

10.F.4. Electrical Conductivity and Diffusion in Fluids

Since electric current is simply electric charge in motion, diffusion of charged particles is accompanied by an electric current.

Consider a dilute solution of charged solute (ions) of charge $z_s e$ in water. For simplicity, we assume T & P are constant throughout the solution.

If the solution is subject to a constant electric field $\mathbf{E} = -\nabla \phi$, (10.165) becomes

$$d u - T d s - \tilde{\mu}_s^e d \rho_s - \tilde{\mu}_w d \rho_w = 0$$

where [see (3) of Exercise 2.7, §2.F.4],

$$\tilde{\mu}_s^e = \frac{z_s}{m_s} F \phi + \tilde{\mu}_s = \text{electrochemical potential of solute} \quad (10.190a)$$

$F = \text{Faraday} = \text{amount of charges in 1 mole of protons}$

In the absence of chemical reactions, the entropy production (10.179a) becomes

$$T \sigma = -\tilde{\mathbf{J}}_s \cdot \nabla_r \tilde{\mu}_s^e - \tilde{\mathbf{J}}_w \cdot \nabla_r \tilde{\mu}_w \quad T = \text{const} \quad (10.190)$$

For T & P constant, the Gibbs-Duhem equation (10.180b) gives [see §10.F.2],

$$\rho_w (\nabla_r \tilde{\mu}_w)_{T,P} + \rho_s (\nabla_r \tilde{\mu}_s^e)_{T,P} = 0 \quad (10.190b)$$

Hence, (10.190) becomes

$$\begin{aligned} T \sigma &= -\tilde{\mathbf{J}}_s \cdot \nabla_r \tilde{\mu}_s^e + \frac{\rho_s}{\rho_w} \tilde{\mathbf{J}}_w \cdot \nabla_r \tilde{\mu}_s^e & T \text{ \& } P \text{ constant} \\ &= -\tilde{\mathbf{J}}_s^D \cdot \nabla_r \tilde{\mu}_s^e & (10.191) \end{aligned}$$

where [see (10.183a)]

$$\tilde{\mathbf{J}}_s^D = \tilde{\mathbf{J}}_s - \frac{\rho_s}{\rho_w} \tilde{\mathbf{J}}_w = \rho_s (\mathbf{v}_s - \mathbf{v}_w) \quad (10.191a)$$

is the ion flux relative to water.

For dilute solution,

$$\rho_s \ll \rho_w \quad \rightarrow \quad \tilde{\mathbf{J}}_s^D \approx \tilde{\mathbf{J}}_s \quad (10.191b)$$

The generalized Ohm's law (10.96) or (10.184) becomes

$$\tilde{\mathbf{J}}_s^D = -\tilde{L}_s \nabla_r \tilde{\mu}_s^e \quad T \text{ \& } P \text{ constant}$$

or

$$\mathbf{J}_s^D = \frac{\tilde{\mathbf{J}}_s^D}{m_s} = -L_s \nabla_r \tilde{\mu}_s^e \quad [L_s = \frac{\tilde{L}_s}{m_s}] \quad (10.192)$$

which, in the absence of the electric field, reduces to [see (10.185) of §10.F.2]

$$\mathbf{J}_s^D = -\frac{RT}{m_s c_s} L_s \nabla_r c_s \equiv -D \nabla_r c_s \quad (10.193)$$

where [c.f. (10.185a)]

$$D = \frac{RT}{m_s c_s} L_s = \text{diffusion coefficient}$$

In the absence of concentration gradients, (10.192) reduces to [see (10.190a)]

$$\mathbf{J}_s^D = -L_s \frac{z_s F}{m_s} \nabla_r \phi = L_s \frac{z_s F}{m_s} \mathbf{E} \quad (10.194)$$

$\approx \mathbf{J}_s$ for dilute solution [see (10.191b)].
 = ion flux [moles / (area · time)].

The correspondent electric current density is

$$\mathbf{J}^e = z_s F \mathbf{J}_s^D = L_s \frac{(z_s F)^2}{m_s} \mathbf{E} \quad (10.195)$$

$$\equiv \kappa \mathbf{E}$$

where

$$\kappa = L_s \frac{(z_s F)^2}{m_s} = \frac{c_s (z_s F)^2}{R T} D \quad (10.196)$$

is the **electric conductivity** of the solution. In terms of the **equivalent conductance**

$$\lambda \equiv \frac{\kappa}{c_s z_s} \quad (10.196a)$$

(10.196) becomes

$$\lambda = \frac{z_s F^2}{R T} D \quad (10.196b)$$

Experimental values of λ & D for some infinitely-diluted singly-charged ions ($z_s = \pm 1$) in water at $T = 25^\circ \text{C}$ can be found in Reichl's Table 10.3.

Exercise 10.8

Consider a very dilute solution of salt $C_{v_c} A_{v_a}$, which dissolves as



where v_a & v_c are stoichiometric coefficients.

Compute the diffusion coefficient for the salt in terms of the diffusion coefficients of the ions in the limit of infinitely dilute solution and uniform T & P throughout the solution.

Answer

The solution is just an electrolyte [see §S.2.E], with A & C being the anion & cation, respectively.

In the absence of temperature gradient and chemical reactions, the entropy production (10.180) becomes

$$T \sigma = -\tilde{\mathbf{J}}_w \cdot \nabla_r \tilde{\mu}_w - \tilde{\mathbf{J}}_c \cdot \nabla_r \tilde{\mu}_c - \tilde{\mathbf{J}}_a \cdot \nabla_r \tilde{\mu}_a \quad T, P = \text{const} \quad (1)$$

while the Gibbs-Duhem equation gives [see (10.190b)]

$$\rho_w \nabla_r \tilde{\mu}_w + \rho_c \nabla_r \tilde{\mu}_c + \rho_a \nabla_r \tilde{\mu}_a = 0 \quad T, P = \text{const} \quad (1b)$$

Putting (1b) into (1) gives

$$\begin{aligned} T \sigma &= -\left(\tilde{\mathbf{J}}_c - \frac{\rho_c}{\rho_w} \tilde{\mathbf{J}}_w \right) \cdot \nabla_r \tilde{\mu}_c - \left(\tilde{\mathbf{J}}_a - \frac{\rho_a}{\rho_w} \tilde{\mathbf{J}}_w \right) \cdot \nabla_r \tilde{\mu}_a \\ &= -\tilde{\mathbf{J}}_c^D \cdot \nabla_r \tilde{\mu}_c - \tilde{\mathbf{J}}_a^D \cdot \nabla_r \tilde{\mu}_a \end{aligned} \quad (2)$$

where [see (10.191a)]

$$\tilde{\mathbf{J}}_j^D = \tilde{\mathbf{J}}_j - \frac{\rho_j}{\rho_w} \tilde{\mathbf{J}}_w$$

$= \rho_j(\mathbf{v}_j - \mathbf{v}_w) =$ mass flux of the type j ion relative to water.

The generalized ohm's law (10.96) is

$$\begin{pmatrix} \tilde{\mathbf{J}}_c^D \\ \tilde{\mathbf{J}}_a^D \end{pmatrix} = -\tilde{\mathbf{L}} \cdot \begin{pmatrix} \nabla_r \tilde{\mu}_c \\ \nabla_r \tilde{\mu}_a \end{pmatrix} = -\begin{pmatrix} \tilde{L}_{cc} & \tilde{L}_{ca} \\ \tilde{L}_{ac} & \tilde{L}_{aa} \end{pmatrix} \cdot \begin{pmatrix} \nabla_r \tilde{\mu}_c \\ \nabla_r \tilde{\mu}_a \end{pmatrix}$$

In the limit of infinitely dilute solution, we may neglect the crossed terms so that

$$\begin{pmatrix} \tilde{\mathbf{J}}_c^D \\ \tilde{\mathbf{J}}_a^D \end{pmatrix} \approx -\begin{pmatrix} \tilde{L}_{cc} & 0 \\ 0 & \tilde{L}_{aa} \end{pmatrix} \cdot \begin{pmatrix} \nabla_r \tilde{\mu}_c \\ \nabla_r \tilde{\mu}_a \end{pmatrix} \quad (3)$$

Since $\mathbf{E} = 0$, the total electric current density is zero:

$$\begin{aligned} \mathbf{J}^D &= z_c F \mathbf{J}_c^D + z_a F \mathbf{J}_a^D = \frac{z_c F}{m_c} \tilde{\mathbf{J}}_c^D + \frac{z_a F}{m_a} \tilde{\mathbf{J}}_a^D \\ &= -\frac{z_c F}{m_c} \tilde{L}_{cc} \nabla_r \tilde{\mu}_c - \frac{z_a F}{m_a} \tilde{L}_{aa} \nabla_r \tilde{\mu}_a = 0 \quad [(3) \text{ used. }] \end{aligned} \quad (4)$$

$$\rightarrow \nabla_r \tilde{\mu}_a = -\frac{z_c m_a}{z_a m_c} \frac{\tilde{L}_{cc}}{\tilde{L}_{aa}} \nabla_r \tilde{\mu}_c \quad (5)$$

The equilibrium condition for the reaction (1a) is [see (2.255) of §S2.E]

$$\begin{aligned} \mu_s &\equiv \mu_{ca} = \nu_c \mu_c + \nu_a \mu_a \\ \rightarrow m_s \tilde{\mu}_s &= \nu_c m_c \tilde{\mu}_c + \nu_a m_a \tilde{\mu}_a \\ m_s \nabla_r \tilde{\mu}_s &= \nu_c m_c \nabla_r \tilde{\mu}_c + \nu_a m_a \nabla_r \tilde{\mu}_a \end{aligned} \quad (6)$$

Using (6) to eliminate $\nabla_r \tilde{\mu}_a$ from (5) gives

$$\begin{aligned} m_s \nabla_r \tilde{\mu}_s &= \left(\nu_c m_c - \nu_a m_a \frac{z_c m_a}{z_a m_c} \frac{\tilde{L}_{cc}}{\tilde{L}_{aa}} \right) \nabla_r \tilde{\mu}_c \\ \rightarrow \nabla_r \tilde{\mu}_c &= \frac{z_a m_c \tilde{L}_{aa}}{\nu_c z_a m_c^2 \tilde{L}_{aa} - \nu_a z_c m_a^2 \tilde{L}_{cc}} m_s \nabla_r \tilde{\mu}_s \end{aligned} \quad (7)$$

Setting $a \leftrightarrow c$ gives

$$\nabla_r \tilde{\mu}_a = \frac{z_c m_a \tilde{L}_{cc}}{\nu_a z_c m_a^2 \tilde{L}_{cc} - \nu_c z_a m_c^2 \tilde{L}_{aa}} m_s \nabla_r \tilde{\mu}_s \quad (8)$$

The particle flux of the salt is

$$\begin{aligned} \mathbf{J}_s^D &= \mathbf{J}_c^D + \mathbf{J}_a^D = \frac{1}{m_c} \tilde{\mathbf{J}}_c^D + \frac{1}{m_a} \tilde{\mathbf{J}}_a^D \\ &= -\frac{1}{m_c} \tilde{L}_{cc} \nabla_r \tilde{\mu}_c - \frac{1}{m_a} \tilde{L}_{aa} \nabla_r \tilde{\mu}_a \quad [(3) \text{ used. }] \\ &= -\frac{1}{m_s} \tilde{L}_s \nabla_r \tilde{\mu}_s \end{aligned} \quad (9)$$

Putting (7-8) into (9) gives

$$\mathbf{J}_s^D = -\frac{(z_a - z_c) \tilde{L}_{aa} \tilde{L}_{cc}}{\nu_c z_a m_c^2 \tilde{L}_{aa} - \nu_a z_c m_a^2 \tilde{L}_{cc}} m_s \nabla_r \tilde{\mu}_s$$

$$\rightarrow \frac{\tilde{L}_s}{m_s^2} = \frac{(z_a - z_c) \tilde{L}_{aa} \tilde{L}_{cc}}{v_c z_a m_c^2 \tilde{L}_{aa} - v_a z_c m_a^2 \tilde{L}_{cc}} \quad (9a)$$

Using [see (10.185a)]

$$\tilde{L}_j = \frac{m_j^2 c_j}{RT} D_j \quad j = c, a, s$$

on (9a) gives

$$c_s D_s = \frac{(z_a - z_c) c_a D_a c_c D_c}{v_c z_a c_a D_a - v_a z_c c_c D_c} \quad (9b)$$

For the reaction (1a) [see (2.235) of §2.D.1],

$$d n_s = \frac{d n_c}{v_c} = \frac{d n_a}{v_a}$$

$$\rightarrow c_c = v_c c_s \quad c_a = v_a c_s \quad [(1a) \text{ implies } v_c, v_a > 0] \quad (9c)$$

(9b) thus becomes

$$\begin{aligned} D_s &= \frac{(z_a - z_c) D_a D_c}{z_a D_a - z_c D_c} \\ &= \frac{(|z_a| + z_c) D_a D_c}{|z_a| D_a + z_c D_c} \quad [z_a < 0 \ \& \ z_c > 0] \end{aligned} \quad (10)$$