which the construction change of the elementary reactant species is the rate-determining step are already well known.

The hydrogen electrode process is one of the most typical of these. Therefore, in this section, let us study the hydrogen electrode as an example. But of course the following ideas as to the activation overpotential can be reached in other cases as well.

The concentration polarization is a reaction process which has a physical meaning of "diffusion", and this diffusion of ionic species near the electrode surface can be the rate-determining step in chemical reaction. On the other hand, the activation overpotential, which now comes into the question, is caused by a catalytic reaction process on the surface of an electrode. The concentration polarization is due to a simple mechanism, while the activation overpotential is supposed to be a complex reaction stage. Accordingly, different investigators have proposed different theories.<sup>2)</sup>

For example, in the case of the hydrogen electrode, where hydrogen ion  $H^+$  is converted finally into gas molecule  $H_2$ , several steps can be considered through this conversion such as:-<sup>3)</sup>



1) Wagner, J. Electrochem. Soc., 98, 116 (1951).

2) J. O'M. Bockis, Chem. Rev., 43, 525 (1948).

3) Yoshizawa, Kagaku-hyoron (Chemical Review in Japan), 11, 208; 271 (1946). Suito, Butsurikagaku no Sinpo (Proc. of Phy. Chem.), 14, 45 (1940).

The whole reaction process is controlled by the slowest of these different steps of reaction. Hence, to understand the potential distribution which is now going to be explained, it seems necessary to discuss these theories in general. But as they hold almost the same concept concerning the existence of an electrical double layer near the electrode surface, it may be sufficient to discuss the question according to any one of these theories, so long as this consideration does not touch upon the mechanism of the polarization phenomena itself.<sup>1)</sup>

For convenience' sake, here is introduced the theory of Horiuti and Polanyi.<sup>2)</sup> According to this theory, hydroxonium ions  $\text{H}\cdot\text{H}_2\text{O}^+$  exist in the solution, keeping a certain distance from the electrode surface, and the ionic species which are nearest to the surface of the electrode from the electrical double layer. Then there takes place a reaction which put a portion of hydrogen spirit and a metal-electron of the electrode together to form an adsorbed hydrogen atom on the electrode surface. This step is the rate-determining. In this case, for the sake of convenience, the potential energy of the system which consists of a hydrogen spirit and a metal electron, and that of the other system which is formed by an adsorbed hydrogen atom and a metal electron, are calculated independently. In the former case, the Coulomb force acts between two species, and when hydrogen spirit reaches as near as the radius of the hydroxonium ion, i.e., the thickness of the double layer (about  $1.5\text{\AA}$ ), hydrogen ion  $\text{H}^+$  can proceed more to the electrode surface, while the water molecule, which forms a hydrated ionic species remains as it was.<sup>3)</sup> And so the potential energy, i.e., the dissociation energy suddenly increases.

The distance between two O-atoms in a water molecule is  $2.09\text{\AA}$  according to Bernal and Fowler<sup>4)</sup> while the thickness of the electrical double layer is concluded to be  $1.5\text{\AA}$  by Frumkin<sup>5)</sup>.

If the electrode potential is risen to  $K$ -fold of the first, the Coulomb potential  $U(r)$  of this system, as a matter of course, becomes,

$$U(r) = -K \cdot e^2 / r, \quad (1)$$

where  $r$  is the average distance between a hydrogen spirit and a metal electron. And moreover, we have

$$dU/dr = K \cdot e^2 / r^2, \quad (2)$$

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- 1) Okada, Yoshizawa and Hine, J. Electrochem. Soc. Japan, **20** 78 (1952).
  - 2) Horiuti and polanyi, Acta Physicochim. U. R. S. S., **2**, 505 (1935).
  - 3) Hine, Yoshizawa and Okada, J. Electrochem. Soc. Japan, **20**, 218 (1952).
  - 4) Bernal and Fowler, J. Chem. Phys., **1**, 515 (1935).
  - 5) Frumkin, Phys. Z. Sowjetunion, **4**, 243 (1933).

hence, the potential curve of this case can be concluded by the first conditions which is shown in Fig. 1.

In the later case, the adsorbed atom is unhydrated, so that the chemical species can reach nearer to the electrode surface than in the former, and its limiting distance is equal to Bohr's radius. The potential energy of this system is approximately equal to an adsorbed energy of the hydrogen atom, which seems to be chemi-sorbed on the electrode surface. And this energy may be calculated in the same way as the van der Waals energy according to the method devised by London and his co-authors concerning the case of the non-activated adsorption of gas on solid surface.<sup>1,2)</sup> So this term is approximately constant for the change of the electrode potential.

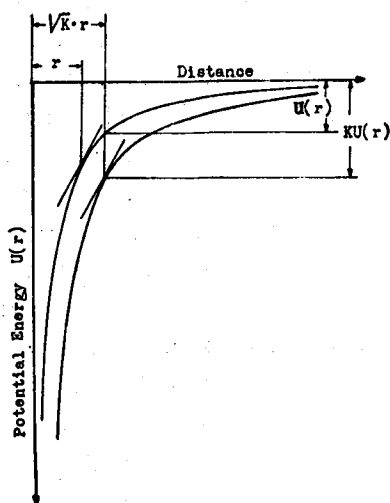


Fig. 1

The above discussions result in the conclusion that the potential barrier for the construction change of the reactant species in question is dependent only on the electrode potential, if the electrode is made of perfectly conductive material. Thus, the potential energies of both a hydrogen ion and a hydrogen atom, perhaps chemi-sorbed, are expressed in functions of the distance from the surface of metal, and figured in two curves, X and Y, respectively, as shown in Fig. 2. Admitting that the double layer is formed as mentioned above, the distance between the hydroxonium ion and the metallic electrons on the electrode surface seems to have an almost constant value. Hence, the curve X is simply given in independence of the form of the electrode, etc., namely, the horizontal axis in Fig. 2 coincides with the direction perpendicular to the electrode surface.

Needless to say, the rotation and the vibration of the species itself were not considered in the above inference and also

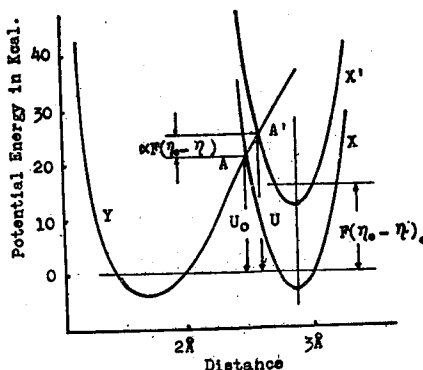


Fig. 2

1) London, Z. Phys., 63, 245 (1930).

2) Lonnard and Jones, Trans. Farad. Soc., 28, 333 (1932).

were ignored the mutual interactions between the two systems, which were referred above.

This idea is applied equally to illustrate theoretical mechanism of the evolution of gaseous chlorine at the surface of the insoluble anode, the electrolytic deposition of metal on the cathode surface, and so forth.

In general we cannot, however, but honour the rate-determining step of the whole reaction not with the name of construction change but diffusion process of ionic species which are carried through the bulk of the solution to the double layer adjacent to the electrode surface on the occasion of the electrolysis of a metallic salt solution, of which the typical example is the metallic copper deposition from an acidic solution of its salt. But we are not free from exceptions, such as the dissolution of metallic iron into hydrochloric acid, when there is no other plausible explanation than the theory that the construction change of elementary species is the rate-determining step.

The diffusion-controlled processes may not be expatiated in this paper, as minute researches are prolofic before our eyes. Nevertheless, the activation overpotential and the concentration polarization can not be separated in practice from each other, for they are inseparably related at the double layer near the electrode surface. For this reason, it is more practical and available to discuss the overpotential in its summerized form than from its mechanism, i.e., how the total polarization is related to the external factors.

### §3. The Flow of the Elementary Reaction

All the discussions here are based upon the assumption that the system of the elementary reaction under consideration satisfies always the restriction of the "thermal equilibrium", the definition originated by Horiuti.<sup>1)</sup> Along with him,<sup>2)</sup> we define the reaction rates of the forward and backward directions as,

$$\vec{v} = \kappa \frac{kT}{h} e^{-\frac{\mu^{\delta*} - \mu^{\delta f}}{RT}}, \quad (1\vec{v})$$

and

$$\overleftarrow{v} = \kappa \frac{kT}{h} e^{-\frac{\mu^{\delta*} - \mu^{\delta b}}{RT}}, \quad (1\overleftarrow{v})$$

respectively, for the elementary particle  $\delta$ , where  $k$  is Boltzmann's constants and  $h$  is Plank's constant;  $\kappa$  is the transmission coefficient, and  $\mu^{\delta}$  represents

1) Horiuti, Hydrogen Electrode Reaction (Phys. Chem., II, Kagaku-jikkengaku (Experimental Chemistry, Series), Kawade Co., Tokyo), p.12 (1950).

2) Horiuti, Theory of Chemical Reaction (Physics X, The Iwanami Series, Iwanami & Co., Tokyo), p. 20.

the chemical potential of  $\delta$ ; and on the shoulder of  $\delta$ , the suffix  $I, F$  and  $*$  mean the initial, the final and the activated system.

Whereas, the chemical potential of  $\delta$  is expressed in,

$$\mu^\delta = \mu_0^\delta + RT \log C^\delta + zFV, \quad (2)$$

where  $\mu_0^\delta$  is the standard chemical potential, i.e., the potential when the concentration of  $\delta$ ,  $C^\delta$ , is equal to unity and the electrical potential,  $V$ , is reduced to naught.

Therefore, the chemical potential of  $\delta$  is, in other word, the change of the free energy of an isothermal system into which 1 mol of  $\delta$  is added reversibly without any external alteration. Accordingly, the reaction rate,  $v$ , is to the effect of the increment or decrement of the chemical species of  $\delta$ , in the system per unit volume and in unit time.

It is sure to endow the treatment with much convenience if we compare this chemical reaction to an "incompressible laminar flow". Such stream lines never cross each other and so the sectional area of this flux at a point corresponds to the inverse number of the intensity of the electrical field there.

Here is introduced a quantity, defined as,

$$\mu_{(v)}^\delta = \bar{\mu}_0^\delta + RT \log Q^\delta + zFV, \quad (3)$$

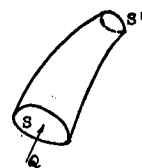


Fig. 3

where  $Q^\delta$  represents the quantity of the species  $\delta$  at the section  $S, V$  is the electrical potential at this point, and  $\bar{\mu}_0^\delta$  is the standard chemical potential of the species  $\delta$  at the section.

That is,  $\bar{\mu}_0^\delta$  is  $\mu_{(v)}^\delta$  in the standard state in equilibrium when one normal line penetrates the section (namely, one species is found there), or when the electrical potential is zero owing to no application of external voltage at  $0^\circ\text{K}$ .

This definition gives the meaning of the chemical potential,  $\mu_{(v)}^\delta$  as the total sum of the chemical potentials of various kinds of the individual chemical species, i.e.,

$$\mu_{(v)}^\delta = \sum_i \mu_{(v)}^{\delta_i} \quad (4)$$

or, in a word, the chemical potential allotted to 1 mol of the species  $\delta_i$  at the section  $S$ .

Thus, we can bring forth a new elementary reaction rate of each direction,

$$\vec{v} = \kappa \frac{kT}{h} e^{-\frac{\mu_{(v)}^{\delta*} - \mu_{(v)}^{\delta I}}{RT}}, \quad (5 \vec{v})$$

and,

$$\overleftarrow{v} = \kappa \frac{kT}{h} e^{-\frac{\mu_{(b)}^{\delta*} - \mu_{(b)}^{\delta F}}{RT}}, \quad (5\overleftarrow{v})$$

respectively. From this expression, we understand  $\overrightarrow{v}$  and  $\overleftarrow{v}$  as the reaction rates for both directions of the species  $\delta$  which crosses the section S per unit time. No entrance or exit of the species is allowed over the boundary of the species is allowed over the boundary of the flux, and hence the constant values of both rates,  $\overrightarrow{v}$  and  $\overleftarrow{v}$ . Now, this flux may be named anew the "Reaction Flux", and  $\overrightarrow{v}$  and  $\overleftarrow{v}$  the "Reaction Velocities for the Flux" of the positive and the negative directions, severally.

The above discussions over one reaction flux can be expanded exactly in the same manner to the whole region between the electrode surfaces where exists the species,—the electrode surfaces themselves and the electrolytic solution.

By means of these reaction rates the current flux for each direction is introduced as,

$$\overrightarrow{i} = zF\overrightarrow{v} \quad \text{and} \quad \overleftarrow{i} = zF\overleftarrow{v} \quad (6\overrightarrow{i}), (6\overleftarrow{i})$$

Surmising that the reaction rate of the process in question is much slower than those of others and accordingly there is partial equilibrium in the other elementary reactions which connect themselves with this process, substitution of eqs. (4) and (5) in eq. (6) gives the following equations in the event that the electrical potential jump is far larger at this process than at the others;

$$\overrightarrow{i} = zF\kappa \frac{kT}{h} Q^{\delta I} e^{-\frac{\overrightarrow{U}_{(b)} + zF(V^* - V^I)}{RT}}, \quad (7\overrightarrow{i})$$

and,

$$\overleftarrow{i} = zF\kappa \frac{kT}{h} Q^{\delta F} e^{-\frac{\overleftarrow{U}_{(b)} + zF(V^* - V^F)}{RT}}, \quad (7\overleftarrow{i})$$

where,

$$\overrightarrow{U}_{(b)} = \mu_0^{\delta*} - \overline{\mu}_0^{\delta I} + RT \log Q^{\delta*}, \quad (8U_{(b)})$$

$$\overleftarrow{U}_{(b)} = \overline{\mu}_0^{\delta*} - \overline{\mu}_0^{\delta I} + RT \log Q^{\delta*}. \quad (8\overleftarrow{U}_{(b)})$$

Supplied with no external voltage and in an equilibrium state,  $Q^{\delta}$  and  $V$  are reduced to  $Q_0^{\delta}$  and  $V_0$ , respectively, and the electrical potential at the specific double layer of the species  $\delta$ ;

$$-\eta_0 = -(V_0^F - V_0^I) = \frac{\overline{\mu}_0^{\delta F} - \overline{\mu}_0^{\delta I}}{zF} + \frac{RT}{zF} \log \frac{Q_0^{\delta F}}{Q_0^{\delta I}} \quad (9)$$

whereas supply of external voltage gives rise to  $\eta$  in the electrical potential of the same point. Upon these premises, we obtain from eq. (7),

$$\vec{i} = \vec{K}_a Q_0^{\delta I} e^{-\frac{zF}{RT} \alpha' (\eta_0 - \eta)}, \quad (10 \vec{i})$$

and,

$$\overleftarrow{i} = \overleftarrow{K}_a Q_0^{\delta F} e^{-\frac{zF}{RT} \alpha (\eta_0 - \eta)}, \quad (10 \overleftarrow{i})$$

where,

$$\vec{K}_a = zF \kappa \frac{kT}{h} e^{-\frac{\vec{U}^{(v)}}{RT}}, \quad \text{and} \quad \overleftarrow{K}_a = zF \kappa \frac{kT}{h} e^{-\frac{\overleftarrow{U}^{(v)}}{RT}} \quad (11 \vec{K}), (11 \overleftarrow{K})$$

$$(a \sim a' = 1). \quad (12)$$

In a reaction system where the diffusion process of the ionic species is the rate-determining step, variation in the electrical field intensity is followed by the change of the current flux,  $i$ , in the bulk of the solution, including the hydrodynamical boundary layer and the diffusion layer in the vicinity of the electrode surface.

Though the electro-magnetic theory cannot be adopted directly when a diffusion layer of ionic species is formed and therefore diffusion of ionic species is at issue, little regard is paid to the potential drop in the layer in the minute research by Kimball.<sup>1)</sup>

#### §4. The Activation Overpotential in the Poly-dimensional Field

In this section, we will see how the concept of the "reaction flux" can be utilized in the explanation of the activation overpotential in the poly-dimensional field.

In equilibrium, no difference in the chemical potential exists between the initial and the final states, so that directly follows,

$$\vec{K}_a Q^{\delta I} = \overleftarrow{K}_a Q^{\delta F} \quad (\text{in equilibrium}). \quad (1)$$

In the next place, the respective net rates of the reaction and of the current flux are shown as,

$$v = \vec{v} \sim \overleftarrow{v}, \quad i = \vec{i} \sim \overleftarrow{i}. \quad (2 v), (2 i)$$

When the external application of voltage is so large as to suppress the electrical potential at the double layer to a sufficiently low value, it turns out that  $\vec{v}$  and  $\overleftarrow{v}$  are no more than the net rates,  $v$ , and  $i$  respectively, ignoring  $\overleftarrow{v}$  and  $\overleftarrow{i}$  in practice. Introduction of this supposition yields the so-called "Tafel's equation",<sup>2)</sup>

$$\pi_a = \frac{RT}{\alpha z F} \log K_a Q^{\delta F} - \frac{RT}{\alpha z F} \log i, \quad (3)$$

1) Kimcall and Glassner, J. Chem. Phys., 8, 815 (1940).

2) Tafel, Z. phys. Chem., 34, 200 (1900); *ibid.*, 50, 641 (1905).



which came from his experimental analysis,<sup>1)</sup> and has been a hot topic in the world of electrochemistry.

### §5. Migration of Ionic Species

Migration of a charged particle such as an ionic species towards the electrical field supplied on it is inevitable consequently discrepancy is caused in its concentration, which is succeeded by its diffusion as the immediate result. The first kinetic analysis of this phenomenon was carried out by Stearn and Eyring.<sup>2)</sup>

In this section we shall confront with the reconsideration of this problem from the view point of the reaction flux.<sup>3)</sup>

Regarding diffusion or migration also as a type of chemical reactions, the reaction rate is stated under the influence of the external force,  $f$ , as,

$$v = K_a' Q^{\delta}(s) e^{-\frac{\beta' f}{RT}} - K_a' Q^{\delta}(s') e^{-\frac{\beta f}{RT}} \quad (1)$$

where  $K_a'$  is the rate constant.

We are free any objection when we express the constant in  $K_a'$ , since diffusion and migration are typical in their reversibility as chemical reactions, i.e.,

$$\vec{K}_a' = \overleftarrow{K}_a'.$$

$Q^{\delta}(s)$  and  $Q^{\delta}(s')$  are respectively equal to the numbers of the species existing on the sections,  $S$  and  $S'$ , which are to be understood as the domains of either side of the potential barrier for the diffusion process. It may be suitable to consider that the interface between the adsorbed atomic layer and the adsorbed ionic layer<sup>4)</sup> constructs the transition surface in this case.<sup>5)</sup> The width of this transition surface, in other words, the distance between right- and the left-hand domains of the potential barrier,  $\lambda$ , can be rationally considered as nearly the same order as the size of the reactant species. The assumption over the similarity of the surface  $S$  and  $S'$  which are set up face to face with such microscopic gap between each other, allows to expand  $Q(s')$  in eq. (1) into  $\lambda$ 's power series,

$$v = K_a' Q^{\delta}(s) e^{-\frac{\beta' f}{RT}} - K_a' \left\{ Q^{\delta}(s) + \lambda \frac{dQ^{\delta}}{dn} \right\} e^{-\frac{\beta f}{RT}}, \quad (2)$$

where  $n$  means the length of the normal direction at the sectional surface  $S$ .

1) Hine, Yoshizawa and Okada, *J. Electrochem. Soc. Japan*, **20**, 218 (1952).

2) Stearn and Eyring, *J. Phys. Chem.*, **44**, 955 (1940).

3) Okada, Yoshizawa and Hine, *J. Electrochem. Soc. Japan*, **20**, 120 (1952). Hine, Yoshizawa and Okada, *ibid.*, **20**, 333 (1952).

4) Kimball, Glastone and Glassner, *J. Chem. Phys.*, **9**, (1940).

5) Hine, Yoshizawa and Okada, *loc. cit.*

When the external force,  $f$ , is supposed to be much smaller than  $RT$ , expansion of the exponential terms in eq. (2) into McLaurin's series easily derives,

$$v = D \left\{ -\frac{zF}{RT} E Q^{\delta}(s) - \frac{dQ^{\delta}}{dn} \right\} \quad (3)$$

where,

$$D = \lambda K_a' \quad (4)$$

at the evaluation of which we must not forget the interaction between the charged ionic species, especially between the species which have opposite signs to each other<sup>2)</sup>, that is to say, in the simplest case of an electrolytic solution, for which we find each one kind of oppositely charged species, the diffusion coefficient,

$$D = \frac{zRT}{F^2} \frac{A_+ A_-}{A_+ + A_-} \quad (5)$$

where  $A_i$  denotes equivalent conductance.

Now, the first term of the right-hand side of eq. (3) shows the degree of the migration of the ionic species, while the second the diffusion on account of the difference in the concentration.

The next subject of our deliberation, then, is in what form of function the second term can be expressed. Approving with Nernst<sup>3)</sup> that the concentration decrement is of linear gradient in the diffusion layer (thickness:  $d$ ),

$$\nabla C^{\delta} = \frac{C_0^{\delta} - C_s^{\delta}}{d} \quad (6)$$

where  $C_0^{\delta}$  represents the concentration at the bulk and  $C_s^{\delta}$  at the electrode surface.

He carried it out for the dissolution of solid bodies. Though actual cases never exhibit such linearity, this bold postulate is able to be nodded assent to, with the introduction of the "reduced thickness", which shall be treated in the coming section.<sup>4)</sup>

Now that  $d$  is always somewhere from  $10^{-1} \sim 10^{-2}$  cm. and, accordingly, no abrupt alteration is ever possible,

$$\frac{dQ^{\delta}}{dn} = \frac{Q_0^{\delta} - Q_s^{\delta}}{d} \quad (7)$$

as the result of the substitution of  $Q^{\delta}$  for  $C^{\delta}$ .

1) Eyring, J. Chem. Phys., 4, 285 (1936).

2) Glasstone, Laidler and Eyring, The Theory of Rate Processes, p.556 (1941).

3) Nernst, Z. phys. Chem., 47, 52 (1904).

4) Hine, Yoshizawa and Okada, not yet in publication.

### § 6. Diffusion Layer

The change of the concentration in the neighbourhood of the electrode is worth consideration in electrochemistry, in the name of the "concentration polarization", which does, however, not arise without the subsistence of the solvent. Therefore the kinetic treatment of it necessarily differs from that of a gaseous phase and three individual processes—Migration, Convection, and Diffusion—are involved in the present case. But, as it is almost beyond the possibility of mathematics to consider simultaneously these processes, this investigation is only performed under special conditions of electrolysis, namely, by supposing that apart from the ions which respond to the electrolysis, there exist many other ions which are independent of the reaction, and that the solution is in vigorous agitation, so that we may neglect the migration of ions and the convection of the solution, to limit the investigation to the concentration polarization caused by diffusion alone.

The following is the theory established by Neyes and Whitney<sup>1)</sup>, Nernst<sup>2)</sup>, Brunner<sup>3)</sup>, and others.

When an electrolytic solution with an initial concentration  $C_0$  is brought to electrolysis, the concentration of the ion in the vicinity of the electrode will undoubtedly suffer change. But once the equilibrium is arrived at, the stationary state continues with  $C_e$  as the concentration at the electrode surface (see Fig. 4), unless constant current density is broken. And then in Fick's diffusion formula,

$$\frac{\partial c}{\partial t} = D \cdot \Delta C(x, y, z), \quad (1)$$

derivative  $\partial C/\partial t$  becomes zero and the formula proves to be Laplace's equation.

Postulating that the electrodes consist of parallel and infinitely expanded planes and that the diffusion of ions is limited within the normal direction at the surface of the electrode, (e.g., the direction of  $y$ ), the question can be simplified to Laplace's equation of one-dimension. Then, the well-known formula,

$$i/zF = D(C_0 - C_e)/d, \quad (2)$$

is derivable upon these premises:

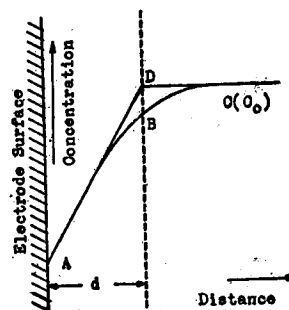


Fig. 4

1) Neyes and Whitney, *Z. phys. Chem.*, **23**, 689 (1897).

2) Nernst, *ibid.*, **47**, 52 (1904).

3) Brunner, *ibid.*, **47**, 56 (1904).

- (1) the solution, again, is effectively stirred, and
- (2) the diffusion layer is formed anew, to the interior of which the change of the concentration is limited.

This concept of the "diffusion layer" at the electrode surface is confirmed experimentally by Nerst<sup>1)</sup>, Akerberg<sup>2)</sup>, Karaoglanoff<sup>3)</sup>, Glasstone<sup>4)</sup>, Wilson and Youtz<sup>5)</sup>, and also by the polarographic method<sup>6)</sup>.

Although the above consideration was made with regard to an one-dimensional field for a heterogeneous reaction, it differs essentially from the basis of eq. (3) of §5, for the latter includes skilfully the migration term as well as the diffusion term.

To return to the main subject, to what does the thickness of the diffusion layer amount? With all the values of 0.001~0.1 cm. asserted by Wilson and Youtz which are, frankly speaking, of little reliability, this intangible object still seems to remain far from elucidation except through an insight into its intrinsic nature including a study of the various factors working in its formation. From this startingpoint, Okada, Yoshizawa and Hine have made researches as to the form of the diffusion layer with no successful result sufficient for general adaptation<sup>7)</sup>.

Although, so far, we have stressed the assumption of uniform concentration in the bulk of the solution, the most modern hydrodynamics is at a loss to analyze convection and agitation, so that we have no other resort to understand various phenomena in the liquid phase than the adoption of a laminar flow. Our stand-point regarding the diffusion layer<sup>8)</sup> is that as the dissolution of an electrolyte is quite uniform in its solution, surrounded by the solvent molecules, the standstill of the ions apart from the solvent is not permissible in case of agitation; while hydrodynamics for viscous fluid teaches well the existence of the boundary layer near a solid surface (the electrode surface), where the ions in question are stagnant. And then, immediately after electrical field is imposed, there occurs diffusion which is seen only within the boundary layer.

For convenience, let us take a parallel flat plate electrode as an example.

- 1) Nerst, *Z. phys. Chem.*, **53**, 1235 (1905).
- 2) Akerberg, *Z. anorg. Chem.*, **31**, 161 (1902).
- 3) Karaoglanoff, *Z. Elektrochem.*, **12**, 5 (1906).
- 4) Glasstone, *Trans. Farad. Soc.*, 299 (1933).
- 5) Wilson and Youtz, *Ind. Eng. Chem.*, **15**, 603 (1923).
- 6) Okada, Yoshizawa and Hine, *J. Electrochem. Soc. Japan*, **19**, 18 (1951).
- 7) Okada, Yoshizawa and Hine, *J. Electrochem. Soc. Japan*, **19**, 18 (1951).
- 8) Okada, Yoshizawa and Hine, *ibid.*, **20**, 120 (1952).

The substantiality of Blasius' solution<sup>1)</sup>, one of the various researches over the boundary layer, it must be noted, confined within the narrow region far from the edge of the electrode; whereas Carrier and Lin<sup>2)</sup> have lately obtained a rigorous solution for the neighbourhood of the leading edge.

According to them, as the exactness of the approximation of Stokes' is very high there, by its introduction as the first approximation the function of a flow becomes,

$$\psi = \psi_0 + \psi_1 + \psi_2 + \dots, \quad (3)$$

where  $\psi_0$  is Blasius' function of the flow, and is employed as the first approximation.  $\psi$  may, therefore, be calculated by the successive method. In the first place,

$$\psi_0 = Ar^{\frac{3}{2}} \left( \cos \frac{\theta}{2} - \cos \frac{3\theta}{2} \right),$$

and

$$\psi_1 = \frac{A^2 r^3}{128} \left[ \theta (\cos \theta - \cos 3\theta) + \log r (3 \sin \theta - \sin 3\theta) \right] + \frac{Ar^3}{40} \left[ \sin 2\theta - 2 \sin \theta \right].$$

On the other hand, the velocity component of Blasius' solution for this direction of the flow at the points distant from the leading edge where his solution is high in its degree of approximation, is expressed in,

$$u_1 = f(\eta), \quad \eta = \frac{y}{x^{1/2}},$$

and,

$$f(\eta) = \alpha \frac{\eta^2}{2!} - \alpha^2 \frac{\eta^5}{2 \cdot 5!} + \dots,$$

where,

$$\alpha = 0.332 : \text{Blasius' Constant},$$

which leads to the following approximation near the electrode surface ( $\theta \approx 0$ ),

$$u_1 \approx ar^{\frac{3}{2}} \theta - a^2 r^2 \frac{\theta^4}{48} + \dots \quad (4)$$

And so, combination of eq. (4) with

$$u_1 + iv_1 = -2i \frac{\partial \psi}{\partial \bar{z}_1}, \quad (\bar{z}_1 : \text{Conjugate Complex of } z_1)$$

derived from eq. (3), yields,

$$u_1 \approx 4Ar^{\frac{1}{2}} \theta + \gamma r^2 \theta^4 + \delta r^2 \log r \cdot \theta^4 + \dots, \quad (5)$$

where  $\theta$  is nearly zero,  $\gamma$  and  $\delta$  are constants.

1) Blasius, Z. Math. Phys., 56, 1 (1908).

2) Carrier and Lin, Quart. Applied Math., 6, 63 (1948).

For the definite value of  $r$ , eqs. (4) and (5) agree with each other, so that,

$$4A = \alpha, \quad \text{i.e., } A = 0.083. \quad (6)$$

Accordingly, the ultimate results are,

$$\begin{aligned} \psi = & 0.083r^{\frac{3}{2}} \left( \cos \frac{\theta}{2} - \cos \frac{2\theta}{2} \right) \\ & + 0.00005r^3 [\theta (\cos \theta - \cos 3\theta)] \\ & + \log \gamma (3 \sin \theta - \sin 3\theta) + 0.00017r^3 [\sin 2\theta - 2 \sin \theta] + \dots, \end{aligned} \quad (7)$$

$$u_1 = 0.083r^{\frac{1}{2}} \left( 5 \sin \frac{\theta}{2} + \sin \frac{3\theta}{2} \right) + \dots. \quad (8)$$

Substituting  $\pi$  for  $\theta$  in eq. (8) at the leading edge, and transforming the solution of eq. (8) from the  $r-\theta$  domain to the  $x-y$  field, we have,

$$u/u_0 = 0.332 u_0 x / \nu. \quad (9)$$

The coordinate,  $d_e$  of the point where  $u=u_0$ , is shown as.

$$d_e = \frac{1}{0.332} \frac{\nu}{u_0} = 3.012 \frac{\nu}{u_0}, \quad (10)$$

in which  $\nu$  is the kinematic coefficient of viscosity.

For example, if we may take up a copper sulfate solution whose concentration is 12.57% in weight percentage (equal to about 1.5N), dynamical viscosity coefficient,  $\mu$ , is 0.0133 poise, specific gravity,  $\rho$ , is 1.13, each at 25°C,<sup>1)</sup> and flow velocity,  $u_0$ , is 10 cm/sec. The thickness of the diffusion layer at the leading edge,  $d_e$ , is calculated to be 0.0035 cm., which agrees well with the data in previous reports by various workers<sup>2)</sup>.

These investigations so appeared to have established a definite idea as to the phenomena of diffusion in the main, that, for the purpose of backing it up, we attempted an experiment of copper deposition employing an electrolytic cell of nearly the same form<sup>3)</sup>. But the result obtained fell far start of what had been expected concerning the rate of the deposition<sup>4)</sup>. As the conclusion, the dishonourable name of "null hypothesis" cannot but be thrown upon the postulate that the diffusion layer accords with the hydrodynamical boundary layer, since the former must be undoubtedly thinner than the latter. Thus we were imposed to inquire this problem again.

1) Jituyō Kagaku Binran (Practical Table for Chemistry, Tokyo), (1948).

2) c. f., Suito, Buturikagaku no Simpo (Proceedings of Physical Chemistry), 15, 37 (1941).

3) Hine, Yamori, Yoshizawa and Okada, The Meeting of The Electrochemical Soc. of Nippon in 1952. 4. 14., No XIX.

4) Okada, Yoshizawa and Hine, J. Electrochem. Soc. Japan, 20, 120 (1952).

**§7. Movement of Ionic Species in a Flow<sup>1)</sup>**

Some consideration have been given to the electrical condition of a flowing solution, but almost in vain, because they take into account both the absolute migration velocity and velocity of the solution at one and the same time.

When an electrolytic solution is flowed parallel to a flat plate electrode, the dynamic stress against an ionic species is divided into,

- (1) the migration force in virtue of the electrical field, and
- (2) the dynamic stress by dint of the fluid flow.

The former corresponds to the absolute migration velocity, whereas the latter is the tangential stress over the ionic species constructing the double layer. According to hydrodynamics, a particle in a viscous fluid may exempt from it. Short numerical scrutiny makes it clear that the absolute migration velocity is of the order of  $10^{-3}$ – $10^{-4}$  cm/sec under unit intensity of the electrical field, while the usual velocity of the fluid flow is about  $10^{-1}$ – $10$  cm/sec. In a word, the latter is far larger than the former. It appears not implausible then that electrical current cannot stream in an agitated fluid since all the ionic species are fetched away under such circumstances. We have never experienced such a phenomenon in practice, though some larger resistance may be encountered. In fact we are impossible to eliminate the effects of natural convection almost equivalent to that of a forced flow in general manipulations.

This apparent inconsistency is unraveled as follows. The absolute migration velocity pertains to an individual particle. But it cannot be free from objections to regard the velocity of a separate particle in the same light with that of the total flow at a fixed point, since hydrodynamics has no eye to distinguish any finer structures beyond the continuous body of the whole of a solution. In consequence we cannot help admitting the snub of hydrodynamics for assistance in the treatment of the behaviour of an ionic species.

At a fixed point, an ionic species may be carried away in an instant, but another species is always ready to fill the position of the preceding one in succession to it to form an invariable condition of the system. A more physico-chemical explanation states that no deformation is possible in the net structure of water molecules in an electrical field, because it is neither possible nor useful to grasp the behaviour of the conductive species within it which show dizzy motions, along the centers (in case of hydroxonium ions) or through (in case of other ordinary ions) the net structure.

If it be so, through what course is the fluid flow influential upon electrode

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1) Hine, Yoshizawa and Okada, not yet in publication.

reactions? Presumably it is the tangential stress on the electrode surface, as the exposition will display by degrees.

### § 8. Flow of the Electrolytic Solution and Arrangement of the Ionic Species on the Electrode Surface and near it

It is well-known from earlier years that reactant species form a double layer on the electrode surface and from there to the bulk of the solution there exists a continuous distribution of the same kind of species.

The potential barrier at the double layer is comparatively high, while that at the diffusion layer is small enough to be neglected<sup>1)</sup>. The arrangement of ions in diffusion layer as a result of dynamical phenomena is almost regular<sup>2)</sup>.

We approximated for convenience's sake the diffusion layer with the hydrodynamical boundary layer, which proved to be erroneous. As there's also a certain distribution is so apt to become uniform, that it seems to be naturally accepted that the diffusion layer is thinner than the boundary layer as visible in Fig. 5. The next object is, then, to obtain the concentration distribution of ionic species in the same way as Blasius did<sup>3)</sup> for the velocity distribution in the boundary layer.

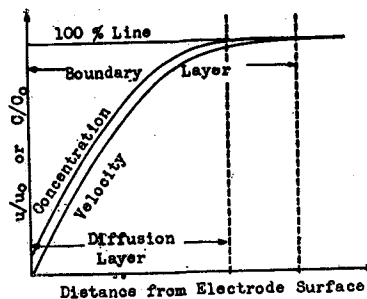


Fig. 5

Before this, a brief review of the effect of flow is to be introduced.

### § 9. Stress on Reactant Species by Flow

No scope for further discussion can be afforded to the fact that we can pay no regard to the existence of dynamical stress upon reactant species placed in a potential field of a solution, as expounded in § 7. For this reason, we make little of the effect of flow upon the electrode reaction in a perfectly non-viscous electrolytic solution, for which, to our great regret, we lack samples to give experimental verification. The effect of flow is, therefore, attributable to the viscosity of the solution, if we are not much mistaken.

Namely, as is well-known, the surface of a body exposed in a flow of a viscous fluid is covered with a boundary layer, where declination of the velocity in the normal direction of the flow makes any two adjacent layers give the

1) Kimball and Glassner, J. Chem., 8, 814 (1940).

2) Okada, Yoshizawa and Hine, J. Electrochem. Soc. Japan, 20, 120 (1952).

3) Blasius, Z. Math u. phys., 56, 1 (1908).



tangential shearing stress to each other,

$$X = \mu \frac{du}{dy}. \quad (1)$$

This results in a slip between the two layers, working on each species ranging on them. Thus the effect is specific for the coordinate in the layer, though by us<sup>1)</sup> it was once erroneously confined to the first layer from the electrode surface—the electrical double layer. Expansion of this primitive idea is enough, however, when an alternating current is supplied of the mechanism is activation-controlled, while further scruple is requested for the treatment of a system where the concentration distribution matters.

### §10. Concentration Distribution in the Diffusion Layer near the Flat Plate Electrode

The classical diffusion theory of responsible for the fundamental differential equation<sup>2)</sup>,

$$\frac{\partial n}{\partial t} = \frac{D}{kT} \operatorname{div} (kT \operatorname{grad} n - \mathbf{K}n). \quad (1)$$

where  $n$  is the quantity of the species in unit volume,  $\mathbf{K}$  is the intensity of the field and  $D$  is, similar to before, the diffusion coefficient which is, generally speaking, independent of the coordinate.

For a two-dimensional flow in the equilibrium state, eq. (1) is rewritten as,

$$kT \left[ \frac{\partial^2 n}{\partial x^2} + \frac{\partial^2 n}{\partial y^2} \right] - \left[ \frac{\partial K_x n}{\partial x} + \frac{\partial K_y n}{\partial y} \right] = 0, \quad (2)$$

where  $K_x$  and  $K_y$  are the components of  $\mathbf{K}$  for the directions  $x$  and  $y$ , respectively. Though eq. (2) is to produce the solution in connection with the boundary conditions,

$$(n) \text{ at the surface of the boundary layer} = n_0: \text{ Constant}, \quad (3)$$

and, from eq. (3), p. 50,

$$\left( \frac{\partial n}{\partial y} \right) \text{ at the surface of the electrode} = - \left( \frac{i}{zFD} + \frac{zFE_s n_s}{RT} \right), \quad (4)$$

the equation is impossible to be solved and analyzed, since it is non-linear as  $K_x$  and  $K_y$  are the functions of  $x$  and  $y$ , severally, and moreover, the boundary condition (3) may be dependent upon the form of the boundary layer. Then let us prove, to be satisfied perforce, the concentration distribution in the

1) Hine, Yoshizawa and Okada, Course of Publication in J. Electrochem. Soc. of Japan.

2) C. f., Toda, Ekitai Kōzōron (The Theory of Liquid), p. 239 (1947), Kyoritu Co., Tokyo.

perpendicular section to the flow. Good approximation seems to be attained at the parts far from the leading edge in whose vicinity the boundary layer may be capable of displacing the diffusion layer. The outlook of the concentration distribution becomes almost open before our eyes, on the adaption of this process at several points.

At the first place the direction  $y$  is taken up, when

$$kT \frac{d^2n}{dy^2} - \frac{dK_y n}{dy} = 0. \quad (5)$$

Now, if it is assumed that  $K_y$  is approximately equal to the term of the electro-static field, it is nearly unrelated to  $y$  except in the neighbourhood of the leading edge. Therefore,

$$kT \frac{d^2n}{dy^2} - K_y \frac{dn}{dy} = 0. \quad (6)$$

The boundary conditions are given as,

$$(n)_{y=d(x)} = n_0, \quad \text{and} \quad (7)$$

$$\left(\frac{dn}{dy}\right)_{y=0} = \frac{\kappa N}{zFD} E_s(x) - \frac{zFE_s}{RT} n_s, \quad (8)$$

where  $d(x)$  expresses the thickness of the boundary layer which is the function of the coordinate  $x$ ,  $E_s$  is the field intensity at the coordinate  $x$  on the electrode surface, and  $\kappa$  is the conductivity which is considered to be constant, independent of the change of the ionic concentration. And, the definition demands,

$$K_y = -z \cdot e \cdot E_s. \quad (9)$$

In consequence, eq. (9) is analyzed as,

$$n = n_0 + \left(n_s - \frac{\kappa NRT}{z^2 F^2 D}\right) \left\{ e^{-\frac{zFE_s(x)}{RT} y} - e^{-\frac{zFE_s(x)}{RT} d(x)} \right\}, \quad (10n)$$

or,

$$c = c_0 + \left(c_s - \frac{\kappa RT}{z^2 F^2 D}\right) \left\{ e^{-\frac{zFE_s(x)}{RT} y} - e^{-\frac{zFE_s(x)}{RT} d(x)} \right\}. \quad (10c)$$

This is converted, by the use of  $c_y=0$ , into,

$$E_s(x) = -\frac{RT}{zF} \frac{1}{d(x)} \log \left( 1 - \frac{z^2 F^2 DC_0}{\kappa RT} \right), \quad (11)$$

which represents the field intensity corresponding to the so-called "limiting current" at the point with  $x$  as its coordinate.

Before the actual enumeration with an example is made, appropriate

assumption is indispensable for the field intensity,  $E_s(x)$ , and the thickness of the boundary layer,  $d(x)$ .

The former is approximated as,

$$E_s(x) = \frac{V_0^*}{a} \frac{1}{\sqrt{(\xi-1)^2}} \quad (12)$$

where,

$$x = 3.183 (\xi - 1 - \log \xi),$$

and the latter, adopting the velocity distribution,

$$u = u_0 \sin \frac{\pi y}{2d}, \quad (13)$$

as,

$$d(x) = \sqrt{\frac{2\pi^2}{4-\pi}} \sqrt{\frac{\nu x}{u_0}} = 4.80 \sqrt{\frac{\nu x}{u_0}} \quad (14)$$

The other conditions for exemplification are as follows:<sup>2)</sup>

Composition of the electrolytic solution:

cry.  $\text{CuSO}_4$  0.6 mol/lit., and conc.  $\text{H}_2\text{SO}_4$  0.5 mol/lit.

Conductivity of the solution: 0.139 mho/cm at 20°C.

Dynamic viscosity coefficient: 1.387 c.p. at 20°C.

Specific gravity: 1.127 at 20°C.

Temperature: 20.6°C. (mean value)

Velocity of flow: 5 cm/sec.

Shown in Fig. 6 is an example of the concentration distribution. It may be possible to understand the outline of the distribution if we make several sheets of such profiles with regard to many points.

Suppose a quantity,  $d^*$ , which is give expression in the equation,

$$d^* = \frac{1}{c_0} \int_0^{y_1} (c_0 - c) dy \quad (15)$$

where  $y_1$  is an arbitrary thickness thicker than that of the boundary layer. The physical meaning of this term may be explicit in the following paragraph.

Figured to the left is the concentration distribution in a section which is elected vertically

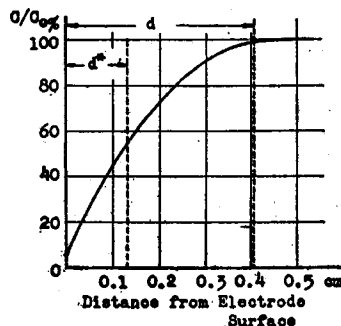


Fig. 6

1) Lamb, Hydrodynamics, p. 686 (1932). Kármán and he employed this to analyze the momentum equation.  
 2) Hine, Yoshizawa and Okada, Course of publication in J. Electrochem. Soc. of Nippon.

to the electrode surface at a point A.

The term  $\int_0^{y_1} c_0 dy$ , in eq. (15), whose graphical expression is the area ABCD, is equivalent to the quantity in a belt-like part with  $y_1$  as its width from the electrode, if the electrolytic solution is perfect fluid and no diffusion takes place. The term,  $\int_0^{y_1} c dy$ , gives the flow through the same belt, when viscosity of the solution causes the concentration distribution shown in Figs. 6 and 7, that is, the area AEFCD.

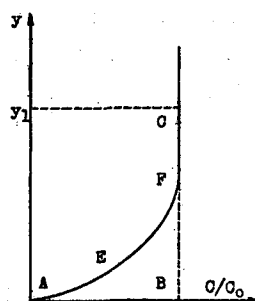


Fig. 7

Therefore, the area ABFE indicates the flows of the perfect and the viscous fluid. On the other hand, at the leading edge and the region without the electrode, the flow must correspond to  $\int_0^{y_1} c_0 dy$ , through the belt between the line of the electrode and the line distant from it by  $y_1$ . And if we properly assume that the velocity of flow is much larger than the diffusion rate of ionic species, the law of continuity comes approximately into existence. Hence, the equi-concentration line which would pass through  $y_1$  in case of perfect fluid, should diverge outwardly by  $\int_0^{y_1} (c_0 - c) dy$ . But, it must be suitable to denote the extent of the deviation with  $\frac{1}{c_0} \int_0^{y_1} (c_0 - c) dy$ , as the velocity and the concentration are both uniform, with constant values of  $u_0$  and  $C_0$ , respectively, in the bulk of the solution. This idea is gained by the extension of the notion of "Displacement Thickness" <sup>1)</sup> concerning viscous fluid to the field of concentration. Thus,  $d^*$  can be naturally named the "Equivalent Thickness of the Diffusion Layer".

For instance, substitution of eq. (11) to eq. (15), leads,

$$d^* = \left( \frac{\kappa RT}{z^2 F^2 D C_0} - \frac{c_0}{c_s} \left[ \frac{RT}{z F E_s} \left( 1 - e^{-\frac{z F E_s d}{RT}} \right) - d \cdot e^{-\frac{z F E_s d}{RT}} \right] \right) \quad (16)$$

which is calculated and figured in Fig. 8, along with  $d$ , for a flat plate electrode.

At all event, this "equivalent thickness" is a fictitious thickness, within which it is imagined possible that the concentration is affected practically by no flow. A better agreement results when it is applied again to the analysis of the data of the copper deposition in § 6, leaving no room for further examination.

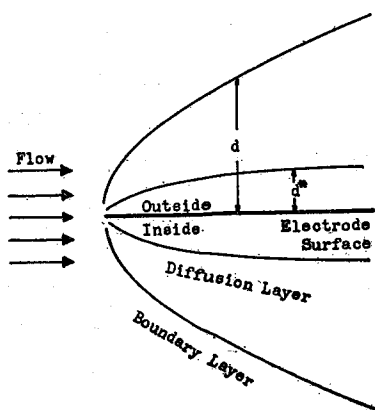


Fig. 8

1) Prandtle, Aerodynamic Theory, Vol. III, p. 89 (1935).

### § 11. Polarizations in the Poly-dimensional Field

We have been taught that there are many types of polarization, an inevitable accessory to an electrode reaction. If we pay our attention exclusively to the concentration polarization, we are still in anxiety shadowed by the activation overpotential originated in the process of the construction change of the species in question, because without it no licence can be granted for the proceedings of the reaction and it precedes the concentration polarization, however small it may be in case of the diffusion-controlled. On the contrary, the polarographical research was not blind in finding the diffusion phenomena in the hydrogen electrode reaction which is typical of the activation-controlled. Moreover, different points on a electrode surface, when the field intensity varies much in accordance with the position. We have so many examples in this line, it is necessary to reduce the whole polarization so as to be analyzed at the same time in spite of the multifariousness of its origin. So it is! The polarization is after all the general name of the phenomena at the double layer which is paved all over the electrode surface, and its qualitative significance to divide it into several types.

In this sense, we are unsparing in the praise of Kimball<sup>1)</sup>, who at all events attempted to debate at once the diffusion phenomena and the construction change of the reactant species, which of these is rate-determining no one knows. We are to follow him in our analysis as you see in the following pages<sup>2)</sup>.

The reaction rate concerning the construction change process has already had its expression in § 7 and § 8, and the rate of the diffusion process has also received in § 7 the baptism of discussion after the manner of Eyring, divided into two parts,—the diffusion term and the migration term. In case of the former is employed without any correction the Nernst equation based upon the linearity of the concentration distribution which is just imitative of the dissolution of solid bodies. But a question necessity arises as to the thickness of the diffusion layer. Let us introduce here the equivalent thickness of the diffusion layer obtained from the view-point of hydrodynamics in the previous section. A physical meaning will be bestowed for the first time under this restriction upon the linear concentration distribution, which has been presumed by Nernst and others upon no trustworthy ground. Now, it is necessary to simplify the domain of the reactant species at the electrode surface to the model of the Helmholtz layer<sup>3)</sup> nearest to the surface with the diffusion layer next to its reaching the

1) Kimball, *J. Chem. phys.*, 8, 199 (1940).

2) Hine, Yoshizawa and Okada, *J. Electrochem. Soc. Japan*, 20, 332 (1952).

3) Helmholtz, *Weid. Ann.*, 1, 338 (1879).

bulk of the solution.  $d^*$  is the thickness of the diffusion layer, where the concentration is of linear distribution and the diffusion potential is negligibly small, as verified elaborately by Kimball and his co-authors<sup>1)</sup>. And the concentrations and the quantities of the species  $\delta$  existing at various sections of the reaction flux are denoted by  $C^\delta$  and  $Q^\delta$ . The suffixes,  $e$ ,  $\sigma$  and  $o$  at the waists of these respectively distinguish the electrode surface, the boundary between the Helmholtz layer and the diffusion layer and the bulk of the solution.

Of course, such assumption about the double layer is not correct under strict survey. For example, according to Horiuti and his cooperators<sup>2)</sup>, among various mechanisms presented by many authors, the hydrogen electrode reaction complies with the quasi-catalytic mechanism in case of nickel cathode, while the electrochemical one with  $H_2^+$  as the intermediate product when the electrode is changed into mercury. And what is more interesting, the mechanism for platinum cathode shifts by degrees from the former to the latter in proportion to the current density. Helmholtz layer introduced here has no capacity to give any authentic explanation to such a singular case which can be possibly made out either by Stern's theory<sup>3)</sup>, or by the idea of the adsorbed atomic layer and the adsorbed ionic layer arranged side by side, developed by Kimball<sup>4)</sup>.

The reaction rate of the construction change and the diffusion process must be equal to each other in this continuous reaction flux, so that from eqs. (2) in § 4, (10) in § 10 and (3) in § 5, we have,<sup>5)</sup>

$$Q_e^\delta = Q_o^\delta \frac{\frac{D}{d^*} + \overleftarrow{K}'_a e^{-\frac{\alpha' z F (\eta_0 - \eta)}{RT}}}{\frac{D}{d^*} - \frac{z F E_s}{RT} D + \overleftarrow{K}'_a e^{-\frac{\alpha z F (\eta_0 - \eta)}{RT}}} \quad (1)$$

This development of idea has no essential difference with Kimball's work, except that Kimball shows the migration term by confining the rate at the diffusion layer only to the velocity of diffusion on account of the difference in the concentration, following Nernst's thought for non-electrical field.

Combination of eq. (1) with eq. (2) in § 4 gives,

$$i = \overleftarrow{K}_o Q_o^\delta \frac{\left(1 - \frac{z F E_s}{RT} d^*\right) e^{\frac{z F (\eta_0 - \eta)}{RT}} - 1}{\left(1 - \frac{z F E_s}{RT} d^*\right) e^{\frac{\alpha z F (\eta_0 - \eta)}{RT}} + \overleftarrow{K}'_a \frac{d^*}{D}} \quad (2)$$

- 1) Kimball and Glassner, J.chem. phys., 8, 815 (1940).
- 2) Horiuti and Okamoto, Sc. P., 28, 231, (1936).
- 3) Stern, Z. Electrochem., 30, 508 (1924).
- 4) Kimball, J. Chem. Phys., 8, 199 (1940).  
Kimball, Glasstone and Glassner, *ibid.*, 9, 91 (1941).
- 5) Okada, Yoshizawa and Hine, J. Electrochem. Soc. Japan., 20, 120 (1952). Hine, Yoshizawa and Okada, *ibid.*, 20 332 (1952).

where,

$$K' = K/zF. \quad (3)$$

This is noting less than our longed-for end, after a whole lot of arguments. It is clear that the polarization,  $\eta_0 - \eta$ , is the function of  $E_s$  and  $d^*$ , both of which are, in turn, dependent upon the coordinate, to make after all the polarization a variable dominated by the coordinate. It would not, however, be a waste of time to call your attention again to the disparity of this derivation from the results of previous works which are simple extensions of one-dimensional discussions and induced from entangled relation of functions, such as the false reasoning that the polarization is a subordinate variable of current density which is also dependent on the coordinate. For these several years, we have fixed our doubts on this problem. Starting at first from the daring hypothesis that the polarization potential is independent of the coordinate, we were successful in acquiring the outline of the electrode phenomena. But its true aspect were never elucidated until the methodology which is applied to get eq. (2) came to be used. It is a quite clear now to what extent the hypothesis surmised at first is applicable. However, we never insist that only the above method is significant. It is presented merely as a tentative plan to bring into analysis the heterogeneous elementary reactions such as the electrode reaction, which rejects direct assaults of mathematics.

### §12. Specialization of the Polarization in the Poly-dimensional Field<sup>1)</sup>

Correct analysis of eq. (2) in §11, is nearly impossible, as it is a transcendental function and the polarization,  $\eta_0 - \eta$ , cannot be converted into an explicit function. Therefore, it is inevitable to neglect smaller terms, comparing the magnitude of the terms with each other under special extreme conditions.

In the first place, in the numerator of the equation, the first term,  $\left(1 - \frac{zFE_s d^*}{RT}\right) e^{\frac{zF(\eta_0 - \eta)}{RT}}$ , is approximated to 1 when the polarization is relatively small, and the increasing polarization is succeeded by the gradual conversion of this term into zero. Secondly, the denominator transforms according to the sort of the rate-determining step of the reaction in question; that is to say, when it is the diffusion-controlled, we have,

$$i = zFQ_0^s \frac{D}{d^*} \left\{ \left(1 - \frac{zFE_s d^*}{RT}\right) e^{\frac{zF(\eta_0 - \eta)}{RT}} - 1 \right\}, \quad (1)$$

1) Hine, Yoshizawa and Okada, not yet in publication.

directly from eq. (2) in § 11,  $\left(1 - \frac{zFE_s}{RT}d^*\right) e^{\frac{zF(\eta_1 - \eta)}{RT}}$  being negligible to  $\frac{i_0 d^*}{K_a}$ . A small deformation of it for the purpose of expressing  $\eta_0 - \eta$  explicitly, gives,

$$\eta_0 - \eta = \frac{RT}{zF} \log \left(1 + \frac{i}{zFQ_0^{\delta}} \cdot \frac{d^*}{D}\right) - \frac{RT}{zF} \log \left(1 - \frac{zFE_s}{RT}d^*\right). \quad (2)$$

In this case, if the "limiting current",  $i_0$ , is attained regarding the reaction system on account of sufficiently high external voltage, eq. (2) becomes,

$$\eta_0 - \eta = \frac{RT}{zF} \log \left(1 - \frac{i}{i_0}\right) - \frac{RT}{zF} \log \left(1 - \frac{zFE_s}{RT}d^*\right), \quad (3)$$

where,

$$i_0 = -zFQ_0^{\delta} \frac{D}{d^*}. \quad (4)$$

The first term of eq. (3) is famous as the Nernst polarization potential<sup>1)</sup>, as the second is the contribution of the migration of the species to the polarization. This equation apparently shows that in the case of the diffusion-controlled, the polarization is under the domination of the coordinate, for not only the field intensity,  $E_s$ , but the equivalent thickness of the diffusion layer,  $d^*$ ,<sup>2)</sup> are the functions of the coordinate. But, even in this case, sufficiently large amount of indifferent electrolytes which are contained in the solution, reduces the term,  $\frac{zFE_s}{RT}d^*$ , negligibly small, compared with 1, and the polarization is only dependent upon the difference in the chemical potential or the concentration; even when it cannot be forget that, to tell the precise,  $i_0$  also included  $d^*$  which varies with the coordinate, to leave the polarization invariably under the shackles of the coordinate, no matter how this effect is trifling, because  $d^*$  is unified except at the leading edge by rapid flowing, with the result of the uniform polarization all over the electrode surface.

And now, turning to the circumstance where the migration factor comes to the front, some pages are to be given to a quantitative exemplification, taking for example the case of the copper sulfate solution again, with semi-infinite parallel plate electrodes as a model of electrolytic cell.<sup>3)</sup> The conditions of the electrolysis are:

Solution: cry.  $\text{CuSO}_4$  150 gr/lit.

dynamic viscosity coefficient 1.277 c.p. at 20°C.

Specific gravity 1.080 at 20°C.

Conductivity 0.0379 mho/cm. at 20°C.

1) see, Butler, *Electrocapillarity*, p. 164 (1940), London.

2) c. f., § 11.

3) Okada, Yoshizawa and Hine, *J. Electrochem, Soc. Japan*, 19, 159 (1952), also see, § 10.



Mean current density: 1.0 amp/dm<sup>2</sup>.

Temperature: 20±0.5°C.

Velocity of flow: 10 cm/sec.

The calculated magnitude of the migration term for this example is shown in Table 1.

Table 1.

Distance from Leading Edge (cm)	Migration Term (mV)	Distance from Leading Edge (cm)	Migration Term (mV)	Distance from Leading Edge (cm)	Migration Term (mV)
1.0	18.6	4.0	22.3	7.0	24.6
2.0	20.8	5.0	23.3	8.0	24.8
3.0	21.5	6.0	24.3	9.0	24.9

We may understand that the magnitudes of the diffusion term and of the migration term are comparable to each other from this table.

Namely, the migration factor is the most important when the polarization is considered for an electrolytic solution with high resistance as in the above mentioned case. Then, the word, polarization, heretofore in use, proves to include the migration term as well as the diffusion term. The actual polarization potentials under the experimental conditions above shown are displayed in Table 2.

Table 2.

Distance / Flow Vel.	0.2cm.	2.0	4.0	6.0	8.0	9.8
3.5 cm/sec	26.1mV.	26.2	26.0	25.9	26.2	25.5
4.5	26.2	26.5	26.0	25.3	26.2	26.0
5.0	26.4	25.4	26.4	25.8	26.0	25.7

Now, what effect can be deduced by the addition of free sulfuric acid into the copper sulfate solution? The following are the experimental conditions:

Solution: cry. CuSO<sub>4</sub> 150 gr/lit., conc. H<sub>2</sub>SO<sub>4</sub> 50 gr/lit.

Kinetic viscosity coefficient 1.587 c.p. at 20°C.

Specific gravity 1.127 at 20°C.

Conductivity 0.1469 mho/cm at 20°C.

Mean current density: 1.376 amp/dm<sup>2</sup>.

Temperature: 20.6°C. (mean value)

Velocity of flow: 3.5 cm/sec., 4.5 cm/sec.

The calculated values of the migration term are about 15 mV, while that of the diffusion term defies calculation for we lack the definition of the unit of the reaction. We may, however, consider to be about 45 mV by difference from the observed total polarization shown in Table 3.

Table 3.

Distance Flow Vel.		0.2 cm	2.0	4.0	6.0	8.0	9.0
	3.5 cm/sec	Inside Surface	33.3mV	32.7	32.8	32.5	31.9
Outside Surface		30.1	30.0	29.9	30.1	29.6	29.0
4.5 cm/sec	Inside Surface	32.9	32.9	32.8	32.7	32.5	32.8
	Outside Surface	30.4	30.1	30.1	29.9	29.7	29.9

Similar analysis is possible for anodic reactions. Shown in Table 4 is the anodic polarization when the above solution is electrolyzed with 0.5 amp/dm<sup>2</sup> as the mean current density.

Table 4.

Distance Flow Vol.		0.2cm.	2.0	4.0	6.0	8.0	9.8
	3.5 cm/sec	Inside Surface	44.0	38.8	40.5	38.6	43.7
Outside Surface		40.7	41.1	39.2	41.8	36.4	39.8
4.5	Inside Surface	39.5	39.1	39.4	37.4	38.1	36.7
	Outside Surface	36.9	36.6	36.7	36.3	36.2	37.5

In short, these considerations make it plain that the migration term of the polarization which has often neglected is large enough to be comparable with the diffusion term, or still larger than it even in conditions with which we are familiar in practice. Accordingly, further discussions are in urgent need to control the polarization better. In the previous arguments the laminar flow is assumed, although such a gentle condition seldom or never takes place practically. For the purpose of uniting the concentration of the electrolytic solution, a propeller-agitator is employed in general, which is known to be not effective as judged not only by common sense or experiences, but by the researches in chemical engineering. Besides, the agitation itself lies outside the strict study of hydrodynamics. Therefore, our above analysis of little use for adaptation in usual cases, but may, we hope, at least help to infer some general concept.

Figured in Fig. 9 is the polarization potential when a propeller-agitated electrolytic solution which consists of cry.  $\text{CuSO}_4$  (150 gr/lit.) and conc.  $\text{H}_2\text{SO}_4$  (10 gr/lit.) is electrolyzed at  $20^\circ\text{C}$ . As was expected, the polarization is not a little affected by the degree of the stirring effect, and we cannot say that the

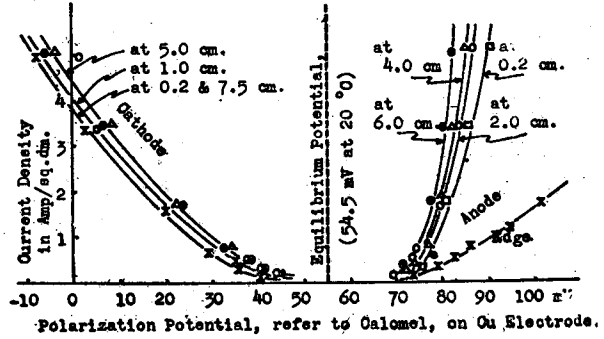


Fig. 9

polarization is always larger as it comes nearer to the leading edge (numbers guided by arrows indicate the distances from the leading edge). The curve labelled as "edge" in the anodic half of the figure means the values which are measured with a capillary tube stuck just at the leading edge. However large the deviation may seem, it must be taken as illustrating the difficulty of observation at the edge rather than something meaningful.

To conclude our considerations with regard to the reaction system where the construction change at the electrical double layer is in partial equilibrium, as in the deposition of copper from its salt solution, we shall study the type of electrode reaction at the reverse extremity to it, i.e., the reaction with the construction change of the species as its rate-determining step, whose striking is hydrogen evolution at the surface of an insoluble electrode from a dilute acid solutions. This process apparently permits to neglect  $\frac{\overleftarrow{K}_a d^*}{D}$  against  $\left(1 + \frac{zFE_s}{RT} d^*\right) e^{\frac{\alpha zF(\eta_0 - \eta)}{RT}}$ , and eq. (2) in §11 deforms,

$$i = \overleftarrow{K}_a Q_a^{\delta} \left\{ e^{-\frac{\alpha zF(\eta_0 - \eta)}{RT}} - \frac{e^{-\frac{\alpha zF(\eta_0 - \eta)}{RT}}}{1 - \frac{zFE_s}{RT} d^*} \right\}. \quad (5)$$

Furthermore, the first term in eq. (5) disappears in comparison with the second, when the applied voltage rises high enough, followed by a decrement of the potential at the double layer,  $\eta$ ; that is,

$$i \approx \overleftarrow{i} = -\overleftarrow{K}_a Q_a^{\delta} \frac{e^{-\frac{\alpha zF(\eta_0 - \eta)}{RT}}}{1 - \frac{zFE_s}{RT} d^*}, \quad (6)$$

or,

$$\eta_0 - \eta = \frac{RT}{\alpha zF} \log \overleftarrow{K}_a Q_a^{\delta} - \frac{RT}{\alpha zF} \log \left( 1 - \frac{zFE_s}{RT} d^* \right) - \frac{RT}{\alpha zF} \log (-\overleftarrow{i}), \quad (7)$$

which is equivalent to the Tafel equation. The conversion of  $i$  into  $\bar{i}$  in the way from eq. (5) to eq. (6) or (7), means that under such a condition there is a perfect substitution of the backward current (the negative current) for the balanced total current.

Attention should be paid to the second term in eq. (7). For example, the diffusion of hydroxonium ions matters little in the hydrogen electrode reaction. This well-acknowledged fact suggests that there is no diffusion layer built at the electrode surface, to say nothing of the hydrodynamical boundary layer, and as the term,  $\frac{zF E_s}{RT} d^*$ , is zero, eq. (7) becomes,

$$\eta_0 - \eta = \frac{RT}{\alpha z F} \log \bar{K}_a Q_a^{\delta} - \frac{RT}{\alpha z F} \log (-\bar{i}), \quad (8)$$

The migration and the diffusion may amount to a considerable problem even concerning hydroxonium ions, when the potential at the double layer is tolerably lowered?

This problem was once offered for universal debatement by Okada and Yoshizawa<sup>1)</sup>, who made observations of the relationship between the current and the electrode potential with the mercury dropping electrode contacting a dilute hydrochloric acid solution. Their polarographic reserch resulted in a curve similar to those for the electrolysis of metal-ion solution. In order to explain this phenomena, they presented a general equation resembling Kimball's<sup>2)</sup> which is seen in § 11 and contains both the construction change process and the diffusion process, by means of the adaptation of Ilkovic's theory<sup>3)</sup> concerning the diffusion process to Bowden's relation<sup>4)</sup> between the current density and the concentration of the species. And some specialization in the equation good accordance with the works by Tafel<sup>5)</sup>, Glasstone<sup>6)</sup> and Bowden<sup>7)</sup>.

It is also admissible that the second term is not to be overlooked when the migration and the diffusion is of importance though the construction change is dominant, e.g., the dissolution and the deposition of metallic nickel by the electrolysis of its salt. Here might lie a cause of various deviation from the Tafel equation often seen in the experiments of the hydrogen electrode reaction.

To make one more reference. Electrolysis with relatively low current density required, strictly speaking, immediate analysis by use of eq. (5), because the elementary reaction of the either side is of the same order, with each order. But the equation is simplified as,

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- 1) Okada and Yoshizawa, J. Ind. Chem. Soc. Japan, **49**, 183 (1946).
  - 2) Kimball, J. Chem. Phys., **8**, 199 (1940), also see 11.
  - 3) Ilkovic, Coll. Czech., **6**, 498 (1934).
  - 4) Bowden, Trans. Farad. Soc., **24**, 473 (1928).
  - 5) Tafel, Z. Phys. Chem., **50**, 641 (1905).
  - 6) Glasstone, J. Chem. Soc., **125**, 2414 (1924).

$$i = \bar{K}_a Q_a^{\delta} \left\{ e^{-\frac{\alpha' z F (\eta_0 - \eta)}{RT}} - e^{-\frac{\alpha z F (\eta_0 - \eta)}{RT}} \right\}, \quad (9)$$

because not only the field intensity,  $E_s$ , is sufficiently small, but also the equivalent thickness of the diffusion layer,  $d^*$ , does not matter much. For instance, figures in Fig. 10 is the hydrogen overpotential at three points on the surface of an iron cathode in a N/20 KOH solution at 20°C, referred to a calomel electrode. Beside the comparative uniformity of polarization, what this figure indicates is this steep arrangement of the values for the point nearest to the leading edge, for which it is dangerous to make a direct amplification of Knorr's view<sup>1)</sup>. Further considerations appear to be requested, as we are not free from all doubts since the concentration of electric flux at the leading edge may possibly give especially great influence of the turbulence of electrical field then by the capillary tube. This has been vartically pointed out by us<sup>2)</sup>, while Drossbach<sup>3)</sup> also recognized it when he electrolyzed molten salts, and another minute investigation was carried out by Piontelli and others<sup>4)</sup>. In passing, the inner and outer radii of our capillary were 100 $\mu$  and 317 $\mu$ , respectively.

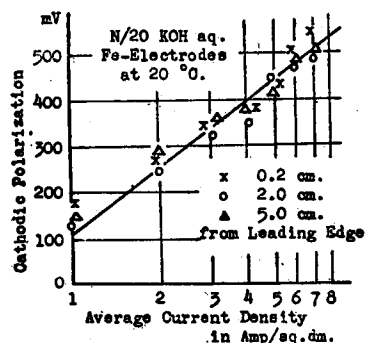


Fig. 10

### §13. Summary

Under the title "Poly-dimensional Problem on Electrode Reaction Process", analysis has been made of the electrode reaction system formed in a poly-dimensional field, introducing the idea of the "reaction flux", which may be employed usefully for other systems of reactant species, as well.

The homogeneous reaction is so perfectly symmetrical, that the analysis of the poly-dimensional problem can be treated as easily as that of the one-dimensional. But this is not case with the heterogeneous reaction and the difficulty in the analysis of poly-dimensional problem exceeds the range of possibility. Dynamical dealings with the heterogeneous reaction have been carried on in the field of catalytic chemistry since days gone by, in connection

1) Knorr, Z. Elektrochem., 40, 38 (1934). Z. Phys. Chem., A 176, 161 (1936).

2) Hine, Yoshizawa and Okada, course of publication in J. Electrochem. Soc. Japan.

3) Drossbach, Z. Elektrochem., 56, 23 (1952).

4) Diontelli, Bianchi and Aletti, *ibid.*, 56, 86 (1952).

with Langmuir's adsorption isotherm<sup>1)</sup>, e.g., those by Butler<sup>2)</sup>, Rideal<sup>3)</sup>, Pease<sup>4)</sup>, Okamoto and others<sup>5)</sup> among which decisive is the research performed lately by Horiuti<sup>6)</sup>. But demands in the field of catalytic chemistry are always fully satisfied by the one-dimensional analysis, for the surface of the catalyst is too extensive to be rivalled by the thickness of the ionic or atomic adsorption layer where elementary reactions take place. It will be, however, quite express that on the occasion of the electrode reaction the circumstances are essentially different, if you see how complex and unarrestable is the relationship between the polarization at a point on the electrode surface and the field intensity, while the latter is dominated by the coordinate of the questioned point and is dominant over the boundary conditions at the electrode surface which is to be indispensably introduced for the analysis. Though there is a detailed research by Okamoto and others for the hydrogen electrode reaction under uniform field intensity<sup>5)</sup>, the question in hand, to our great regret, is the through aspect under non-uniform field intensity.

The reaction flux thus dwelt upon still involve various questions for consideration. One of these is the unit of the flux,—an important problem that wait for inquiry. Here we offer a tentative plan for it:

Though the reactions in the neighbourhood of the electrode surface are to be summed up, as has been repeatedly stated, convenience required to specialize the rate equation as you see in §12; so the unit reaction flux is to be defined as to enable the specialization.

Many suggestions were obtained from the idea of the Faraday flux in electrostatics.

The author would like to express his sincere gratitude to Prof. Shinzo Okada and Assist. Prof. Shiro Yoshizawa for their kindly advices and helpful discussions.

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- 1) Langmuir, *J. Am. Chem. Soc.*, **38**, 2221 (1916).
  - 2) Butler, *Trans. Fared. Soc.*, **19**, 659; 729 (1923-'24).
  - 3) Rideal, *J. Chem. Soc.*, 309 (1922).
  - 4) Pease, *J. Am. Chem. Soc.*, **45**, 1196; 2235 (193 23).
  - 5) Okamoto, Horiuti and Hirota, *Sci. P.*, **29**, 223 (1936).
  - 6) Horiuti, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **1**, 8 (1948).