Theoretical Analysis of Polarographic Waves. II. Reduction of Complex Metal Ions

By Hiroaki MATSUDA and Yuzo AYABE

(Received July 6, 1955)

Introduction

In polarographic literature there are numerous papers dealing with the current-voltage curves due to the reduction of complex metal ions, but satisfactory quantitative treatments reported up to date are almost all based on the fact that the net electrode reaction takes place reversibly[1,2]. Recently, from the viewpoint of chemical kinetics, R. Tamamushi and N. Tanaka[3] attempted a theoretical analysis of the polarographic wave, especially of the irreversible type, which was obtained by the oxidation and reduction of complex metal ions. However, since they have applied the concept of Nernst's diffusion layer to the diffusion process taking place in the region very close to the surface of the dropping mercury electrode, their result cannot be quantitatively adapted to the present problem.

In the present paper, taking into account the movement of the solution caused by the expansion of the mercury drop, we shall attempt to solve the corresponding diffusion problem, which involves the electrolytic reduction of complex metal ions as the boundary condition, and then derive a general equation of the instantaneous current during the drop age for any point along the wave. Moreover, a general expression for the current-voltage curve will be given and its characteristics in several special cases will be discussed in some detail.

Formulation of the Problem

According to the pioneering investigations of N. Bjerrum and his coworkers[4], the formation of complex metal ions always occurs stepwise and the various species of complex metal ions coexist in a given solution, the stability of the individual species being characterized by a series of consecutive dissociation constants of the form:

$$K_\nu=\frac{(f_{\nu-1}C_{\nu-1})(f_{\mathrm{X}}C_{\mathrm{X}})}{(f_\nu C_\nu)}\quad(\nu=1,2,\cdots\cdots,N)\qquad(1)$$

In this expression, C_ν and C_{X} denote the concentrations of the complex metal ion in the form of $\mathrm{MX}_\nu{}^{(n-\nu b)+}$ and of the complexing agent X^{-b}, respectively, f's are the corresponding activity coefficients and N is the maximum number of the ligands taken up.

Now, consider the reduction to the metallic state (amalgam) of complex metal ions of a metal that is soluble in mercury. The net electrode reaction may be represented by

$$\mathrm{MX}_\nu{}^{(n-\nu b)+}+ne+\mathrm{Hg}\rightleftarrows\mathrm{M(Hg)}+\nu\mathrm{X}^{-b}\qquad(2)$$
$$(\nu=N,N-1,\cdots\cdots,1,0)$$

where M(Hg) represents the amalgam formed on the electrode surface and n is the number of electrons associated with the electrode reaction.

In this reaction, various possible types of kinetic mechanism may be considered. From the information as to the formation of complex metal ions, it seems safe to assume that the net electrode reaction described above takes place according to the following scheme:

(1) dissociation and association processes

$$\left.\begin{array}{l}\mathrm{MX}^{(n-\nu b)+}\rightleftarrows\mathrm{MX}_{\nu-1}{}^{[n-(\nu-1)b]+}+\mathrm{X}^{-b}\\(\nu=N,N-1,\cdots\cdots,p+1)\\\mathrm{MX}_{\mu-1}{}^{[n-(\mu-1)b]+}+\mathrm{X}^{-b}\rightleftarrows\mathrm{MX}_\mu{}^{(n-\mu b)+}\\(\mu=p,p-1,\cdots\cdots,1)\end{array}\right.\qquad(3)$$

(2) electron transfer process

$$\mathrm{MX}_\mu{}^{(n-pb)+}+ne+\mathrm{Hg}\rightleftarrows\mathrm{M(Hg)}+p\mathrm{X}^{-b}\qquad(4)$$

In this scheme, it is assumed that the complex metal ions $\mathrm{MX}_\nu{}^{(n-\nu b)+}$ $(\nu=N,N-1,\cdots\cdots,p+1)$ and $\mathrm{MX}_\mu{}^{(n-\mu b)+}$ $(\mu=p-1,p-2,\cdots\cdots,1,0)$ successively dissociate and associate up to the form $\mathrm{MX}_p{}^{(n-pb)+}$ in the vicinity of the electrode surface, respectively, and the species $\mathrm{MX}_p{}^{(n-pb)+}$ thus produced is electrolytically reduced to the amalgam.

If we accept the foregoing assumptions as to the kinetic mechanism of the reduction of complex metal ions, the concentration distributions of the various species of complex metal ions and of the amalgam can be determined by solving the following system of differential equations[5,6]:

---

[1] I.M. Kolthoff and J.J. Lingane, "Polarography" (1952), vol. 1, p. 211.

[2] D.D. DeFord and D.N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).

[3] R. Tamamushi and N. Tanaka, This Bulletin, **23**, 110 (1950).

[4] J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

[5] D. MacGillavry and E.K. Rideal, *Rec. trav. chim.*, **56**, 1013 (1937).

[6] J. Koutecky, *Collection Czechoslov. Chem. Communs.*, **18**, 597 (1953).

$$\frac{\partial C_N}{\partial t}=D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_N}{\partial r}\right)-\frac{a^3}{3r^2}\frac{\partial C_N}{\partial r}$$
$$-\rho_N(C_N-\sigma_N C_{N-1}),\ (r>r_0) \tag{5}$$

$$\frac{\partial C_\nu}{\partial t}=D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_\nu}{\partial r}\right)-\frac{a^3}{3r^2}\frac{\partial C_\nu}{\partial r}$$
$$+\rho_{\nu+1}(C_{\nu+1}-\sigma_{\nu+1}C_\nu)-\rho_\nu(C_\nu-\sigma_\nu C_{\nu-1}),\ (r>r_0) \tag{6}$$
$(\nu=N-1,\ N-2,\cdots\cdots,\ 2,1)$,

$$\frac{\partial C_0}{\partial t}=D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_0}{\partial r}\right)-\frac{a^3}{3r^2}\frac{\partial C_0}{\partial r}$$
$$+\rho_1(C_1-\sigma_1 C_0),\ (r>r_0) \tag{7}$$

$$\frac{\partial C_a}{\partial t}=D_a\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_a}{\partial r}\right)-\frac{a^3}{3r^2}\frac{\partial C_a}{\partial r},$$
$$(r<r_0) \tag{8}$$

where

$$\rho_\nu=k_\nu f_\nu, \tag{9}$$
$$\sigma_\nu=(f_X C_X)(f_{\nu-1}/f_\nu)/K_\nu \tag{10}$$
$$(\nu=N,N-1,\cdots\cdots,\ 2,1).$$

In these equations, r is the distance from the center of the mercury drop, t is the time elapsed after the development of the drop has begun; r_0 is the radius of the mercury drop, which is given by

$$r_0=(3m/4\pi d)^{1/3}t^{1/3}=at^{1/3},$$

where m is the constant rate of flow of mercury uot of the capillary and d is the density of mercury; D and D_a are the diffusion coefficients of the complex metal ions $MX_\nu^{(n-\nu b)+}(\nu=N,N-1,\cdots\cdots,1,0)$ in the solution and of the metal atoms M(Hg) in the amalgam, respectively; $C_\nu(\nu=N,N-1,\cdots\cdots,1,0)$ and C_a are the concentrations of $MX_\nu^{(n-\nu b)+}(\nu=N,N-1,\cdots\cdots,1,0)$ and M(Hg) at any point in the corresponding diffusion layers, respectively; C_X is the concentration of X^{-b}, which is assumed to be constant since the solution usually contains an excess of the complexing agent; f's are the corresponding activity coefficients; k_ν and $K_\nu(\nu=N,N-1,\cdots\cdots,1)$ are the rate and equilibrium constants of the consecutive dissociation processes, respectively.

The initial and boundary conditions are given by

$$\left.\begin{array}{ll} t=0,\ r>r_0: & C_\nu={}^*C_\nu\ (\nu=N,N-1,\cdots\cdots,1,0) \\ t=0,\ r<r_0: & C_a=0 \end{array}\right\} \tag{11}$$

$t>0,\ r=r_0$:

$$D\frac{\partial C_p}{\partial r}=D_a\frac{\partial C_a}{\partial r}=\frac{i(t)}{nFq} \tag{12}$$
$$D\frac{\partial C_\nu}{\partial r}=0\ \left(\begin{array}{l}\nu=N,N-1,\cdots\cdots,p+1,\\ p-1,\cdots\cdots,1,0\end{array}\right) \tag{13}$$

where ${}^*C_\nu(\nu=N,N-1,\cdots\cdots,1,0)$ are the concentrations of $MX_\nu^{(n-\nu b)+}(\nu=N,N-1,\cdots\cdots,1,0)$ in the bulk of the solution, which fulfill the conditions:

$${}^*C_\nu=\sigma_\nu{}^*C_{\nu-1}\ (\nu=N,N-1,\cdots\cdots,1), \tag{14}$$

since the equilibrium states of the consecutive dissociation and association processes expressed by Eq. (3) are assumed to be attained in the bulk of the solution; $i(t)$ is the current flowing through the electrode surface; F is the faraday; q is the surface area of the dropping mercury electrode, which is given by $4\pi r_0^2$. The conditions expressed by Eq. (13) result from the fact that $MX_\nu^{(n-\nu b)+}$ $(\nu=N,N-1,\cdots\cdots,p+1,\ p-1,\cdots\cdots,1,0)$ cannot participate in the electron transfer process.

It is very difficult to obtain an exact solution of the system of differential equations described above. Therefore, in the present paper our discussion will be restricted to a case when the following assumptions are satisfied.

(a) The thickness of the diffusion layer is very much less than the diameter of the mercury drop. Thus, the approximate procedure used in the previous paper[7] can be available.

(b) $\rho_\nu(1+\sigma_\nu)t\gg 1\,(\nu=N,N-1,\cdots\cdots,1)$. This assumption, which is satisfied by sufficiently rapid consecutive reactions in solution, seems to be available for many cases of the reduction of complex metal ions.

Let us now introduce the substitution:

$$x=r^3-r_0^3=r^3-a^3t \tag{15}$$
$$y=t^{7/3} \tag{16}$$
$$C=\sum_{\nu=0}^{N}C_\nu \tag{17}$$

$$g_\nu=C_\nu-\sigma_\nu C_{\nu-1}\ (\nu=N,N-1,\cdots\cdots,\ 1) \tag{18}$$

Then, considering the assumptions (a) and (b), we obtain in place of Eqs. (5), (6), (7) and (8)

$$\frac{\partial C}{\partial y}=\frac{27}{7}a^4D\frac{\partial^2 C}{\partial x^2}\ (x>0) \tag{19}$$

$$0=\frac{27}{7}a^4D\frac{\partial^2 g_N}{\partial x^2}-\frac{3}{7}y^{-4/7}\rho_N(1+\sigma_N)g_N$$
$$+\frac{3}{7}y^{-4/7}\rho_{N-1}\sigma_N g_{N-1}\ (x>0) \tag{20}$$

$$0=\frac{27}{7}a^4D\frac{\partial^2 g_\nu}{\partial x^2}+\frac{3}{7}y^{-4/7}\rho_{\nu+1}g_{\nu+1}$$
$$-\frac{3}{7}y^{-4/7}\rho_\nu(1+\sigma_\nu)g_\nu+\frac{3}{7}y^{-4/7}\rho_{\nu-1}\sigma_\nu g_{\nu-1}\ (x>0) \tag{21}$$
$$(\nu=N-1,\ N-2,\cdots\cdots,\ 3,2)$$

$$0=\frac{27}{7}a^4D\frac{\partial^2 g_1}{\partial x^2}+\frac{3}{7}y^{-4/7}\rho_2 g_2$$
$$-\frac{3}{7}y^{-4/7}\rho_1(1+\sigma_1)g_1\ (x>0) \tag{22}$$

$$\frac{\partial C_a}{\partial y}=\frac{27}{7}a^4D\frac{\partial^2 C_a}{\partial x^2}\ (x<0) \tag{23}$$

The initial and boundary conditions (11), (12) and (13) can be written as follows, after being rearranged:

$$\left.\begin{array}{ll} y=0,\ x>0: & \left\{\begin{array}{l} C={}^*C \\ g_\nu=0\ (\nu=N,N-1,\cdots\cdots,\ 1) \end{array}\right. \\ y=0,\ x<0: & C_a=0 \end{array}\right\} \tag{24}$$

---

[7] H. Matsuda and Y. Ayabe, This Bulletin, 28, 422 (1955).

$y>0,\ x=0:$

$$\left\{\begin{array}{l} 3a^2y^{2/7}D\dfrac{\partial C}{\partial x}=-3a^2y^{2/7}D\dfrac{1}{\sigma_{p+1}}\dfrac{\partial g_{p+1}}{\partial x} \\ =3a^2y^{2/7}D\dfrac{\partial g_p}{\partial x}=3a^2y^{2/7}D_a\dfrac{\partial C_a}{\partial x}=i(y)/nFq \qquad (25) \\ \dfrac{\partial g_\nu}{\partial x}=0\ \begin{pmatrix}\nu=N,N-1,\cdots\cdots p+2,\\ p-1,\cdots\cdots,\ 1\end{pmatrix} \qquad (26)\end{array}\right.$$

Derivation of the Equation for the Instantaneous Current

The solutions of the differential equations (19) and (23), which satisfy the initial and boundary conditions (24) and (25), have been obtained in the previous paper[7]. According to our results, the values of the functions C and C_a at the electrode surface, designated by $^\circ C$ and $^\circ C_a$ respectively, can be expressed as

$$^\circ C={}^*C-\sqrt{\frac{3}{7\pi}}\frac{1}{\sqrt{D}}\int_0^y\frac{u^{-2/7}[i/nFq]}{\sqrt{y-u}}du \qquad (27)$$

$$^\circ C_a=\sqrt{\frac{3}{7\pi}}\frac{1}{\sqrt{D_a}}\int_0^y\frac{u^{-2/7}[i/nFq]}{\sqrt{y-u}}du \qquad (28)$$

The system of differential equations (20) (21) and (22) can be solved by means of method similar to that used in the problem of the linear N coupled oscillators[8]. The values of the functions $g_\nu(\nu=N,N-1,\cdots\cdots,1)$ at the electrode surface, denoted by $^\circ g_\nu$, are given by

$$^\circ g_\nu=\frac{[i/nFq]}{\sqrt{D}}G_\nu\ (\nu=N,N-1,\cdots\cdots,1) \qquad (29)$$

where G_ν is a complicated function of σ_N, $\sigma_{N-1},\cdots\cdots,\sigma_1$ and $\rho_N,\rho_{N-1},\cdots\cdots,\rho_1$.

Upon using the relations expressed by Eqs. (17), (18), (27) and (29), we obtain the following expression for the concentration at the electrode surface of $MX_p^{(n-pb)+}$ which participates in the electron transfer process:

$$^\circ C_p=\frac{(\prod\limits_{\nu=1}^{p}\sigma_\nu)}{\sigma}\Big\{{}^*C-\frac{[i/nFq]}{\lambda_l\sqrt{D}}-\sqrt{\frac{3}{7\pi}}\frac{1}{\sqrt{D}}$$
$$\times\int_0^y\frac{u^{-2/7}[i/nFq]}{\sqrt{y-u}}du\Big\} \qquad (30)$$

where

$$\sigma=1+\sum_{\nu=1}^{N}(\prod_{\mu=1}^{\nu}\sigma_\mu)=1+\sum_{\nu=1}^{N}(f_XC_X)^\nu(f_0/f_\nu)(\prod_{\mu=1}^{\nu}1/K_\mu) \qquad (31)$$

$$(1/\lambda_l)=\sum_{\nu=p+1}^{N}\{1+\sum_{k=\nu+1}^{N}(\prod_{j=\nu+1}^{k}\sigma_j)\}G_\nu$$
$$-\sum_{\nu=1}^{p}\Big\{\sum_{k=1}^{\nu}\Big(\prod_{j=k}^{\nu}\frac{1}{\sigma_j}\Big)\Big\}G_\nu \qquad (32)$$

(λ_e is a complicated function of $\sigma_N,\sigma_{N-1},\cdots\cdots,\sigma_1$ and $\rho_N,\rho_{N-1},\cdots\cdots,\rho_1$, and can be related in a simple manner to the average value of the limiting current, $\bar{i}_l$, as shown later. See Eq. (48). Hence, if one gives up any discussion on the behavior of the limiting current, it is not necessary to obtain an explicit expression of the dependence of λ_l on $\sigma_N,\sigma_{N-1},\cdots\cdots,\sigma_1$ and $\rho_N,\rho_{N-1},\cdots\cdots,\rho_1$.)

The current flowing through the electrode surface depends on the electrode potential and the concentrations at the electrode surface of the substances which participate in the electron transfer process. According to the reaction rate theory[9], the current flowing can be expressed as

$$[i/nFq]=k_f^0(f_p{}^\circ C_p)e^{-\frac{\alpha nF}{RT}E}$$
$$-k_b^0(f_a{}^\circ C_a)(f_XC_X)^pe^{\frac{(1-\alpha)nF}{RT}E} \qquad (33)$$

where E is the electrode potential measured with respect to the normal hydrogen electrode; α is the transfer coefficient; k_f^0 and k_b^0 are the forward (reduction) and reverse (oxidation) rate constants of the electron transfer process at the potential of the normal hydrogen electrode, respectively.

Substituting the relations expressed by Eqs. (28) and (30) into Eq. (33) and rearranging them, we obtain Volterra's integral equation of the second kind:

$$[i/nFq]=\sqrt{D}{}^*C\lambda$$
$$\times\Big[1+\frac{k_b^0f_a(\prod\limits_{\nu=1}^{p}K_\nu)/\sqrt{D_a}}{k_f^0f_0/\sqrt{D}}\sigma e^{\frac{nF}{RT}E}\Big]^{-1}$$
$$-\sqrt{\frac{3}{7\pi}}\lambda\int_0^y\frac{u^{-2/7}[i/nFq]}{\sqrt{y-u}}du \qquad (34)$$

where

$$\lambda=\lambda_l\frac{\dfrac{k_f^0f_0}{\sigma\sqrt{D}}e^{-\frac{\alpha nF}{RT}E}+\dfrac{k_b^0f_a}{\sqrt{D_a}}(\prod\limits_{\nu=1}^{p}K_\nu)e^{\frac{(1-\alpha)nF}{RT}E}}{(f_0/f_p)[\lambda_l/(\prod\limits_{\nu=1}^{p}\sigma_\nu)]+\dfrac{k_f^0f_0}{\sigma\sqrt{D}}e^{-\frac{\alpha nF}{RT}E}} \qquad (35)$$

In order to obtain a description of our problem formulated by means of dimensionless parameters, we make the substitution:

$$[i/nFq]=\sqrt{D}{}^*C\lambda$$
$$\times\Big[1+\frac{k_b^0f_a(\prod\limits_{\nu=1}^{p}K_\nu)/\sqrt{D_a}}{k_f^0f_0/\sqrt{D}}\sigma e^{\frac{nF}{RT}E}\Big]^{-1}\cdot\psi \qquad (36)$$

---

[8] J.C. Slater and N.H. Frank, "Introduction to Theoretical Physics" (1933), p. 107.

[9] S. Glasstone, K.J. Laidler and H. Eyring, "The Theory of Rate Processes" (1941), p. 575.

$$\begin{aligned}\xi&=\lambda y^{3/14}\\ \eta&=\lambda u^{3/14}\end{aligned}\tag{37}$$

Then, we obtain

$$\psi(\xi)=1-2\sqrt{\frac{7}{3\pi}}\int_0^{\xi}\frac{\eta^{7/3}\psi(\eta)}{\sqrt{\xi^{14/3}-\eta^{14/3}}}d\eta\tag{38}$$

This integral equation has already been solved in the previous paper7), and its solution has been there expressed in the form of power series of ξ.

Hence, considering the relations expressed by Eqs. (36) and (37), replacing the surface area of the dropping mercury electrode q with $4\pi r_0^2=4\pi(3m/4\pi d)^{2/3}\ t^{2/3}$, and rearranging it, we obtain for the instantaneous current during the drop age

$$i=i_d\left[1+\frac{k_b^0 f_a(\prod\limits_{\nu=1}^{p}K_\nu)/\sqrt{D_a}}{k_f^0 f_0/\sqrt{D}}\sigma e^{\frac{nF}{RT}E}\right]^{-1}_{\cdot}$$

$$\times\sqrt{\frac{3\pi}{7}}(\lambda\sqrt{t})\psi(\lambda\sqrt{t})\tag{39}$$

where i_d represents the Ilkovic equation for the instantaneous limiting diffusion current. The values of the function $\sqrt{3\pi/7}\times(\lambda\sqrt{t})\times\psi(\lambda\sqrt{t})$ for various values of $\lambda\sqrt{t}$ are tabulated in Table 1 of the previous paper7).

According to DeFord and Hume2), the half-wave potential of the reversible wave due to the reduction of complex metal ions, denoted by $E_{1/2}^{r}$, is given by

$$E_{1/2}^{r}=E^0-2.3\frac{RT}{nF}\log\frac{f_a/\sqrt{D_a}}{f_0/\sqrt{D}}-2.3\frac{RT}{nF}$$

$$\times\log\left\{1+\sum_{\nu=1}^{N}(f_XC_X)^\nu(f_0/f_\nu)(\prod_{\mu=1}^{\nu}1/K_\mu)\right\}\tag{40}$$

where E^0 is the standard potential of the reduction of the simple metal ion M^{n+} to the amalgam state. Since the standard potential of the electron transfer process expressed by Eq. (4), which is given by 2.3 (RT/nF) $\log(k_f^0/k_b^0)$, can be related with E^0 according to

$$2.3\frac{RT}{nF}\log\frac{k_f^0}{k_b^0}=E^0+2.3\frac{RT}{nF}\log(\prod_{\nu=1}^{p}K_\nu),$$

Eq. (40) can be rewritten as follows, by using the abbreviation expressed by Eq. (31):

$$E_{1/2}^{r}=2.3\frac{RT}{nF}\log\frac{k_f^0 f_0/\sqrt{D}}{k_b^0 f_a(\prod\limits_{\nu=1}^{p}K_\nu)/\sqrt{D_a}}$$

$$-2.3\frac{RT}{nF}\log\sigma.$$

Consequently, $\dfrac{k_b^0 f_a(\prod\limits_{\nu=1}^{p}K_\nu)/\sqrt{D_a}}{k_f^0 f_0/\sqrt{D}}\sigma e^{\frac{nF}{RT}E}$ and λ can be, respectively, expressed as

$$\frac{k_b^0 f_a(\prod\limits_{\nu=1}^{p}K_\nu)/\sqrt{D_a}}{k_f^0 f_0/\sqrt{D}}\sigma e^{\frac{nF}{RT}E}=e^\zeta\tag{41}$$

$$\lambda=\frac{1+e^\zeta}{[(f_0/f_p)/(\prod\limits_{\nu=1}^{p}\sigma_\nu)]\Lambda^{-1}e^{\alpha\zeta}+\lambda_l^{-1},}\tag{42}$$

where

$$\zeta=(nF/RT)(E-E_{1/2}^{r}),\tag{43}$$

$$\Lambda=\left\{\frac{k_f^0 f_0}{\sigma\sqrt{D}}\right\}^{1-\alpha}\left\{\frac{k_b^0 f_a}{\sqrt{D_a}}(\prod_{\nu=1}^{p}K_\nu)\right\}^{\alpha}_{\cdot}\tag{44}$$

Hence, Eq. (39) can be transformed into the form

$$i=\frac{i_d}{1+e^\zeta}\sqrt{\frac{3\pi}{7}}(\lambda\sqrt{t})\cdot\psi(\lambda\sqrt{t}),\tag{45}$$

with λ defined by Eq. (42). This is the general expression showing the instantaneous current during the drop age for any point along the wave.

Derivation of the Equation for the Current-Voltage Curve

Upon integrating Eq. (45) with respect to t from zero to the drop time τ and dividing it by τ, we obtain for the average value of the current flowing

$$\bar{i}=\frac{1}{1+e^\zeta}\sqrt{\frac{3\pi}{7}}\frac{1}{\tau}\int_0^\tau i_d(\lambda\sqrt{t})\psi(\lambda\sqrt{t})dt.$$

After writting $\xi=\lambda\sqrt{t}$ and rearranging it, we obtain

$$\bar{i}=\frac{\bar{i}_d}{1+e^\zeta}\sqrt{\frac{3\pi}{7}}(\lambda\sqrt{\tau})^{-7/3}\int_0^{\lambda\sqrt{\tau}}\psi(\xi)\xi^{7/3}d\xi\tag{46}$$

where $\bar{i}_d$ represents the Ilkovic equation for the average value of the limiting diffusion current.

As shown in the previous paper7), the function $\sqrt{7\pi/3}(\lambda\sqrt{\tau})^{-7/3}\times\int_0^{\lambda\sqrt{\tau}}\psi(\xi)\xi^{7/3}d\xi$ can be, with sufficient accuracy, approximated by $(\lambda\sqrt{\tau})^{1.04}/[1.13+(\lambda\sqrt{\tau})^{1.04}]$. For the sake of simplicity, although with a little less accuracy, we replace $(\lambda\sqrt{\tau})^{1.04}/[1.13+(\lambda\sqrt{\tau})^{1.04}]$ with $(\lambda\sqrt{\tau})/[1.12+(\lambda\sqrt{\tau})]$*). Accordingly, Eq. (46) can be reduced to

---

* Replacing the exact function with $(\lambda\sqrt{\tau})/[1.12+(\lambda\sqrt{\tau})]$ causes an error by one unit in the second decimal. On the other hand $(\lambda\sqrt{\tau})^{1.04}/[1.13+(\lambda\sqrt{\tau})^{1.04}]$ is coincident with the exact function up to three units in the third decimal.

$$\bar{i}=\frac{\bar{i}_d}{1.12\{[(f_0/f_p)/(\prod_{\nu=1}^{p}\sigma_\nu)](\Lambda\sqrt{\tau})^{-1}e^{\alpha\zeta}+(\lambda_l\sqrt{\tau})^{-1}\}+1+e^{\zeta}} \tag{47}$$

As the electrode potential becomes sufficiently negative, i.e., $\zeta\to-\infty$, $\bar{i}$ approaches the limiting value, $\bar{i}_l$, which is given by

$$\bar{i}_l=\frac{\bar{i}_d}{1+1.12(\lambda_l\sqrt{\tau})^{-1}} \tag{48}$$

Eq. (48) shows that the limiting current, $\bar{i}_e$, is proportional to $\bar{i}_d$, (hence to $^*C$), and the proportional factor is dependent on $\lambda_l\sqrt{\tau}$.

When the relation expressed by Eq. (48) is substituted into Eq. (47), we obtain

$$\bar{i}=\frac{\bar{i}_d}{1.12[(f_0/f_p)/(\prod_{\nu=1}^{p}\sigma_\nu)](\Lambda\sqrt{\tau})^{-1}e^{\alpha\zeta}+(\bar{i}_d/\bar{i}_l)+e^{\zeta}} \tag{49}$$

This is the general equation of the current-voltage curve for the reduction of complex metal ions.

In the following, we discuss in some detail the charactetistics of the current-voltage curve in several special cases.

(A) When the Electron Transfer Process takes place reversibly.—In the first place, let us consider a case in which the value of $\Lambda\sqrt{\tau}$ is greater than $50\times[(f_0/f_p)/(\prod_{\nu=1}^{p}\sigma_\nu)]\times(\bar{i}_l/\bar{i}_a)^{1-\alpha}\alpha^{\alpha}(1-\alpha)^{1-\alpha}$. Then, since it can easily be shown that

$$(\bar{i}_a/\bar{i}_l)\exp(-\alpha\zeta)+\exp(1-\alpha)\zeta$$
$$>(\bar{i}_a/\bar{i}_l)^{1-\alpha}\alpha^{-\alpha}(1-\alpha)^{-(1-\alpha)}$$

for any value of ζ, Eq. (49) can be transformed into the form

$$\bar{i}=\frac{\bar{i}_a}{(\bar{i}_a/\bar{i}_l)+e^{\zeta}}.$$

By solving the above equation with respect to E, we obtain

$$E=E^r_{1/2}-2.3\frac{RT}{nF}\log\frac{\bar{i}_l}{\bar{i}_a}-2.3\frac{RT}{nF}\log\frac{\bar{i}}{\bar{i}_l-\bar{i}}, \tag{50}$$

where $E^r_{1/2}$ is defined by Eq. (40). This is the equation of the current-voltage curve corresponding to the reversible electron transfer process. Eq. (50) shows that a plot of $-E$ versus $\log\bar{i}/\bar{i}_l-\bar{i})$ should produce a straight line with a slope equal to 2.3 $RT/nF(=59/n$ mV. at 25°C). This fact is a criterion for the reversibility of the electron transfer process.

The half-wave potential, $E_{1/2}$, is given by

$$E_{1/2}=E^r_{1/2}-2.3\frac{RT}{nF}\log\frac{\bar{i}_l}{\bar{i}_a}, \tag{51}$$

as it comes from Eq. (50).

Furthermore, consider a case when the limiting current is completely controlled by the diffusion process, i.e., $\bar{i}_l=\bar{i}_d$. Then, Eq. (50) can easily be reduced to the simple form

$$E=E^r_{1/2}-2.3\frac{RT}{nF}\log\frac{\bar{i}}{\bar{i}_d-\bar{i}}. \tag{52}$$

This is quite the same as the result obtained when the net electrode reaction takes place reversibly. Detailed discussions on this case have been set down by many workers1,2).

(B) When the Electron Transfer Process takes place irreversibly.—In the case of $\Lambda\sqrt{\tau}<2\times10^{-2(1+\alpha)}[(f_0/f_p)/(\prod_{\nu=1}^{p}\sigma_\nu)]\ (\bar{i}_l/\bar{i}_d)$, $\bar{i}$ is smaller than about 2 per cent of the limiting current, $\bar{i}_e$, in the range of $\zeta>-4.6$ and the appreciable value of $\bar{i}$ is observed only for the values of ζ for which the condition $\zeta<-4.6$ is satisfied. Then, since it is found that

$$\exp\zeta<10^{-2}\quad\text{for }\zeta<-4.6,$$

Eq. (49) becomes

$$\bar{i}=\frac{\bar{i}_d}{1.12[(f_0/f_p)/(\prod_{\nu=1}^{p}\sigma_\nu)](\Lambda\sqrt{\tau})^{-1}e^{\alpha\zeta}+(\bar{i}_d/\bar{i}_l)}$$

Upon solving the above equation with respect to E, we obtain

$$E=E^r_{1/2}+2.3\frac{RT}{\alpha nF}\left\{\log\left[\left(\frac{f_p}{f_0}\prod_{\nu=1}^{p}\sigma_\nu\right)\Lambda\sqrt{\tau}\right]\right.$$
$$\left.-0.049-\log\frac{\bar{i}_l}{\bar{i}_d}-\log\frac{\bar{i}}{\bar{i}_e-\bar{i}}\right\}.$$

When the relations expressed by Eqs. (10), (31), (40) and (44) are substituted into the foregoing equation, we obtain

$$E=2.3\frac{RT}{\alpha nF}\left\{\log\frac{k^0_f f_p}{\sqrt{D}}\sqrt{\tau}-0.049-\log\frac{\bar{i}_l}{\bar{i}_d}\right.$$
$$-\log\left[\sum_{\nu=0}^{N}(f_\mathrm{X}C_\mathrm{X})^{\nu-p}(f_p\prod_{\mu=1}^{p}K_\mu)/(f_\nu\prod_{\mu=0}^{\nu}K_\mu)\right]$$
$$\left.-\log\frac{\bar{i}}{\bar{i}_l-\bar{i}}\right\}, \tag{53}$$

where it is defined that $K_0=1$. This is the same equation as that obtained by neglecting the effect of the reverse (oxidation) process. It is evident from Eq. (53), that a plot of $-E$ versus $\log\bar{i}/(\bar{i}_l-\bar{i})$ is linear and the inclination of this line is found to be 2.3 $RT/\alpha nF(=59/\alpha n$ mV. at 25°C). Consequently, if this plot is carried out and the tangent of the line thus obtained is determined, the value of αn can be calculated.

From Eq. (53) the half-wave potential, $E_{1/2}$, can be obtained as

$$E_{1/2}=2.3\frac{RT}{\alpha nF}\left\{\log\frac{k_f^0 f_p}{\sqrt{D}}\sqrt{\tau}-0.049-\log \bar{i}_l/\bar{i}_d\right)$$

$$-\log\left[\sum_{\nu=0}^{N}(f_X C_X)^{\nu-p}(f_p\prod_{\mu=1}^{p}K_\mu)/(f_\nu\prod_{\mu=0}^{\nu}K_\mu)\right]\Bigg\}. \tag{54}$$

Eq. (54) shows that if the consecutive dissociation constants K_ν ($\nu=N, N-1,\cdots\cdots, 1$) are known, the form of the complex metal ion that participates in the electron transfer process, i.e., p, can be determined from the dependence of the half-wave potential, $E_{1/2}$, on the activity of the complexing agent, and the forward rate constant of the electron transfer process, k_f^0, calculated from the measured value of the half-wave potential, $E_{1/2}$.

Let us consider a case in which only the species $MX_s^{(n-sb)+}$ predominates in the bulk of the solution in the region in question of the concentration of the complexing agent, i.e., when the condition $^*C_s \gg {}^*C_\nu(\nu=N, N-1, \cdots\cdots, S+1, S-1,\cdots\cdots, 1, 0)$ is satisfied. Then, by considering the relations expressed by Eq. (14), Eq. (54) can be reduced to the simple form

$$E_{1/2}=2.3\frac{RT}{\alpha nF}\left\{\log\left[\frac{k_f^0 f_s}{\sqrt{D}}\frac{(\prod_{\mu=0}^{s}K_\mu)}{(\prod_{\mu=1}^{p}K_\mu)}\sqrt{\tau}\right]\right.$$

$$\left.-0.049-\log(\bar{i}_l/\bar{i}_d)-(S-p)\log(f_X C_X)\right\} \tag{55}$$

In this case it is evident from Eq. (55), that a plot of $-E_{1/2}-2.3(RT/\alpha nF)\log(\bar{i}_l/\bar{i}_d)$ versus $\log(f_X C_X)$ should produce a straight line with a slope equal to $2.3(RT/\alpha nF)(S-p)$ $(=59(S-p)/\alpha n$ mV. at 25°C).

Unfortunately, few experimental data sufficient for the testing of the validity of Eqs. (53) and (54) are at present available to the authors. As an example of the application of the theoretical results described above, only the irreversible reduction of the ammonia-nickel complex ion, which has been recently studied by K. Morinaga[10], will be treated in the present paper. K. Morinaga has shown that the reduction of the ammonia-nickel complex ion takes place irreversibly at the dropping mercury electrode and the limiting current is completely controlled by the diffusion process. He has also found that the log plot gives a good straight line, as predicted by Eq. (53), and the slope of the line thus obtained is 41.$_5$ mV. (average), from which he has calculated the value of α resulting in 0.71. Furthermore, he has measured the half-wave potential as a function of the ammonia concentration in the range of 0.2 to 3 M. His experimental results are shown in Fig. 1 in which the circles are experimental points. The curves in this graph are theoretical ones calculated by means of Eq. (54) on the assumption that $N=6$ and $p=2$. J. Bjerrum[4] has determined the consecutive dissociation constants for the ammonia-nickel system and shown that the constants determined by direct experiment are given as $K_1=10^{-2.80}$, $K_2=10^{-2.24}$, $K_3=10^{-1.73}$, $K_4=10^{-1.19}$, $K_5=10^{-0.75}$ and $K_6=10^{-0.04}$, respectively, and those corrected on statistical grounds are $K_1=10^{-2.02}$, $K_2=10^{-1.84}$, $K_3=10^{-1.60}$, $K_4=10^{-1.32}$, $K_5=10^{-1.15}$ and $K_6=10^{-0.81}$, respectively. Theoretical curves I and II in Fig. 1 have been calculated by using the former and latter values of the consecutive dissociation constants, respectively. In these calculations, the half-wave potential at $C_{NH_3}=0.995$ N (-1.033 V vs. SCE) has been taken as the standard, and all activity coefficients which appear in Eq. (54) have been taken as if equal to unity since they are at present unavailable. The fairly good agree-

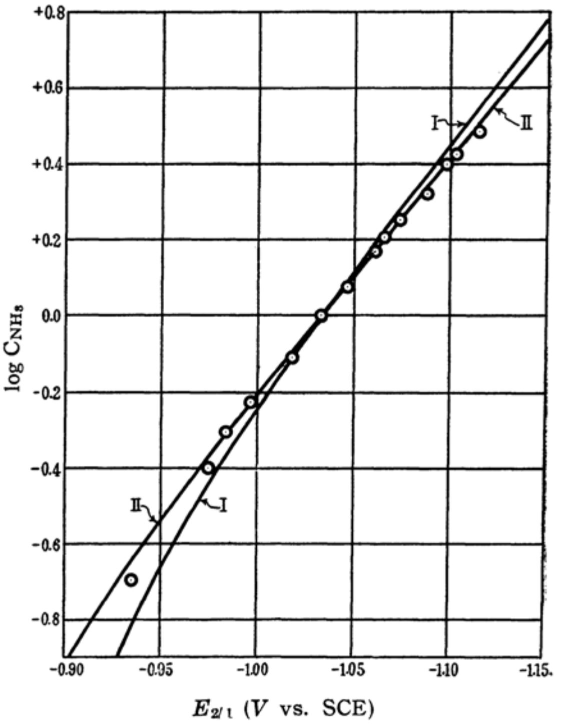

Fig. 1. Half-wave potentials of the ammonia-nickel complex ion as a function of the ammonia concentration in 0.1 M KNO_3. The curves are theoretical ones and the circles are experimental points.

---

[10] K. Morinaga, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*) (in Japanese), **76**, 133 (1955).

ment of the experimental points with the theoretical curve II shows that the species $Ni(NH_3)_2^{++}$ participates in the electron transfer process, the transfer coefficient being equal to 0.71. Moreover, taking the statistically corrected values for the consecutive dissociation constants, 0.89×10^{-5} cm²/sec.* for the diffusion coefficient of the ammonia-nickel complex ion and 4–5 sec for the drop time, we have calculated the value of the forward rate constant of the electron transfer process, k_f^0, with the aid of the measured value of −1.033 V. vs. SCE (−0.787 V. vs. NHE) for the half-wave potential at the ammonia concentration equal to 0.995 N. The result obtained is

$$\log k_f^0 = -16.8 \ (k_f^0:\ \text{cm./sec.}).$$

For the reduction of the hydrated nickel ion, K. Morinaga has shown that the log plot produces a good straight line with a slope equal to 72 mV. and the half-wave potential is −1.047 V vs. SCE (−0.801 V. vs. NHE). Using these data, we have also calculated the forward rate constant, k_f^0, and the transfer coefficient, α, with the aid of the theory developed in the previous paper[7]. The results obtained are

$$\alpha = 0.40,\ \log k_f^0 = -13.7 \ (k_f^0:\ \text{cm./sec.}).$$

In this calculation we have taken 0.69×10^{-5} cm²/sec. for the diffusion coefficient of the hydrated nickel ion and 4–5 sec. for the drop time.

It is seen from the results obtained above that the complex formation of the hydrated nickel ion with ammonia decreases the forward rate constant of the electron transfer process and on the other hand increases the transfer coefficient.

Summary

Under the assumption that the electrolytic reduction of the complex metal ions at the dropping mercury electrode follows the mechanism expressed by Eqs. (3) and (4), the general expression of the current-voltage curve has been derived by solving the corresponding diffusion problem with the same accuracy as the Ilkovic equation, and the special two cases corresponding to the reversible and irreversible electron transfer process have been discussed in some detail. Moreover, as an example of the application of the present theory, the irreversible reduction of the ammonia-nickel complex ion has been analysed by the aid of the experimental data given by K. Morinaga. A fairly good agreement between the experimental data and the theoretical results has been obtained, and it has been found that the species $Ni(NH_3)_2^{++}$ participates in the electron transfer process with the forward rate constant equal to $10^{-16.8}$ cm./sec. and the transfer coefficient equal to 0.71.

Government Chemical Industrial Research Institute, Tokyo

---

* According to the experimental results of K. Morinaga[10], the ratio of the diffusion limiting current of the ammonia-nickel complex ion to that of the hydrated nickel ion, which is equal to the ratio of the square roots of the corresponding diffusion coefficients, is given as 2.52/2.22. Since the diffusion coefficient of the hydrated nickel ion at infinite dilution is 0.69×10^{-5} cm²/sec., the diffusion coefficient of the ammonia-nickel complex ion may be calculated as 0.89×10^{-5} cm²/sec.