

# *The film model for determining the effect of ionic migration in electrochemical systems*

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The film model is used to examine the effect of ionic migration on the concentration of ionic species and on the electrolyte potential profiles inside the Nernst layer.

A general analytical solution is obtained which allows the variation of the limiting current density with the total concentration of the species present in the electrolyte to be demonstrated. Two cases are considered depending on whether the product is soluble in the electrolyte or not. Specific examples are given for the reduction of cupric ions (cations) or ferricyanide ions (anions), respectively in H<sub>2</sub>SO<sub>4</sub> and KOH electrolyte.

## Nomenclature

$C_j$	concentration of ionic species inside the diffusion layer	$t_j$	transport number
$C_{j0}$	concentration of ionic species in the bulk	$x$	normal coordinate
$C_A, C_B$	concentration of the reactant and product inside the diffusion layer	$y$	$= \exp \left[ -\frac{F}{RT} (\phi - \phi_\delta) \right]$ as defined in Equation 36
$D_j$	molecular diffusion coefficient	$z_j$	charge number of species $j$
$F$	Faraday's constant	$z_{AB}$	mutual charge number defined in Equation 11
$i$	current density	$z$	number of electrons involved in the reaction
$n$	exponent of $D_j$		
$i_L, i_{L0}$	limiting current densities		
$r$	ratio $\frac{C_{H^+}}{2C_{SO_4^{2-}}}$ or $\frac{C_{OH^-}}{C_{K^+}}$		
$T$	temperature	<i>Greek letters</i>	
$r'$	$= C_{B0}/C_{A0}$	$\delta$	diffusion layer thickness
		$\phi, \phi_\delta$	electrical solution potential

## 1. Introduction

In an electrolysis cell, the specific flux of an ionic species results, on the whole, from three contributions: 1. migrational transport in the electric field, 2. diffusion and 3. natural or forced convection of the electrolyte.

The rigorous treatment of these three transport mechanisms can only be carried out for certain cases with a specific geometry (rotating disc, mercury drop electrode) and simple hydrodynamics (laminar flow), more particularly, under the following limiting conditions:

(a) the case of the electrolyte containing one or more ionic substances at a high concentration and which does not react with the electrodes. The addition of this inert electrolyte reduces the electric field and the contribution of ionic migration of a reactive species at a low concentration then becomes negligible when considering the diffusion-convection mechanisms.

(b) the case of a binary electrolyte. The use of the electroneutrality condition then leads to a conservation equation identical to that which characterizes non-electrolytic systems and thus overcomes the problem of ionic migration.

The problem has been widely discussed in other papers [1, 2], and more particularly by Newman [3, 4] and other authors [5, 6].

However, in various different important applications such as the treatment of waste water which is slightly conducting and organic electrosynthesis, the electrolyte is only present at low or medium concentrations and the phenomenon of ionic migration modifies the working current densities, usually favourably.

The object of this work is to examine quantitatively the effect of transport by migration starting with the Nernst stagnant diffusion layer model frequently used in physical chemistry or in chemical engineering. This approximation allows us to ignore the convective mechanism inside the diffusion layer, the thickness,  $\delta$ , of which depends on the hydrodynamic conditions prevailing in the neighbourhood of the electrode.

For interphase mass transfer (e.g. gas-liquid, liquid-liquid), different simple models have been described in the literature:

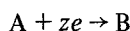
(a) the renewal theory which predicts that the boundary-layer thickness,  $\delta$ , is proportional to the square root of the diffusion coefficient  $D$ ,

(b) the film theory where  $\delta$  is supposed to be the same for all species.

In fact, experimental mass transfer results show that  $\delta$  is proportional to  $D^n$  with  $0$  (film theory)  $< n < 1/2$  (renewal theory).

For the rotating disc system, for example, the effective diffusion-layer thickness varies with the cube root of  $\delta$ . However, the assumption of constant diffusion thickness of all species is frequently used in chemical engineering, which leads to an important simplification of the mathematical treatment. The effect of this assumption upon the results has been described in gas-liquid absorption studies [7-9] which show that no significant error exists even in the case of different diffusion coefficients.

For a reaction mechanism of the type



two cases will be discussed successively:

1. the A and B species are ionic (e.g. the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  or  $\text{Fe}(\text{CN})_6^{3-}$  to  $\text{Fe}(\text{CN})_6^{4-}$ ), and B also participates in the transport
2. only species A is ionic (as in e.g. the reduction of a metal, electrolytic production of a gas or of an insoluble substance).

## 2. Case of a 'Redox' reaction with two substances soluble in the electrolyte

Following the Nernst model, the concentration gradients of A and B and all the ionic species,  $j$ , of the electrolyte can only occur inside the diffusion layer of thickness  $\delta$ .

The equations of conservation of species present in solution are expressed by  $\text{div } \vec{N}_j = 0$  for all  $j$ , where  $\vec{N}_j = -D_j \text{grad. } C_j - z_j F (D_j/RT) C_j \text{grad. } \phi$  is the specific flux of  $j$  made up of two terms, one of diffusion and one of ionic migration (the contribution of convection is zero throughout all the thickness  $\delta$ ).

In a one-dimensional system, the conservation equations become:

$$N_j = -D_j \frac{dC_j}{dx} - z_j F \frac{D_j}{RT} C_j \frac{d\phi}{dx} = 0 \quad \text{for } j \neq A \text{ or } B \quad (1a)$$

$$N_A = -D_A \frac{dC_j}{dx} - z_A F \frac{D_A}{RT} C_A \frac{d\phi}{dx} = \frac{i}{zF} \quad (1b)$$

$$N_B = -D_B \frac{dC_B}{dx} - z_B F \frac{D_B}{RT} C_B \frac{d\phi}{dx} = -\frac{i}{zF} \quad (1c)$$

where  $i$  is the negative current density.

The condition of electroneutrality relates the various local concentrations:

$$\sum_{\text{all } j} z_j C_j = 0 \quad (2)$$

The solution of Equations 1a–c leads to concentration profiles of  $j$  expressed as a function of potential  $\phi$ .

$$C_j = C_{j0} \exp \left[ -\frac{z_j F}{RT} (\phi - \phi_\delta) \right] \quad (3)$$

where  $\phi_\delta$  stands for the electric potential when  $x = \delta$ .

The summation over all species as shown in Equations 1 gives:

$$\sum_{j \neq A, B} z_j C_{j0} \exp \left[ -\frac{z_j F}{RT} (\phi - \phi_\delta) \right] = -z_A C_A - z_B C_B \quad (4)$$

We then easily obtain, from Equations 1b and c and the derivative of Equation 4:

$$\frac{d(C_A + C_B)}{dx} = \frac{F}{RT} \frac{d\phi}{dx} \sum_{j \neq A, B} z_j C_{j0} \exp \left[ -\frac{z_j F}{RT} (\phi - \phi_\delta) \right] + \frac{i}{zF} \left( \frac{1}{D_B} - \frac{1}{D_A} \right) \quad (5)$$

which, by integration between the limits of the diffusion layer, gives:

$$C_A + C_B = \sum_{\text{all } j} C_{j0} + \frac{i}{zF} \left( \frac{1}{D_B} - \frac{1}{D_A} \right) (x - \delta) - \sum_{j \neq A, B} C_{j0} \exp \left[ -\frac{z_j F}{RT} (\phi - \phi_\delta) \right] \quad (6)$$

The elimination of  $C_A$  in Expressions 4 and 6 allows us to express  $C_A$  and  $C_B$  as functions of  $x$  and  $\phi$ , that is

$$C_A = \frac{z - z_A}{z} \sum_{\text{all } j} C_{j0} + \left( \frac{z - z_A}{z} \right) \frac{i}{zF} \left( \frac{1}{D_B} - \frac{1}{D_A} \right) (x - \delta) + \left( \frac{z_A - z}{z} \right) \sum_{j \neq A, B} C_{j0} \exp \left[ -\frac{z_j F}{RT} (\phi - \phi_\delta) \right] - \frac{1}{z} \sum_{j \neq A, B} z_j C_{j0} \exp \left[ -\frac{z_j F}{RT} (\phi - \phi_\delta) \right] \quad (7)$$

$$C_B = \frac{z_A}{z} \sum_{\text{all } j} C_{j0} + \left( \frac{z_A}{z} \right) \frac{i}{zF} \left( \frac{1}{D_B} - \frac{1}{D_A} \right) (x - \delta) - \left( \frac{z_A}{z} \right) \sum_{j \neq A, B} C_{j0} \exp \left[ -\frac{z_j F}{RT} (\phi - \phi_\delta) \right] + \left( \frac{1}{z} \right) \sum_{j \neq A, B} z_j C_{j0} \exp \left[ -\frac{z_j F}{RT} (\phi - \phi_\delta) \right] \quad (8)$$

We then calculate  $(dC_B/dx)$  by differentiation

$$\frac{dC_B}{dx} = \left( \frac{z_A}{z} \right) \frac{i}{zF} \left( \frac{1}{D_B} - \frac{1}{D_A} \right) + \left( \frac{z_A}{z} \right) \frac{F}{RT} \frac{d\phi}{dx} \sum_{j \neq A, B} z_j C_{j0} \exp \left[ -\frac{z_j F}{RT} (\phi - \phi_\delta) \right] - \frac{1}{z} \frac{F}{RT} \frac{d\phi}{dx} \sum_{j \neq A, B} z_j^2 C_{j0} \exp \left[ -\frac{z_j F}{RT} (\phi - \phi_\delta) \right] \quad (9)$$

Combining Equations 1c, 8 and 9 then leads to a first order differential equation in the two variables  $x$  and  $\phi$  of the form:

$$\frac{dx}{d\phi} + ax = \frac{1}{b}f(\phi) \quad (10)$$

with

$$a = +\frac{F}{RT} \left[ \left( \frac{1}{D_A} - \frac{1}{D_B} \right) / \left( \frac{1}{z_B D_A} - \frac{1}{z_A D_B} \right) \right] = +\frac{F}{RT} z_{AB} \quad (11)$$

$$b = \frac{i}{zF} \left( \frac{z_A}{D_A} - \frac{z_B}{D_B} \right) \frac{RT}{F} \quad (12)$$

and

$$f(\phi) = (z_A + z_B) \sum_{j \neq A, B} z_j C_{j0} \exp \left[ -\frac{z_j F}{RT} (\phi - \phi_\delta) \right] - z_A z_B \sum_{j \neq A, B} C_{j0} \exp \left[ -\frac{z_j F}{RT} (\phi - \phi_\delta) \right] \\ - \sum_{j \neq A, B} z_j^2 C_{j0} \exp \left[ -\frac{z_j F}{RT} (\phi - \phi_\delta) \right] + z_A z_B \sum_{\text{all } j} C_{j0} - z_A z_B \frac{i}{zF} \left( \frac{1}{D_B} - \frac{1}{D_A} \right) \delta \quad (13)$$

The general solution of the differential equation Equation 10 is the following

$$x \exp \left( \int a d\phi \right) = \int \frac{1}{b} f(\phi) \exp \left( \int a d\phi \right) d\phi + \text{constant} \quad (14)$$

where the constant can be determined using the condition  $\phi = \phi_\delta$  when  $x = \delta$ . Thus integration from  $\phi = \phi_\delta$  to  $\phi$  and  $x = \delta$  to  $x$  yields the following:

$$x \exp(a\phi) - \delta \exp(a\phi_\delta) = \frac{1}{b} \int_{\phi_\delta}^{\phi} f(\phi) \exp(a\phi) d\phi \quad (15)$$

We then obtain the relationship giving the profile of the potential in the diffusion layer:

$$\frac{i}{zF} \left( \frac{1}{D_B} - \frac{1}{D_A} \right) (x - \delta) = \left\{ \exp \left[ -\frac{F}{RT} z_{AB} (\phi - \phi_\delta) \right] - 1 \right\} \sum_{\text{all } j} C_{j0} \\ + z_{AB} \sum_{j \neq A, B} \frac{f(j, \phi) C_{j0}}{z_j - z_{AB}} \left[ \frac{z_j^2}{z_A z_B} - z_j \left( \frac{1}{z_A} + \frac{1}{z_B} \right) + 1 \right] \quad (16)$$

with

$$f(j, \phi) = \exp \left[ -\frac{F}{RT} z_{AB} (\phi - \phi_\delta) \right] - \exp \left[ -\frac{z_j F}{RT} (\phi - \phi_\delta) \right] \quad (17)$$

This analytical expression, coupled with Relationships 3, 7 and 8, for  $C_j$ ,  $C_A$  and  $C_B$  allows us to calculate the concentration profiles of all species in the diffusion layer and to define the influences of the current density and the concentration of the species inside the solution on the deformation of these profiles. It allows us, in particular, to determine the variation of the limiting current density (for which  $C_{A|x=0} = 0$ ) when the overall concentration of the electrolyte increases.

In addition, we point out that to our knowledge, no theoretical expression of this kind has been proposed up to now, and that the only two assumptions made in this calculation are

- (a) the use of a stagnant diffusion layer thickness independent of diffusion coefficient
- (b) the approximation of a dilute solution in the expression for the specific flux of each ionic species.

It should be noted however that an analysis for the particular case of three ionic species in a stagnant diffusion layer was developed by Hsueh and Newman [10].

### 3. The case of a mechanism of reduction of a metallic species or production of gaseous or insoluble product

Under these conditions species B does not take part in the mechanism of ionic transport in solution and the problem is mathematically more simple. The starting expressions are the same as above, without Expression 1c.

The general procedure of the calculation is identical, and the main results are shown below:

(a) Expression 17 is replaced by:

$$\frac{i}{z_A F D_A} (x - \delta) = \sum_{\text{all } j} C_{j0} + \frac{1}{z_A} \sum_{j \neq A} z_j C_{j0} \exp \left[ -\frac{z_j F}{RT} (\phi - \phi_\delta) \right] - \sum_{j \neq A} C_{j0} \exp \left[ -\frac{z_j F}{RT} (\phi - \phi_\delta) \right] \quad (18)$$

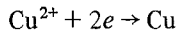
(b) Expression 7 is replaced by:

$$C_A = -\frac{1}{z_A} \sum_{j \neq A} z_j C_{j0} \exp \left[ -\frac{z_j F}{RT} (\phi - \phi_\delta) \right] \quad (19)$$

### 4. Examples of applications

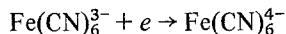
Figs. 1–7 giving the concentration and electric potential profiles inside the diffusion layer are given as examples and allow us to illustrate the preceding developments:

(a) Figs. 1–4 correspond to the reaction mechanism



the supporting electrolyte being sulphuric acid

(b) Figs. 5–7 correspond to the reduction of ferricyanide ions



the supporting electrolyte being KOH

The numerical values of the parameters are shown in Table 1.

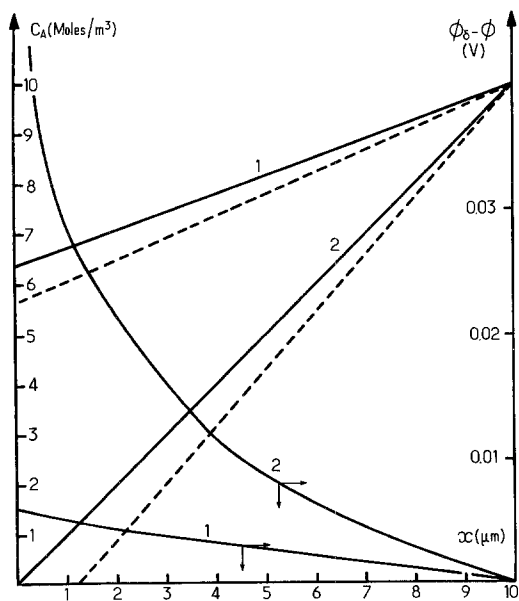


Fig. 1.  $\text{CuSO}_4$  system: Concentration and potential profiles inside the diffusion layer. No supporting electrolyte:  $[\text{CuSO}_4] = 10^{-2} \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 0 \text{ M}$ .  $1 - i = -100 \text{ A m}^{-2}$ ;  $2 - i = -277 \text{ A m}^{-2}$ .

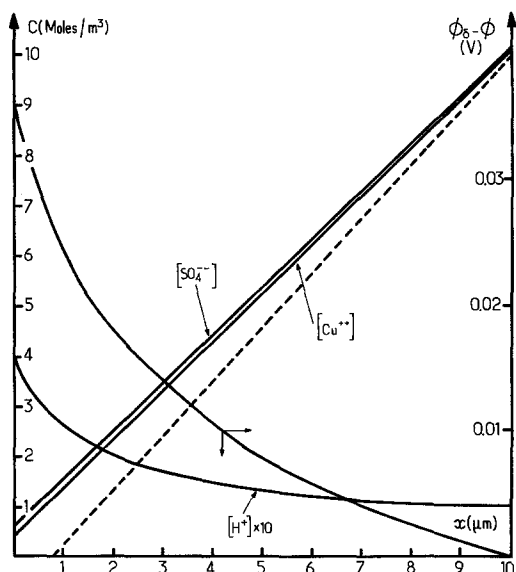


Fig. 2.  $\text{CuSO}_4 + \text{H}_2\text{SO}_4$  system: Concentration and potential profiles inside the diffusion layer.  $[\text{CuSO}_4] = 10^{-2} \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 5 \times 10^{-5} \text{ M}$ ,  $i = -260 \text{ A m}^{-2}$ .

#### 4.1. Reduction of A to an insoluble B species

Fig. 1 concerns the case of a binary electrolyte  $\text{CuSO}_4$  in the absence of the supporting electrolyte.

We again find the classical expressions:

$$C_A = C_{\text{SO}_4^{2-}} \quad (\text{equation of electroneutrality}) \quad (20)$$

$$C_A - C_{A0} = \frac{-i}{2zFD_A}(x - \delta) \quad (21)$$

and

$$\phi_\delta - \phi = -\frac{RT}{2F} \ln \left[ 1 - \frac{i}{2zFD_A C_{A0}}(x - \delta) \right] \quad (22)$$

The limiting current density  $i_L = -277 \text{ A m}^{-2}$  is twice as high as that obtained when there is a high

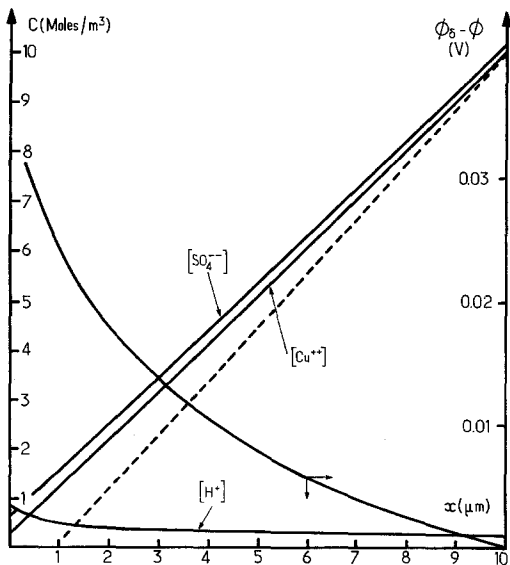


Fig. 3.  $\text{CuSO}_4 + \text{H}_2\text{SO}_4$  system:  $[\text{CuSO}_4] = 10^{-2} \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 10^{-4} \text{ M}$ ,  $i = -260 \text{ A m}^{-2}$ .

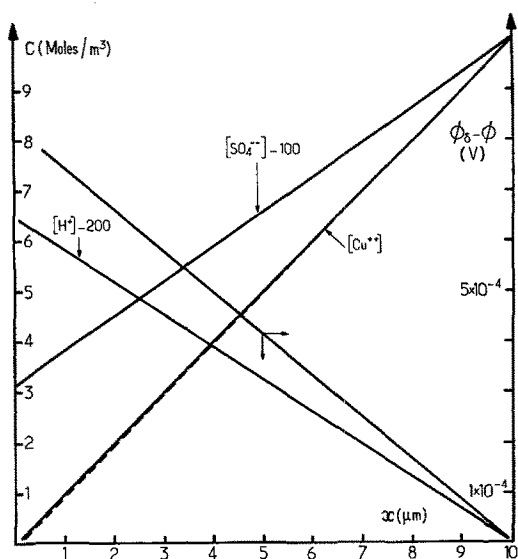


Fig. 4.  $\text{CuSO}_4 + \text{H}_2\text{SO}_4$  system:  $[\text{CuSO}_4] = 10^{-2} \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 0.1 \text{ M}$ ,  $i = -145 \text{ A m}^{-2}$ .

concentration of supporting electrolyte. Ionic migration then has a favourable effect on the maximum rate of the electrochemical reaction.

The profiles shown in dotted lines correspond to the classical use of transport numbers, the values of which are assumed to be constant and equal to those inside the solution [11], that is:

$$D_A \frac{dC_A}{dx} - \frac{it_A}{z_A F} = -\frac{i}{z_A F} \quad \text{with } i < 0 \quad (23)$$

or

$$C_A - C_{A0} = \frac{i}{z_A F D_A} (t_A - 1)(x - \delta) \quad (24)$$

with

$$t_A = \frac{z_A^2 D_A C_{A0}}{\sum_{\text{all } j} z_j^2 D_j C_{j0}} = \frac{[i_A]}{[i]} \quad \text{in solution} \quad (25)$$

For low concentrations of sulphuric acid (see Figs. 2 and 3), the difference between the real profile and that resulting from the use of transport numbers is important but becomes indistinguishable for values of the order of  $0.1 \text{ M H}_2\text{SO}_4$  (Fig. 4).

It should be noted that increasing the concentration of the supporting electrolyte tends to cause the profiles of the electric potential  $\phi$  and that of the concentration in  $\text{H}^+$  to be more linear.

Fig. 8a gives the variations in the ratio  $i_L/i_{L0}$  between the limiting current density at a given concen-

Table 1. Parameters for the electrolytes depicted in Figs. 1-4 and 5-7

Electrolyte	Diffusion coefficients ( $\text{m}^2 \text{s}^{-1}$ )	$\delta$ ( $\mu\text{m}$ )	T (K)	$i_{L0}$ ( $\text{A m}^{-2}$ )
$\text{CuSO}_4, \text{H}_2\text{SO}_4$ $\text{Cu}^{2+} + 2e \rightarrow \text{Cu}$ $Z_A = Z = 2$	$\left\{ \begin{array}{l} D_{\text{Cu}^{2+}} = 0.72 \times 10^{-9} \\ D_{\text{SO}_4^{2-}} = 1.06 \times 10^{-9} \\ D_{\text{H}^+} = 9.3 \times 10^{-9} \end{array} \right\}$	10	300	-138.9
$\text{K}_3\text{Fe}(\text{CN})_6, \text{K}_4\text{Fe}(\text{CN})_6, \text{KOH}$ $\text{Fe}(\text{CN})_6^{3-} + e \rightarrow \text{Fe}(\text{CN})_6^{4-}$ $Z_A = -3, Z_B = -4, Z = 1$	$\left\{ \begin{array}{l} D_A = 0.9 \times 10^{-9} \\ D_B = 0.74 \times 10^{-9} \\ D_{\text{K}^+} = 2 \times 10^{-9} \\ D_{\text{OH}^-} = 5.3 \times 10^{-9} \end{array} \right\}$	10	300	-86.84

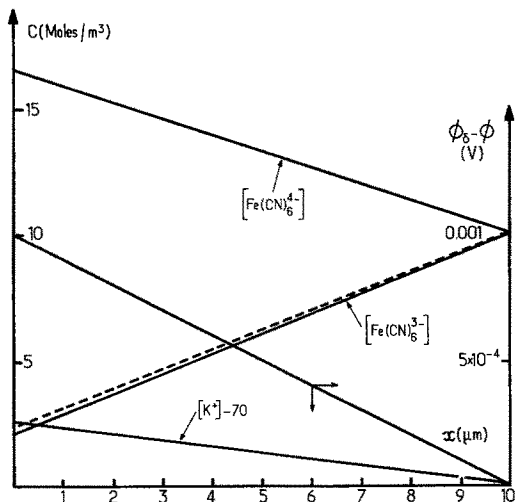


Fig. 5.  $\text{K}_3\text{Fe}(\text{CN})_6$ - $\text{K}_4\text{Fe}(\text{CN})_6$  system: Concentration and potential profiles. No supporting electrolyte:  $[\text{K}_3\text{Fe}(\text{CN})_6] = [\text{K}_4\text{Fe}(\text{CN})_6] = 10^{-2} \text{ M}$ ,  $[\text{KOH}] = 0 \text{ M}$ ,  $i = -60 \text{ A m}^{-2}$ .

tration in acid  $i_L$  and that obtained at a high concentration corresponding to an excess of supporting electrolyte  $i_{L0}$  as a function of the parameter  $r = C_{\text{H}^+}/2C_{\text{SO}_4^{2-}}$  defined by Newman [1].

In the particular case given here, the ratio varies between 1 and 2 and the gain remains greater than 20% as long as  $r$  is lower than 0.5. The choice of the optimal value for the supporting electrolyte is the result of a compromise between the increase in the overall rate of reaction and the reduction of the electrical conductivity of the solution, which leads to an over-consumption of electrical energy by the ohmic drop.

The theoretical expressions of  $i_L/i_{L0}$  can be derived by writing  $C_A = 0$  when  $x = 0$ .

We therefore easily obtain from Equation 18 and Equation 19 (where  $z_1$  and  $z_2$  refer to  $\text{SO}_4^{2-}$  and  $\text{H}^+$ , respectively).

$$\exp\left[-\frac{z_j F}{RT}(\phi - \phi_\delta)\right]_{x=0} = \left(-2r \frac{z_2}{z_1}\right)^{-z_j/(z_2 - z_1)}$$

$$\frac{i_L}{i_{L0}} = 1 - \frac{z_A}{z_1 + 2rz_2} \left\{ 1 + 2r - (2r)^{-z_1/(z_2 - z_1)} \left[ \left(\frac{-z_2}{z_1}\right)^{-z_1/(z_2 - z_1)} + \left(\frac{-z_2}{z_1}\right)^{-z_2/(z_2 - z_1)} \right] \right\} \quad (26)$$

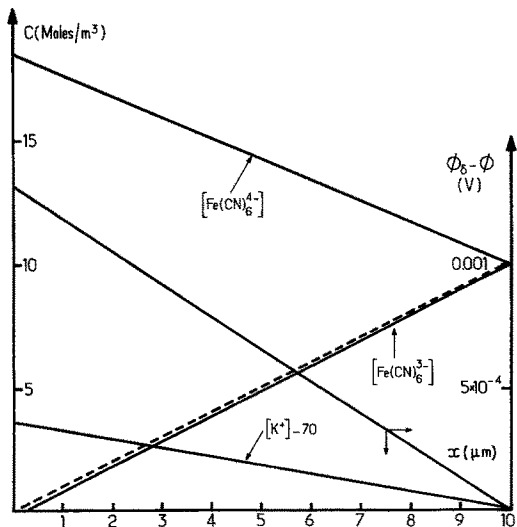


Fig. 6.  $\text{K}_3\text{Fe}(\text{CN})_6$ - $\text{K}_4\text{Fe}(\text{CN})_6$  system: Concentration and potential profiles at the limiting current density ( $r = 0$ ).  $[\text{K}_3\text{Fe}(\text{CN})_6] = [\text{K}_4\text{Fe}(\text{CN})_6] = 10^{-2} \text{ M}$ ,  $[\text{KOH}] = 0 \text{ M}$ ,  $i = -80.15 \text{ A m}^{-2}$ .



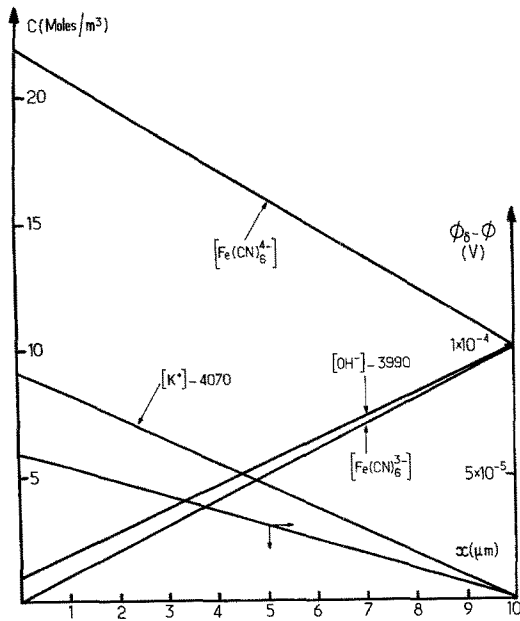


Fig. 7.  $K_3Fe(CN)_6-K_4Fe(CN)_6$  system: Concentration and potential profiles at the limiting current density with an excess of supporting electrolyte:  $[K_3Fe(CN)_6] = [K_4Fe(CN)_6] = 10^{-2}$  M,  $[KOH] = 4$  M,  $i = -86.84$  A  $m^{-2}$ .

with  $r = C_{20}/2C_{10}$

and

$$\frac{\Delta C_2}{2C_{A0}} = \frac{C_2|_{x=0} - C_{20}}{2C_{A0}} = \frac{rz_A}{z_1 + 2rz_2} \left[ 1 - \left( -2r \frac{z_2}{z_1} \right)^{-z_2/(z_2-z_1)} \right] \tag{28}$$

Fig. 8b gives the variations with  $(r)^{1/2}$  of the last parameter representing the normalized difference of the concentration of  $H^+$  over the entire thickness of the diffusion layer. It should be noted that the analytical solutions obtained for  $i_L/i_{L0}$  and  $\Delta C_2/2C_{A0}$  do not differ greatly from those given by Newman [1] for the rotating disc, using a numerical method for the computer calculation.

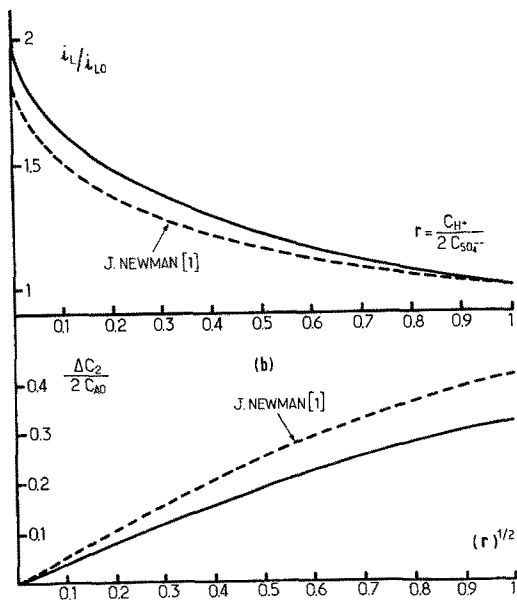


Fig. 8.  $CuSO_4 + H_2SO_4$  system: (a) calculated variations of  $i_L/i_{L0}$  with  $r$ , (b) calculated variations of  $\Delta C_2/2C_{A0}$  with  $(r)^{1/2}$ .

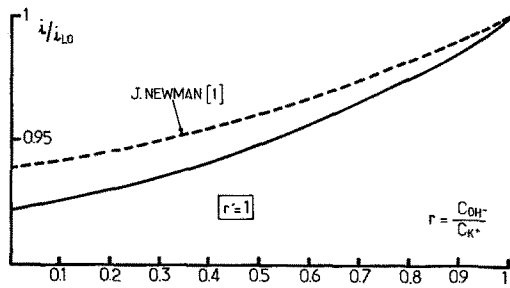


Fig. 9.  $K_3Fe(CN)_6$ - $K_4Fe(CN)_6$  system: Calculated variations of  $i_L/i_{L0}$  with  $r = C_{OH^-}/C_{K^+}$  and comparison with the results of the rotating disc electrode.

#### 4.2. Reduction of A to a soluble B species

The results for the reduction of ferricyanide ions to soluble ferrocyanide are shown in Figs. 5-7 and have an additional interest owing to the negative charge of the A species.

The diffusion mechanisms of A to the electrode and of migration in the electric field are opposite, contrary to the case of the  $Cu^{2+}/Cu$  couple. The 'chemical force' dragging the reactive species toward the electrode is always greater than the electric force, but the limiting current density is then lower than that obtained when the supporting electrolyte is present in large excess (of the order of  $87 A m^{-2}$  for the numerical values of Table 1).

However, just as Newman [1] mentioned for the rotating disc, the relative difference is low, considering the presence of  $K^+$  ions coming from the dissociation of  $K_3Fe(CN)_6$  and  $K_4Fe(CN)_6$ .

Fig. 6, for example, shows that in the absence of KOH, the limiting current density is about  $80 A m^{-2}$ , which is very close to the value of  $87 A m^{-2}$  when KOH is in excess.

The use of transport numbers, which are assumed to be constant throughout the thickness of the Nernst layer, allows us to write the following relationships:

$$\frac{dC_A}{dx} = -\frac{i}{FD_A} \left( \frac{1}{z} - \frac{t_A}{z_A} \right) \quad (29)$$

that is

$$C_A - C_{A0} = -\frac{i}{FD_A} \left( \frac{1}{z} - \frac{t_A}{z_A} \right) (x - \delta) \quad (30)$$

and

$$\frac{dC_B}{dx} = \frac{i}{FD_B} \left( \frac{t_B}{z_B} + \frac{1}{z} \right) \quad (31)$$

that is

$$C_B - C_{B0} = \frac{i}{FD_B} \left( \frac{t_B}{z_B} + \frac{1}{z} \right) (x - \delta) \quad (32)$$

The corresponding profiles for A have been drawn in dotted lines in Figs. 5-7 and represent very small differences when compared with the real profiles. It should, however, be noted that, even in the absence of KOH, the value of the transport number,  $t_A$ , for A is only 0.238 and the correction term  $[(1/z) - (t_A/z_A)]$ , is only 1.079. The effect of the ionic migration is therefore minimized by the necessary presence of the  $K^+$  ions.

The general analytical solution (Equations 7 and 17) can be used to determine the variations of the ratio  $i_L/i_{L0}$  with the parameter

$$r = C_{OH^-}/C_{K^+} = C_{20}/C_{10} \quad (33)$$

as well as those of

$$\frac{C_{20} - C_{2|x=0}}{C_{B0}} = \frac{\Delta C_2}{C_{B0}} \quad (34)$$

(see Figs. 10 and 11).

Putting  $C_A = 0$  when  $x = 0$  in Equation 7 and replacing the expression found in Equation 17, we get the following simple equation:

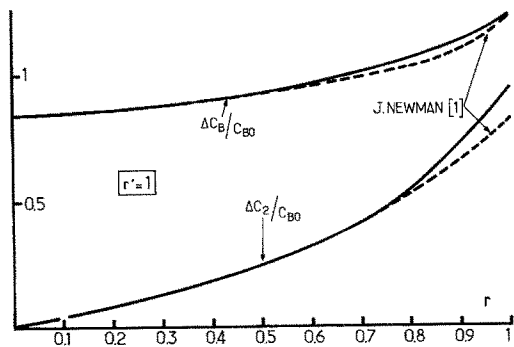


Fig. 10.  $K_3Fe(CN)_6$ - $K_4Fe(CN)_6$  system: Calculated variations of  $\Delta C_B/C_{B0}$  and  $\Delta C_2/C_{B0}$  with  $r$ . Comparison with the results of the rotating disc electrode.

$$\begin{aligned}
 & \exp \left[ -\frac{z_1 F}{RT} (\phi - \phi_\delta) \right]_{x=0} \left\{ \frac{z_1}{z_B} - 1 - \left( \frac{z_{AB}}{z_1 - z_{AB}} \right) \left[ \frac{z_1^2}{z_A z_B} - z_1 \left( \frac{1}{z_A} + \frac{1}{z_B} \right) + 1 \right] \right\} \\
 & + r \exp \left[ -\frac{z_2 F}{RT} (\phi - \phi_\delta) \right]_{x=0} \left\{ \frac{z_2}{z_B} - 1 - \left( \frac{z_{AB}}{z_2 - z_{AB}} \right) \left[ \frac{z_2^2}{z_A z_B} - z_2 \left( \frac{1}{z_A} + \frac{1}{z_B} \right) + 1 \right] \right\} \\
 & + \exp \left[ -\frac{F z_{AB}}{RT} (\phi - \phi_\delta) \right]_{x=0} \left\{ \left( \frac{z_{AB}}{z_1 - z_{AB}} \right) \left[ \frac{z_1^2}{z_A z_B} - z_1 \left( \frac{1}{z_A} + \frac{1}{z_B} \right) + 1 \right] \right. \\
 & \left. + \left( \frac{r z_{AB}}{z_2 - z_{AB}} \right) \left[ \frac{z_2^2}{z_A z_B} - z_2 \left( \frac{1}{z_A} + \frac{1}{z_B} \right) + 1 \right] + (1+r) - \frac{(1+r')(z_1 + z_2 r)}{z_A + r' z_B} \right\} = 0 \quad (35)
 \end{aligned}$$

with  $r' = C_{B0}/C_{A0}$  and  $z_1 = 1$  and  $z_2 = -1$ . By putting

$$y = \exp \left[ -\frac{F}{RT} (\phi - \phi_\delta) \right]_{x=0} = \frac{C_{A|x=0}}{C_{A0}} \quad (36)$$

an expression of the following form is obtained:

$$Ay + \frac{rB}{y} + Cy^{z_{AB}} = 0 \quad (37)$$

with

$$A = \frac{z_1}{z_B} - 1 - \left( \frac{z_{AB}}{z_1 - z_{AB}} \right) \left[ \frac{z_1^2}{z_A z_B} - z_1 \left( \frac{1}{z_A} + \frac{1}{z_B} \right) + 1 \right] \quad (38)$$

$$B = \frac{z_2}{z_B} - 1 - \left( \frac{z_{AB}}{z_2 - z_{AB}} \right) \left[ \frac{z_2^2}{z_A z_B} - z_2 \left( \frac{1}{z_A} + \frac{1}{z_B} \right) + 1 \right] \quad (39)$$

$$\begin{aligned}
 C = & \left( \frac{z_{AB}}{z_1 - z_{AB}} \right) \left[ \frac{z_1^2}{z_A z_B} - z_1 \left( \frac{1}{z_A} + \frac{1}{z_B} \right) + 1 \right] + \left( \frac{r z_{AB}}{z_2 - z_{AB}} \right) \left[ \frac{z_2^2}{z_A z_B} - z_2 \left( \frac{1}{z_A} + \frac{1}{z_B} \right) + 1 \right] \\
 & + 1 + r - \frac{(1+r')(z_1 + r z_2)}{z_A + r' z_B} \quad (40)
 \end{aligned}$$

For each value of  $r$  between 0 and 1, the solution to this equation gives the value of  $y$  at the surface of the electrode: the corresponding limiting current density is then obtained from Expression 7 in which  $C_{A|x=0} = 0$ :

$$\frac{i_L \left( \frac{1}{D_B} - \frac{1}{D_A} \right) \delta}{zF} = (1+r') + \left( \frac{z_A + r' z_B}{r-1} \right) \left( 1 - y + \frac{y}{z_B} \right) + r \left( \frac{z_A + r' z_B}{r-1} \right) \left( 1 + \frac{1}{y} - \frac{1}{y z_B} \right) \quad (41)$$

Furthermore in the presence of a supporting electrolyte in excess, we have:

$$i_{L0} = z_A F \frac{D_A}{\delta} C_{A0} \quad (42)$$

and therefore:

$$\frac{i_L}{i_{L0}} = \frac{D_B}{D_B - D_A} \left[ (1 + r') + \left( \frac{z_A + r' z_B}{r - 1} \right) \left( 1 - y + \frac{y}{z_B} \right) + r \left( \frac{z_A + r' z_B}{r - 1} \right) \left( 1 - \frac{1}{y} - \frac{1}{y z_B} \right) \right] \quad (43)$$

By combining Expression 3 for  $j = 2$ , the definitions of  $r$  and  $r'$  and the electroneutrality condition in the bulk, we also obtain:

$$\frac{\Delta C_2}{C_{B0}} = r \frac{z_A + r' z_B}{r'(r - 1)} \left( 1 - \frac{1}{y} \right) \quad (44)$$

and in the same way:

$$\frac{\Delta C_B}{C_{B0}} = \frac{C_{B|x=0} - C_{B0}}{C_{B0}} = \frac{1}{r' z_B} \left( \frac{z_A + r' z_B}{r - 1} \right) \left( \frac{r}{y} - y \right) - 1 \quad (45)$$

An important specific example is that for  $r = 0$ , that is, in the absence of a supporting electrolyte. From Equation 37, we get directly:

$$y = \exp \left[ -\frac{F}{RT} (\phi - \phi_\delta) \right] = \left( -\frac{C}{A} \right)^{1/1 - z_{AB}} \quad (46)$$

that is:

$$y_{r=0} = \left\{ \left[ \frac{r' + 1}{z_A + r' z_B} - \left( \frac{z_{AB}}{1 - z_{AB}} \right) \left( \frac{1}{z_A z_B} - \frac{1}{z_A} - \frac{1}{z_B} + 1 \right) \right] - 1 \right. \\ \left. / \left[ \left( \frac{-z_{AB}}{1 - z_{AB}} \right) \left( \frac{1}{z_A z_B} - \frac{1}{z_A} - \frac{1}{z_B} + 1 \right) - 1 + \frac{1}{z_B} \right] \right\}^{1/1 - z_{AB}} \quad (47)$$

For the numerical conditions of Table 1,  $y_{r=0} = 1.051$  and the corresponding value of  $i_L/i_{L0}$  is 0.923.

For  $r' = 1$ , i.e. equal concentrations of ferri- and ferrocyanide, Figs. 9 and 10, show the variations of  $i_L/i_{L0}$ ,  $\Delta C_2/C_{B0}$  and  $\Delta C_B/C_{B0}$  with  $r$ , and compare the results with the numerical solutions for the rotating disc obtained by Newman [1]. The relative differences are reasonably small, although the two geometries (rotating disc and layer of constant thickness) differ considerably. It should be noted that, for a given value of  $r$ , the numerical values of the three variables of Figs. 9 and 10, deduced from our analytical approach, are absolutely identical to those deduced by the numerical solution of the basic differential equations.

This complete agreement confirms the general analytical solution obtained in this work.

## 5. Conclusions

We have used the diffusion layer model as used in chemical engineering and proposed by Nernst in physical chemistry to examine the influence of ionic migration on the concentration profiles of reactive or inert ionic species and on the profile of the electric potential.

The good agreement observed between the present model based on the film theory and the numerical solutions for the rotating disc electrode obtained by Newman shows that the assumption of constant diffusion-layer thickness for all species is sufficiently good for chemical engineering calculations even when the diffusion coefficients of the ionic species are very different.

The analytical solution obtained displays a general character and allows, in particular, to show quantitatively how the limiting current density varies with the total concentration of the species making up the inert electrolyte. The application of this model can be considered for all electrochemical reactors with forced, turbulent convection of the electrolyte intended to be used for the treatment of dilute solutions.

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