KINETIC CURRENTS IN POLAROGRAPHY PART – I–LINEAR DIFFUSION TO THE DME FOR PSEUDO FIRST ORDER CATALYZED PROCESSES

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The methods that have been developed for solving the differential equations that have been formulated for cases involving chemical reactions occuring parallel to the electrode process are very difficult. In the present work a simple method of solving the equation is presented. Two new variables $s = xt^{2/3}/2\sqrt{3D/7}$ and $T = 1/4\ t^{7/3}$ are introduced, and the equation is transformed. The boundary conditions for the transformed differential equation are formulated and the equation is solved by the Laplace Transform method. Expressions for $C_A(x,t)$ and $C_B(x,t)$ and for $(i_t)_{total}/(i_d)_t$ are given. It is shown that when $k = 0$, the equations transform to those obtained for the case of linear diffusion to a growing electrode.

In addition to electrode processes which are controlled by the rate of diffusion or the rate electrode reaction, there are processes controlled by a chemical reaction occurring at the electrode surface. Such currents are called kinetic currents. In this paper reactions which occur parallel to the electrode process <1> and which can be represented by the following scheme are discussed.

$$A + ne \rightleftharpoons B, \qquad B + X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A$$

where k_1 and k_2 are the rate constants of the forward and the backward processes. Usually $k_2 << k_1$ and hence the chemical reaction can be taken as unidirectional. Since the substance X is usually present in excess, the chemical reaction is considered pseudo - first - order reaction. The current for the reduction of A consists of two parts, namely (i) due to diffusion of A to the electrode surface and (ii) due to regeneration of A by reaction of B with X. This type of kinetic current which is produced due to regeneration of the depolarizer is called catalytic current. Brdicka and Wiesner-<2,3> treated the problem of catalytic current by the approximate method based on the concept of reaction layer. A more rigorous treatment has been possible when the problem is treated on the basis of differential equations.

NOTATIONS

$C_A(x,t)$: Concentration of the substance A at a distance x from the electrode surface at time t

$C_A(0,t)$: Concentration of the substance A at the electrode surface at time t ($^{\circ}C_A$ but in the present case O)

$^{*}C_A$: Bulk concentration of A

$C_B(x,t)$: Concentration of the substance B at a distance x from the electrode surface at time t.

$C_B(x,0)$: Initial concentration of the substance B ($^{*}C_B$ in the present case O)

C_X : Concentration of X which is regarded constant.
All C' s in mole in cm^{-3}

D_A and D_B: Diffusion coefficients of A and B in $cm^2\ sec^{-1}$. D : Common diffusion coefficient since $D_A \simeq D_B$.

A : Area of the electrode.

P : Variabe in Laplace transformation.

L(C) : Laplace transform of C.

L^{-1} u : Inverse transform of u

$s = xt^{2/3}/(2\sqrt{(3/7)\,D})$: new variable

$T = (1/4)t^{7/3}$: new variable (t in seconds)

k_1 and k_2 : rate constants of the forward and the backward processes of the parallel chemical reaction between B and X to generate A. k's in $mole^{-1}\ cm^3\ sec^{-1}$

Differential Equations

When the current is governed only by the linear diffusion of A to the stationary electrode surface, the following differential equation holds :

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2}$$

The change in the concentration of A due to chemical reaction alone is

$$\frac{\partial C_A}{\partial t} = k_1 C_X C_B - k_2 C_A$$

For combined effect of diffusion and reaction, the following differential equation can be written.

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} + k_1 C_X C_B - k_2 C_A \quad \ldots.(1)$$

Similarly one can write for B

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} - k_1 C_X C_B + k_2 C_A \quad \ldots.(2)$$

Replacing D_A and D_B by common D and $k_1 C_X$ by k since C_X is constant and noting that $k_2 << k_1$, one can write

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial x^2} + kC_B \quad \ldots.(3)$$

$$\frac{\partial C_B}{\partial t} = D \frac{\partial^2 C_B}{\partial x^2} - kC_B \quad \ldots.(4)$$

The initial and the boundary conditions are

$C_A(x,0) = {}^*C_A$: $C_B(x,0) = 0$;
$C_A(0,t) = 0$ (limiting current region):

$C_A(x,t) = {}^*C_A$ as $x \longrightarrow \infty$ .....(5)

It may be pointed out that since the concentration of B is zero to start with and is produced by the reduction of A

$$C_B(x,t) = {}^*C_A - C_A(x,t) \quad \ldots.(6)$$

For a growing electrode one has to add the convective terms to the diffusion portion of the differential equation as formulated by Ilkovic<4>. Equation (3) & (4) take the form

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial x^2} + \frac{2}{3}\frac{x}{t}\frac{\partial C_A}{\partial x} + kC_B \quad \ldots.(7)$$

$$\frac{\partial C_B}{\partial t} = D \frac{\partial^2 C_B}{\partial x^2} + \frac{2}{3}\frac{x}{t}\frac{\partial C_B}{\partial x} - kC_B \quad \ldots.(8)$$

The initial and the boundary conditions are the same as above.

Equations (3) and (4) have been solved by Laplace transform method by Delahay and Stiehl<5> and Miller<6> but full details are not available. The generalized form of the differential equations (1) & (2) for stationary electrode (including both k_1 and k_2) have been solved by Koutecky and Brdicka<7> by the Laplace transform method. Equations (7) and (8) have been solved by Koutecky<8> by the method of dimensionless parameters but the method is complicated. The Laplace transform method developed by Henke and Hans<9>, for solving equations (7) and (8) is also complicated. Hence work was undertaken to examine the possibilities of converting the partial differential equations (7) and (8) into standard forms by the technique of change of variables and then solve by the Laplace transform method. In the present paper a simple Laplace transform method for solving differential equations (7) and (8) is presented.

THEORETICAL

(i) Transformation Of The Differential Equation.

The differential equation (7) can not be solved unless C_B is expressed in terms of C_A . Replacing C_B by ${}^*C_A - C_A$, the differential equation takes the form

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial x^2} + \frac{2}{3}\frac{x}{t}\frac{\partial C_A}{\partial x} + k({}^*C_A - C_A) \quad (7a)$$

In the above differential equation x and t are independent variables. Subrahmanya<10> has expressed

$\partial C_A/\partial t$, $\partial^2 C_A/\partial x^2$ & $(2x/3t)(\partial C_A/\partial x)$

in terms of new independent variables s & T using chain rule. This results in the following transformations.

$$\frac{\partial C_A}{\partial t} = \frac{\partial C_\Lambda}{\partial T} \cdot \frac{1}{4} \cdot \frac{7}{3} \cdot t^{4/3} + \frac{\partial C_A}{\partial s} \cdot \frac{2}{3} \cdot \frac{s}{t} \quad ..(9)$$

$$D \frac{\partial^2 C_A}{\partial x^2} = D \frac{t^{4/3}}{\left[2\sqrt{(3/7)D}\right]^2} \cdot \frac{\partial^2 C_A}{\partial s^2} \quad ...(10)$$

$$\frac{2}{3} \cdot \frac{x}{t} \cdot \frac{\partial C_A}{\partial x} = \frac{2}{3} \cdot \frac{s}{t} \cdot \frac{\partial C_A}{\partial s} \quad .....(11)$$

Substituting the above in the differential equation 7a, one gets

$$\frac{\partial C_A}{\partial T} = \frac{\partial^2 C_A}{\partial s^2} + k\,(^*C_A - C_A) \quad .....(7b)$$

(ii) Initial and Boundary Conditions for Equation (7b)

The initial & boundary conditions for equation (3) which also holds for equation(7) is already written under equation(5)and C_B is expressed in terms of C_Λ in equation(6).

For equation 7b with transformed variables (Present work) the following initial and boundary condiions can be given.

$$C_A(s,0) = {}^*C_\Lambda : C_A(0,T) = 0$$
$$C_A(s,T) = {}^*C_\Lambda \text{ as } s \text{ -----> } \infty \quad .....(5a)$$

Subrahmanya<10> has examined the significance of boundary conditions given above. He has pointed out that the new variable (s) suggest that we are considering the value of C_A at different concentric spheres from the surface of the electrode. It is pointed out that changes in t are similar to changes in T.

(iii) Solution of the Equation (7b)

The equation<7b> is a partial differential equation with constant coefficients and the Laplace transform method has been used to solve this equation.

We define the Laplace transform of $C_\Lambda(s,T)$ (abbreviated as L C(s,T)) as

$$u(s,p) = \int_0^\infty \exp(-pT)\, C_A(s,T)\, dT \quad ..(12)$$

Then $L \frac{\partial C_\Lambda}{\partial T} = -C_\Lambda(s,0) + pu(s,p)$ ....(13)

$$L \frac{\partial^2 C_A}{\partial s^2} = \frac{d^2 u(s,p)}{ds^2} \quad .....(14)$$

$$L\ k\ {}^*C_A = k\ {}^*C_A / p \quad .....(15)$$

The partial differential equation is transformed to

$$\frac{d^2 u}{ds^2} - (p+k)\,u = -\frac{p+k}{p}\,{}^*C_A \quad ...(16)$$

since $^*C_\Lambda$ is the value of the function $C_A(s.T)$ when T = 0.

The solution of equation (16) is

$$u = u_c + u_p$$

$$= A_1 \exp(+\sqrt{p+k}.s) + A_2 \exp(-\sqrt{p+k}.s) + \frac{-\left(\frac{p+k}{p}\right)}{-(p+k)}\,{}^*C_\Lambda$$

$$= A_1 \exp(+\sqrt{p+k}.s) + A_2 \exp(-\sqrt{p+k}.s) + {}^*C_A/p \quad .(17)$$

Since the concentration of A does not increase indefinitely with an increase in the value of s, $A_1 = 0$. Since C_Λ (0,T) is zero, u(0,p) is also zero. Hence $A_2 = -(^*C_\Lambda/p)$.

Therefore

$$u = {}^*C_A/p \cdot \exp(-\sqrt{p+k}.s) + {}^*C_A/p \quad ...(18)$$

$$C_A(s,T) = L^{-1}\, u(s,p)$$

$$= L^{-1} - {}^*C_A/p[\exp(-\sqrt{p+k}.s)] + L^{-1}\,({}^*C_A/p) \quad ..(19)$$

On the basis of the Laplace transforms given in Table of transforms <11,12> and using the relevant theorem concerning transforms containing (p+k), the following can be written

$$L^{-1} - {}^*C_A \frac{\exp(-\sqrt{p+k}\ .\ s)}{p+k-k}$$

$$= {}^*C_A \exp(-kT) \left\{ \frac{1}{2} \exp(kT) \right.$$

$$\left[\exp(-\sqrt{k}.s)\ \operatorname{erfc}\left(s/(2\sqrt{T}) - \sqrt{kT}\right)\right.$$

$$\left.\left. + \exp(+\sqrt{k}.s)\ \operatorname{erfc}\left(s/(2\sqrt{T}) + \sqrt{kT}\right)\right]\right\} \quad ....(20)$$

The Laplace transform of a constant is constant divided by p . Therefore

$$L^{-1} \quad ({}^{*}C_A / p) = {}^{*}C_A$$

The following expression for C_A (s,T) can now be written :

$$C_A(s,T) = {}^{*}C_A \left\{ 1 - 1/2 \exp(-\sqrt{k}.s) \left[1 - \operatorname{erf}\left(s/2\sqrt{T} - \sqrt{k.T} \right) \right] - 1/2 \exp \sqrt{k}.s \left[1 - \operatorname{erf}\left(s/(2\sqrt{T}) + \sqrt{kT} \right) \right] \right\} \quad \ldots(21)$$

In terms of the old coordinative system, we have the following expression

$$C_A(x,t) = {}^{*}C_A \left\{ 1 - \frac{1}{2} \exp\left(-\sqrt{\frac{7}{12}\frac{k}{D}} t^{4/3} \right).x \left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{3Dt/7}} - \frac{1}{2}\sqrt{kt^{7/3}} \right) \right] - \frac{1}{2} \exp\frac{\sqrt{7\ kt^{4/3}}}{\sqrt{12\ D}}.x \left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{3Dt/7}} + \frac{1}{2}\sqrt{kt^{7/3}} \right) \right] \right\} \quad \ldots(22)$$

The above equation gives C_A as a function of x and t. The instantaneous current at any time is given by the equation $i_t = nFAD(\partial C_A/\partial x)_{x=o}$ The value of $(\partial C_A / \partial x)_{x=o}$ can be obtained by differentiating the expression for $C_A(x,t)$ given above with respect to x and putting x = 0 in the resulting expression. It may be pointed out that in the course of differentiation one comes across differentiation of error integral which involves differentiation under integral sign and one typical example is given below.

$$\frac{\partial}{\partial x}\left(\frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{3Dt/7}} - \frac{1}{2}\sqrt{kt^{7/3}}} e^{-u^2} du \right) = \frac{2}{\sqrt{\pi}} \exp -\left(\frac{x}{2\sqrt{3Dt/7}} - \frac{1}{2}\sqrt{kt^{7/3}} \right)^2 \frac{1}{2\sqrt{3Dt/7}} \quad \ldots(23)$$

The rest of the operation are normal. The expression for $(\partial C_A/\partial x)_{x=0}$ is given below.

$$\left(\frac{\partial C_A}{\partial x}\right)_{x=0} = {}^{*}C_A \left\{ \left(\frac{7}{12}\frac{k}{D} t^{4/3} \right)^{1/2} \operatorname{erf} \sqrt{\frac{kt^{7/3}}{4}} + \frac{\exp\left[(-kt^{7/3})/4 \right]}{\sqrt{3\ \pi\ Dt/7}} \right\} \quad \ldots(24)$$

It may be pointed out that by introducing the condition that parallel chemical reaction is not taking place, $k_1 = 0$ (hence k= 0 in equations 22 and 24) the following equations are obtained.

$$C_A(x,t) = {}^{*}C_A \operatorname{erf}(x/2\sqrt{3Dt/7}) \quad \ldots(22a)$$

$$\left(\frac{\partial C_A}{\partial x}\right)_{x=o} = \frac{{}^{*}C_A}{\sqrt{3\ \pi Dt/7}} \quad \ldots(24a)$$

The equations 22a and 24a are identical with those obtained for the case of linear diffusion to a growing electrodes<10>.

The following equation can be written for C_B (x,t).

$$C_B(x,t) = {}^{*}C_A - C_A(x,t)$$

$$= {}^{*}C_A/2 \left\{ \exp -\sqrt{\frac{7}{12}\frac{k}{D}} t^{4/3}\ x \left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{3Dt/7}} - \frac{1}{2}\sqrt{kt^{7/3}} \right) \right] + \exp\sqrt{\frac{7}{12}\frac{k}{D}} t^{4/3}.x \left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{3Dt/7}} + \frac{1}{2}\sqrt{kt^{7/3}} \right) \right] \right\} \quad \ldots(25)$$

The instantaneous total current (with parallel chemical reaction) at any time t during droplife is given by

$$(i_t)_{total} = nF\ AD(\partial C_A/\partial x)\ x=o$$

$$= nF\ AD\ {}^{*}C_A \left\{ \left(\frac{7}{12}\frac{k}{D} t^{4/3} \right)^{1/2} \operatorname{erf} \sqrt{\frac{kt^{7/3}}{4}} + \frac{1}{\sqrt{3\ \pi Dt/7}} \exp\left(\frac{-kt^{7/3}}{4} \right) \right\} \quad \ldots(26)$$

The instantaneous diffusion current (without parallel chemical reaction)) at any time t during droplife is

$$(i_d)_t = n\ F\ A\ D \left(\partial C_A/\partial x \right)_{\substack{x=o \\ k=o}}$$

$$= nFAD\ {}^{*}C_A \frac{1}{\sqrt{3\ \pi Dt/7}} \quad \ldots(27)$$

Introducing the variable $\lambda = kt^{7/3}/4$, we get the following expression for $(i_t)_{total} / (i_d)_t$ for linear diffusion to a growing electrode.

$$\frac{(i_t)_{total}}{(i_d)_t} = \lambda^{1/2}\left[\Pi^{1/2}\,\mathrm{erf}\,\lambda^{1/2} + \frac{\exp(-\lambda)}{\lambda^{1/2}}\right] \quad (28)$$

A similar expression has been given by Delahay<13> in the case of linear diffusion to a stationary electrode. In a subsequent paper the implications of the equations obtained in the present paper will be discussed.

REFERENCES

1. J. Heyrovsky and J. Kuta, *Principles of Polarography*, p.380,(1966),Academic Press, New York and London. P 380.
2. R. Brdicka and K. Weisner, *Collection Czechoslov.Chem.Communs.*,12 (1947) 39.
3. R. Brdicka and K. Weisner, *Colln. Czech. Chem. Communs.*, 12 (1947) 139.
4. D. Ilkovic, *J. Chim. Phy.*, 38 (1938) 129.
5. P. Delahay and G.I. Stiehl, *J. Amer. Chem. Soc.*, 74 (1952) 3500.
6. S.I. Miller, *J. Amer. Chem. Soc.* 74, (1952) 4130.
7. J. Koutecky and R. Bridcka, *Colln. Czechoslov. Chem. Communs.*, 12, (1947) 337.
8. J. Koutecky, *Colln. Czech. Chem. Communs.*, 18 (1953) 311.
9. K.H. Henke and W. Hans, *Z. Electro-Chem.* 57, (1955) 676.
10. R.S. Subrahmanya, Canadian *J. Chem*, 60 (1962) 296.
11. H.S. Carslaw and J.C. Jaeger, *Conduction of Heat in Solids* (1947) Oxford.
12. A.V. Luikov, *Analytical Heat Diffusion Theory* (1968),Academic Press, New York and London.
13. P. Delahay, *New Instrumental Methods in Electrochemistry*, p 102 (1954) Interscience, New York.

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