Title
THE ROLE OF IONIC MIGRATION IN ELECTROLYTIC MASS TRANSPORT: DUTUSIVITIES OP [Fe(CN)6]3- AND [Fe(CN)6]1*- IN KDH AND NaOH SOLUTIONS

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The Role of Ionic Migration in Electrolytic Mass Transport; Diffusivities of $[\text{Fe(CN)}_6]^{3-}$ and $[\text{Fe(CN)}_6]^{4-}$ in KOH and NaOH Solutions

By Stanley L. Gordon, John S. Newman, Charles W. Tobias
The Role of Ionic Migration in Electrolytic Mass Transport; Diffusivities of $[\text{Fe(CN)}_6]^{3-}$ and $[\text{Fe(CN)}_6]^{4-}$ in KOH and NaOH Solutions

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(Eingegangen am 29. Oktober 1965)

The role of migration in ionic mass transport is discussed, and a rigorous method is presented for the evaluation of the contribution of migration when a constant potential gradient can be assumed to exist in the mass transfer boundary layer.

The influence of supporting electrolytes is shown to depend on the relative mobilities of all ionic species present in the solution.

Theoretical results are applied to the $K_3[\text{Fe(CN)}_6]-K_4[\text{Fe(CN)}_6]-\text{KOH}$ or NaOH systems. Limiting currents were measured by a rotating disk electrode, and the apparent diffusivities calculated from these measurements were corrected taking into account the influence of the presence of nonreacting ionic species. It is shown that the corrected product, $D\mu$, shows only a slight dependence on ionic strength over a large range of concentrations

\[
\frac{D\mu}{T} = (2.34 + 0.014 I) \times 10^{-10} (\text{cm}^2/\text{sec}) \text{ poise}^2/\text{K}
\]

for $[\text{Fe(CN)}_6]^{3-}$, and

\[
\frac{D\mu}{T} = (1.87 + 0.034 I) \times 10^{-10} (\text{cm}^2/\text{sec}) \text{ poise}^2/\text{K}
\]

where $I$ is the ionic strength of the solution.

It is shown that the corrected product, $D\mu$, shows only a slight dependence on ionic strength over a large range of concentrations.

The theoretical results are applied to the $K_3[\text{Fe(CN)}_6]-K_4[\text{Fe(CN)}_6]-\text{KOH}$ or NaOH systems. Limiting currents were measured by a rotating disk electrode, and the apparent diffusivities calculated from these measurements were corrected taking into account the influence of the presence of nonreacting ionic species. It is shown that the corrected product, $D\mu$, shows only a slight dependence on ionic strength over a large range of concentrations.

where $\dot{j}_i$ is the concentration of species $i$, $D_i$ is the ionic diffusivity, $e$ is the electronic charge, $F$ is Faraday's constant, $I$ is the current density, $N_i$ is the ionic flux, $t$ is the time, $U_i$ is the ionic mobility, $v$ is the velocity of the fluid, $z_i$ is the number of charges on an ion, and $\Phi$ is the potential.

Within the mass transfer boundary layer the concentrations of all ions change due to migration, diffusion, and convective fluxes [equation (1)]. Ions that migrate towards the electrode must diffuse away if they are not involved in the electrode reaction. The concentration of each ionic species departs from the bulk value, but the solution, to a good approximation, remains electrically neutral at all points [equation (4)].

The potential gradient, the driving force for migra-
tion, at any point in the solution is obtained by combining equations (1), (3), (4) and solving for $\nabla \Phi$.

$$
\nabla \Phi = -\frac{I}{K} - \frac{F \sum_{i=1}^{m} z_i D_i \epsilon \gamma_i}{K}
$$

where

$$
K = F \sum_{i=1}^{m} U_i \epsilon \gamma_i \xi_i
$$

which is commonly known as the solution conductivity.

The potential gradient is composed of an ohmic drop and a term which includes the concentration gradients and the conductivity. The second term, which appears in all electrolytic systems where concentration gradients and diffusivity differences exist, is the diffusion potential.

To understand more fully the effect of migration, consider the cathodic discharge of a metal ion. Assume that a large amount of supporting electrolyte, relative to the reacting ion, is present, and that therefore the migration flux is negligible. In the bulk of a well-stirred solution, the concentration remains practically uniform because the swiftly moving fluid rapidly replenishes the loss due to diffusion. As the electrode is approached, the fluid velocity decreases and the concentration gradients increase because the total flux is constant at steady state [equation (2)]. Concentration gradients attain maxima at the electrode surface where the fluid velocity is zero.

The contribution of migration can be increased by decreasing the amount of supporting electrolyte. As in the supporting electrolyte case, the fluid velocity decreases in the vicinity of the electrode. However, a migration velocity (towards the electrode for the metal deposition case being considered) affects the entire concentration profile. The reacting ion in the faster moving lamina migrates to the slower lamina nearer the electrode, therefore shifting the concentration profile towards the electrode surface as shown in Fig. 1.

The change in the concentration profile of the reacting ion is of interest because the limiting current $I_L$ is directly related to the concentration gradient at the interface. Combining equations (1) and (3), one obtains

$$
I_L = n F D_1 \epsilon \gamma_1
$$

where the subscript 1 denotes the reactant*).

**Quantitative Calculation of the Limiting Current for a Special Case**

Until this point a consideration of the physical model has not been necessary, but a quantitative analysis can be performed only for a specific flow system. The rotating disk electrode is one of the few physical models where the velocity distribution is known within the vicinity of the surface [2].

*) Note that the term involving the electric field vanishes because under limiting current conditions the concentration of the reacting ion approaches zero at the solution-electrode interface.

The limiting current, including the migration contributions, to a rotating disk electrode can be calculated for a constant potential gradient in the mass transfer boundary layer. A constant potential gradient is possible if all ionic diffusivities are equal and if the solution contains enough supporting electrolyte so that the conductivity remains essentially constant through the boundary layer. Then the potential gradient from equation (5) will be (at limiting current)

$$
\nabla \Phi = -\frac{I_L}{Kb^*}
$$

Applying a constant potential and eliminating the flux between equation (2) and equation (1), one obtains at steady state for the reactant

$$
D_1 \nabla^2 c_1 = (v - U_1 \epsilon \gamma_1 \nabla \Phi) \frac{d c_1}{d y}
$$

where the divergence of the velocity was eliminated by the continuity condition and the fluid properties were assumed to be constant.

For the rotating disk electrode, equation (9) can be simplified further. Levich [2] has proposed that the concentration is a function of only one dimension, $y$, which is the perpendicular distance from the plane of the disk, and therefore

$$
D_1 \frac{d^2 c_1}{d y^2} = (v - U_1 \epsilon \gamma_1 \frac{d \Phi}{d y}) \frac{d c_1}{d y}
$$

In equation (10) $v$ and $d \Phi/d y$ are known as functions of $y$. These functions do not involve $c_1$ or its derivatives. Therefore, we have a linear second-order differential equation which can be readily solved for $c_1$ and related to the limiting current, $I_L$. The solution to equation (10) which satisfied the boundary conditions:

- $y = 0, \ c_1 = 0$ for $I = I_L$
- $y = \infty, \ c_1 = c_1^0$

**gives following expression for the bulk concentration of the reactant:**

$$
c_1^0 = \left(\frac{d c_1}{d y}\right)_0 \int_{-\infty}^{+\infty} \text{exp} \left( \int_{-\infty}^{y} \left( v - U_1 \epsilon \gamma_1 \frac{d \Phi}{D_1} \right) \frac{d \xi}{d y} \right) \frac{d y}{d \xi}.
$$
The fluid velocity component, \( v \), in equation (11) is [4]

\[
v = (\omega a)^{1/3} \times \left[ -0.510 \left( \frac{\omega}{v} \right)^{1/3} t^3 + 0.333 \left( \frac{\omega}{v} \right)^{1/3} t^3 - 0.103 \left( \frac{\omega}{v} \right)^{1/3} t^3 + \cdots \right] (12)
\]

where \( \omega \) is the angular velocity of the disk and \( v \) is the kinematic viscosity of the solution.

The development is simplified by letting

\[
x = \frac{2}{\alpha}.
\]

According to Levich: \( \delta_1 = \delta_B (Sc)^{-1/6} \) (diffusion boundary layer), and \( \delta_H = 1.805 (\nu/\omega)^{1/6} \) (hydrodynamic boundary layer), where \( Sc = \nu D_1 \) (Schmidt number).

With this variable transformation equations (11) and (12) yield

\[
\delta_1^2 = \left( \frac{d_1}{d_f} \right)^2 \delta_1 \times \int_0^\infty \exp(-x^3 + 0.884 (Sc)^{-1/6} x^4) \exp\left(-\frac{U_1 e z_1 P \Phi \delta_1}{D_1} \right) d x. (13)
\]

The value of the limiting current, from equation (7) and equation (13), is:

\[
I_L = -\frac{nF D_1 c_b}{\delta_1 M_1} (14)
\]

where

\[
M_1 = \int_0^\infty \exp(-x^3 + 0.884 (Sc)^{-1/6} x^4 - 0.939 (Sc)^{-1/6} x^6) \times \exp\left(-\frac{U_1 e z_1 P \Phi \delta_1}{D_1} \right) d x. (15)
\]

The migration integral, \( M_1 \), is a function of the parameter \( -\frac{U_1 e z_1 P \Phi \delta_1}{D_1} \) which can be related to solution properties by the application of equations (7), (11)

\[
\frac{U_1 e z_1 P \Phi \delta_1}{D_1} = -\frac{U_1 e z_1 I_i \delta_i'}{K^b D_1} - \frac{n_{t_1}}{z_1 M_1},
\]

where \( t_1 \) is the transference number of the reacting ion in the bulk.

\[
t_1 = \frac{U_1 e z_1 c_b}{\Sigma U_1 e z_1 c_i}
\]

Equation (15) can be expanded into an infinite series of gamma functions. When evaluated, neglecting cross products and higher terms in \( Sc^{-1/6} \) one obtains:

\[
M_1 = .893 + .2661 Sc^{-1/6} + .4513 \frac{n_{t_1}}{z_1 M_1} + .1667 \left( \frac{n_{t_1}}{z_1 M_1} \right)^2.
\]

Fig. 2 gives the values of \( M_1 \), for large Schmidt numbers, as a function of \( n_{t_1}/z_1 \).

**Comparison of Migration Correction Methods**

A comparison can be made between the commonly used migration correction and the present results. By equating the migration flux to the product, \( t_1 I_i/z_1 F \), we have

\[
I_L \left( 1 - \frac{n_{t_1}}{z_1} \right) = -n F D_1 P \phi (17)
\]

for an arbitrary mass transport system. With the effective film thickness, \( \delta_i' \), for the rotating disk electrode [3], equation (17) becomes

\[
I_L = -\frac{n F D_1 c_b}{.893 \left( 1 - \frac{n_{t_1}}{z_1} \right) \delta_i'} (18)
\]

(since \( \delta_i' = \frac{c_b}{\delta_i' (893 \delta_i') \delta_i) \) whereas from equation (14) and equation (16), at small \( t_1 \) and large \( \delta_i \) we have

\[
I_L = -\frac{n F D_1 c_b}{.893 \left( 1 - .566 n_{t_1} \right) \delta_i'. (19)
\]

The transference number appears in a rigorous solution as, approximately, the arithmetic average over the boundary layer \( t_i = 0 \) at the electrode surface. In equation (18) the \( t_i \) was considered to be constant.

To clarify further the role of ionic migration the effect of a changing potential gradient within the boundary layer should be estimated.

**Effect of Changing Potential Gradient on Mass Transfer**

The interfacial potential gradient can be estimated for an arbitrary number of ions by allowing the interfacial concentrations to be represented by

\[
\phi' = \frac{\beta_i}{c_i} \phi \delta_i' (20)
\]

where \( \delta_i' \) is the equivalent diffusion film thickness. To satisfy electroneutrality all \( \delta_i' \) must be equal when a linear representation such as equation (20) is used for \( \phi' \).

At \( I = I_L \), \( \phi' = 0 \), hence

\[
\phi' = \left( \phi_1 - \beta_i \right) \phi_1 (21)
\]

where

\[
\phi_1 = \frac{\phi}{c_i}
\]

and

\[
\beta_i = \frac{V \phi'}{V \phi}.
\]

By eliminating the potential gradient between the flux equations for the non-discharging ions, applying the Nernst-Einstein relationship \( (D_1 = k T U_i) \), eliminating the interfacial concentrations by equation (21) and solving for \( \beta_i \), we obtain:

\[
\frac{n_{t_1}}{z_1} = \frac{\delta_{i'}}{\delta_i'}.
\]

*) Note: Setting \( t_i = 0 \) in equation (16) gives the relationship \( M_1 = .893 + .2661 Sc^{-1/6} \), which compares with the commonly used Gregory and Riddiford correction [18].
Case 1. Ion discharge (deposition) reaction

\[ \beta_i = \frac{z_i Y_i}{z_i Y_i + \beta_3 (z_1 - z_3)} \]

and since

\[ \sum_{m=1}^{2} z_i \beta_i = 0 \quad \text{and} \quad \sum_{m=1}^{2} z_i Y_i = 0 \]

by electroneutrality, \( \beta_3 \) is given by

\[ z_1 + \beta_3 \sum_{m=1}^{2} \frac{z_i Y_i (z_1 - z_m)}{z_2 Y_2 + \beta_3 (z_2 - z_3)} = 0 \]

and analogously for

Case 2. Oxidation - Reduction \( \text{[Ox}^{+z_1} + (z_1 - z_3) e^- \text{=} Red^{+z_2}] \)

\[ z_1 + z_2 \]

\[ + \beta_2 \sum_{m=1}^{2} \frac{z_i Y_i (z_1 - z_m)}{z_3 Y_3 + \beta_3 (z_3 - z_2)} = 0 \]

\[ \beta_2 = \frac{-(D_1/D_2) z_2 Y_2 (z_1 - z_2) + z_2 Y_2 \beta_1}{z_2 Y_2 + \beta_3 (z_2 - z_3)} \]

and

\[ \beta_1 = \frac{-z_1 Y_1 \beta_1}{z_2 Y_2 + \beta_3 (z_2 - z_3)} \]

The interfacial potential gradient can be written as

\[ \frac{V \Phi_0}{K^b} = -\frac{I_t}{k_b} \frac{[1 + I^*]}{[1 + \alpha]} \]

where

\[ \alpha = \frac{K^a - K^b}{K^b} = -\frac{\sum U_j e x_j \beta_i}{\sum U_j e x_j Y_i} \]

from equation (6) and equation (21) and

\[ I^* = \frac{-n}{nD_1} \left( \sum_{m=1}^{2} \frac{z_i D_i}{z_1 Y_1} \right) \beta_i \]

A rigorous calculation of a proper average potential gradient across the mass transfer boundary layer could be a complex and, perhaps, an impossible task by analytic techniques. For purposes of illustration, an arithmetic average gradient has been selected. Physically an arithmetic average would not provide a proper weighting of the more influential interfacial potential gradient where the fluid velocity approaches zero and migration and diffusion prevail. However, this analysis is only intended to provide additional insight into the effect of a change in potential gradient within the boundary layer. This average gradient is

\[ \frac{V \Phi_{av}}{K^b} = -\frac{I_t}{K^b} \left( 1 + \frac{1 + I^*}{1 + \alpha} \right) \left( \frac{1}{2} \right) \]  

(22)

The results for \( M_t \) remain the same as for a constant potential gradient if an effective transference number is defined. Applying the potential gradient of equation (22), we arrive at the following equation for the effective transference number

\[ t'_e = \frac{t_e}{2} \left( 1 + \frac{1 + I^*}{1 + \alpha} \right) \]  

(23)

which embodies corrections for a diffusion potential and conductivity changes in the boundary layer that appear in real systems.

Numerical Illustrations for an Average Potential Gradient

Calculations were performed for several typical electrolytes. The parameters \( \beta_i, I^*, \alpha, \) and \( t'_e \) were calculated from limiting ionic conductances at 25.0°C [5]. Since only ratios of ionic properties are involved, the use of limiting conductances is not too unrealistic and is suitable for illustrative purposes. The results of these calculations are shown in Table 1.

In Table 1 the effective transference number \( t'_e \) and the transference number in the bulk, \( t_e \), are compared. If the supporting electrolyte is a better conductor than the reacting ion, the diffusion potential is positive, thereby increasing the effective transference number. At the other extreme, as shown in Table 1, the diffusion potential is negative, hence \( t'_e < t_e \).

Conclusions

1. The changing concentrations in the mass transfer boundary layer are important in determining the contribution of ionic migration to the limiting current. For the special case of a constant potential gradient, the limiting current, including migration effects, can be calculated rigorously.

2. The diffusion potential contributes to the electric field which promotes migration. Although an approximate calculation was used to illustrate the effect of the diffusion potential, additional insight about the capacity of various supporting electrolytes for suppressing ionic migration was obtained by evaluating effective transference numbers for some typical ternary and quaternary electrolyte systems.

b) Densities and Viscosities of Aqueous Solutions of \( K_4 Fe(CN)_{6} \), \( K_3 Fe(CN)_{6} \), KOH (or NaOH), and the Diffusion Coefficients of the Ferro- and Ferriyanide Ions

Density, viscosity, and diffusivity data were obtained in equimolar ferro-ferricyanide solutions (0.01-0.20 molar) in the presence of NaOH or KOH (0.0-3.5 molar).

Solution Preparation and Analysis

Solutions were prepared with distilled water and reagent grade chemicals. Ferricyanide ion was titrated with thiosulfate [6] and ferrocyanide was determined by a back titration [7]. Hydroxyl ion was titrated with standard HCl to a bromthymol blue endpoint.

Densities and Viscosities

Experiments

Densities and viscosities were determined by standard techniques (pycnometer and U-tube viscometer [8], respectively). All solutions were thermostated to 25.00 ± 0.05°C before and during measurements.

Results

A second degree polynomial involving \( C_{redox} \) (average of ferri- and ferrocyanide concentrations) and \( C_{KOH} \) or \( C_{NaOH} \) was fitted to the data by a least-squares technique. A total of 26 points for KOH supported solutions and 28 points for NaOH solutions were used in the curve fitting.
Table 1
Effect of supporting ionic species on the effective transference numbers of reacting ions for various concentration levels

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Ion</th>
<th>$z$</th>
<th>$\lambda^o$</th>
<th>$\gamma_0$</th>
<th>$\beta_0$</th>
<th>$\beta_4$</th>
<th>$\beta_4$</th>
<th>$\lambda^*$</th>
<th>$\alpha$</th>
<th>$t_1$</th>
<th>$t_1'$</th>
<th>$I_{L}\bar{I}_{D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4\text{OH}^- + \text{O}_2 + 2\text{H}_2\text{O} + 4e^-$</td>
<td>OH\textsuperscript{-}</td>
<td>−1</td>
<td>−197.6</td>
<td>100</td>
<td>1/2</td>
<td>−1/2</td>
<td>−7035</td>
<td>−0.0158</td>
<td>0.0165</td>
<td>0.0121</td>
<td>1.006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na\textsuperscript{+}</td>
<td>+1</td>
<td>50.1</td>
<td>50</td>
<td>1/2</td>
<td>−1/2</td>
<td>−7035</td>
<td>−0.0310</td>
<td>0.0324</td>
<td>0.0239</td>
<td>1.012</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cl\textsuperscript{-}</td>
<td>−1</td>
<td>67.3</td>
<td>20</td>
<td>1/2</td>
<td>−1/2</td>
<td>−7035</td>
<td>−0.0730</td>
<td>0.0763</td>
<td>0.0580</td>
<td>1.030</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H\textsuperscript{+}</td>
<td>+1</td>
<td>+349.8</td>
<td>100</td>
<td>1/2</td>
<td>−1/2</td>
<td>−7035</td>
<td>−1.332</td>
<td>1.392</td>
<td>1.105</td>
<td>1.057</td>
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</tr>
<tr>
<td></td>
<td>Cl\textsuperscript{-}</td>
<td>−1</td>
<td>−76.3</td>
<td>10</td>
<td>1/2</td>
<td>−1/2</td>
<td>−7035</td>
<td>−0.2268</td>
<td>0.2371</td>
<td>0.0029</td>
<td>1.105</td>
<td></td>
</tr>
<tr>
<td></td>
<td>K\textsuperscript{+}</td>
<td>+1</td>
<td>+73.5</td>
<td>5</td>
<td>1/2</td>
<td>−1/2</td>
<td>−7035</td>
<td>−0.1031</td>
<td>0.1028</td>
<td>0.0738</td>
<td>1.038</td>
<td></td>
</tr>
<tr>
<td>$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$</td>
<td>Cu\textsuperscript{2+}</td>
<td>+2</td>
<td>50.0</td>
<td>100</td>
<td>2/3</td>
<td>−2/3</td>
<td>4.303</td>
<td>0.0004</td>
<td>0.0025</td>
<td>0.0089</td>
<td>1.004</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SO\textsuperscript{2-}</td>
<td>−2</td>
<td>−80.0</td>
<td>20</td>
<td>2/3</td>
<td>−2/3</td>
<td>4.303</td>
<td>0.0011</td>
<td>0.0122</td>
<td>0.0439</td>
<td>1.022</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H\textsuperscript{+}</td>
<td>+1</td>
<td>+349.8</td>
<td>10</td>
<td>2/3</td>
<td>−2/3</td>
<td>4.303</td>
<td>0.1031</td>
<td>0.2373</td>
<td>0.0588</td>
<td>1.028</td>
<td></td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$</td>
<td>Cu\textsuperscript{2+}</td>
<td>+2</td>
<td>50.0</td>
<td>100</td>
<td>2/3</td>
<td>−2/3</td>
<td>4.303</td>
<td>0.0011</td>
<td>0.0122</td>
<td>0.0439</td>
<td>1.022</td>
<td></td>
</tr>
<tr>
<td></td>
<td>K\textsuperscript{+}</td>
<td>+1</td>
<td>+73.5</td>
<td>5</td>
<td>2/3</td>
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<td>4.303</td>
<td>0.1031</td>
<td>0.2373</td>
<td>0.0588</td>
<td>1.028</td>
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</tr>
</tbody>
</table>

Systems containing three ionic species

Systems containing four ionic species

Systems containing five ionic species

*) Solutions are equimolar ferrocyanide and ferricyanide.
The equations and their associated standard errors of estimate are:

a) Potassium hydroxide as a supporting electrolyte.

\[ \mu (cp) = 0.8937 + 0.6178 \text{Creodox} + 0.1064 \text{C}_{\text{KOH}} + 0.00656 \text{C}_{\text{KOH}} \text{Creodox} \]  
(24)

Standard Error of Estimate = 0.012 cp.

\[ \theta [g/cm^3] = 0.9971 + 0.3996 \text{Creodox} + 0.0275 \text{C}_{\text{KOH}} - 0.0013 \text{C}_{\text{KOH}} \text{Creodox} \]  
(25)

Standard Error of Estimate = 0.0030 g/cm³.

b) Sodium hydroxide as a supporting electrolyte.

\[ \mu (cp) = 0.8937 + 0.6969 \text{Creodox} + 0.1539 \text{C}_{\text{NaOH}} + 0.0235 \text{C}_{\text{NaOH}} \text{Creodox} \]  
(26)

Standard Error of Estimate = 0.014 cp.

\[ \theta [g/cm^3] = 0.9971 + 0.3966 \text{Creodox} + 0.0275 \text{C}_{\text{NaOH}} - 0.0013 \text{C}_{\text{NaOH}} \text{Creodox} \]  
(27)

Standard Error of Estimate = 0.0011 g/cm³.

Ranges of validity: Creodox (0.01 - 0.20 M) and C_{KOH}, C_{NaOH} (0.0 - 3.5 M).

The viscosity data as represented by equations (21-2) and (26) agree within 1% with the data by Eisenberg et al. [15], and those reported in Lange's Handbook of Chemistry [16]. The density data as represented by equations (25) and (27) agree within a few tenths of a percent with those reported by Eisenberg et al [15], and by Hitchcock et al. [17].

**Diffusivities**

**Experiment**

The rotating disk electrode has been used for the measurement of ionic diffusion coefficients including those of the ferrocyanide and ferricyanides ions [9-12]. This tool was first analysed by Levich [2] for a binary electrolyte, and then treated by Hogge and Kraichman [13] for a completely flooded electrolyte.

The theory developed in part a) for partially flooded systems where migration effects cannot be neglected was used to determine the diffusivity of the reacting ion from limiting current measurements by a rotating disk electrode. The equation used is:

\[ D_1 = \left( \frac{1}{2} \right) \frac{1.805 \text{I}_{z}^{1/4} M_0^{7/4}}{n F c T} \]  
(28)

obtained by substituting into equation (14) the expression for \( \delta_1 \):

\[ \delta_1 = 1.805 \left( \frac{\nu}{\sigma} \right)^{1/4} \left( \frac{D}{\nu} \right)^{1/4} \]  

Migration effects are included in the parameter \( M_0 \) which contains the effective transference number (see part a) of the reacting ion. \( M_0 \) has a value of 0.893 + 0.2661 Sc^{-1/2} when the transference number of the reacting ion is zero.

The electrode was a 1 cm Pt disk embedded in epoxy resin and attached to an aluminium spindle rotated at precisely controlled speeds between 600 and 3600 rpm. Fig. 3 and 4 are schematic drawings of the apparatus.

**Results**

From the limiting current measurements the diffusivities of ferri- and ferrocyanide ions were determined by equation (28). The data were correlated in the form of the Stokes-Einstein parameter, \( D_1 \mu / T \), as a function of the ionic strength \( \Gamma \).

\[ \Gamma = \left( \frac{1}{2} \right) \sum_{i=1}^{m} \varepsilon_i \]  
(29)

Preliminary calculations performed on the data of Newson and Riddiford [14] indicated that \( D_1 \mu / T \) was independent of \( \mu \) and \( T \) at \( \Gamma = \text{const.} \)
Although temperature was not a variable in the present study, the parameter \( D \mu / T \) should be independent of temperature since the behavior of the ferro- or ferricyanide ion should be similar in this respect to that of the large tri-iodide ion.

A least squares fit of the data (values obtained with KOH or NaOH) agreed within range of experimental error, \( \pm 4\% \) gives the following empirical relationships and standard errors of estimate:

\[
\frac{D \mu}{T} (\text{ferri}) = (0.234 + 0.0014 T) \times 10^{-3} \text{ cm}^2 \text{ poise sec}^{-1} K^{-1} \pm 0.005 , \tag{30}
\]

\[
\frac{D \mu}{T} (\text{ferro}) = (0.187 + 0.0034 T) \times 10^{-3} \text{ cm}^2 \text{ poise sec}^{-1} K^{-1} \pm 0.007 , \tag{31}
\]

As a comparison, the data of Eisenberg et al. [15] at \( C_{\text{NaOH}} = 2 \text{ M}, T = 5.15 \text{ M} \), gives

\[
\frac{D \mu}{T} (\text{ferri}) = 0.250 \times 10^{-3} \text{ cm}^2 \text{ poise sec}^{-1} K^{-1}
\]

and

\[
\frac{D \mu}{T} (\text{ferro}) = 0.215 \times 10^{-3} \text{ cm}^2 \text{ poise sec}^{-1} K^{-1}
\]

whereas equations (30) and (31) give, at this ionic strength,

\[
\frac{D \mu}{T} (\text{ferri}) = 0.240 \times 10^{-3} \text{ cm}^2 \text{ poise sec}^{-1} K^{-1}
\]

and

\[
\frac{D \mu}{T} (\text{ferro}) = 0.202 \times 10^{-3} \text{ cm}^2 \text{ poise sec}^{-1} K^{-1}
\]

Although no conclusion can be reached about the discrepancies between the data presented, the inherent errors in the diffusion capillary technique used by Eisenberg et al. could be responsible for the differences. These empirical relationships are considered to be adequate representations of the data for use in mass transfer studies, and are reliable within the error estimates presented.

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Nomenclature

Lower Case Letters

- \( c \) = concentration - moles/cm\(^3\)
- \( e \) = electronic charge - coulombs
- \( g \) = parameter - dimensionless
- \( j \) = index of series - dimensionless
- \( k \) = Boltzmann constant - erg/deg
- \( m \) = total number of species - dimensionless
- \( n \) = number of electron reacting
- \( t \) = time - sec
- \( t \) = transference number - dimensionless
- \( v \) = fluid velocity - cm/sec
- \( x \) = transformed variable - dimensionless
- \( y \) = co-ordinate axis - cm
- \( z \) = charge on an ion - dimensionless

Upper Case Letters

- \( C \) = concentration - moles/liter
- \( D \) = diffusion coefficient - cm\(^2\)/sec
- \( F \) = Faraday constant - coulombs/equiv
- \( I \) = current density - amp/cm\(^2\)
- \( I^* \) = "diffusion current" - dimensionless

Greek Letters

- \( \alpha \) = fractional conductivity change - dimensionless
- \( \beta \) = relative concentration gradient - dimensionless
- \( \gamma \) = relative concentration - dimensionless
- \( \delta \) = hydrodynamic boundary layer - cm
- \( \delta_t \) = diffusion boundary layer - cm
- \( \epsilon \) = equivalent diffusion thickness - cm
- \( \epsilon \) = dielectric constant - dimensionless
- \( \lambda \) = ionic conductance - \( \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \text{ equiv}^{-1} \)
- \( \mu \) = ionic conductivity - cm\(^2\) ohm\(^{-1}\) sec\(^{-1}\)
- \( \nu \) = kinematic viscosity - cm\(^2\) sec\(^{-1}\)
- \( \xi \) = variable of integration - cm
- \( \zeta \) = variable of integration - cm
- \( \omega \) = density - gm/cm\(^3\)
- \( \phi \) = electric potential - volt
- \( \omega \) = angular frequency - radians/sec
- \( \Gamma \) = ionic strength - moles/liter

Subscripts and Superscripts

- \( b \) = bulk
- \( i \) = index of species
- \( 0 \) = interfacial property
- \( L \) = limiting current

Bibliography
