

## 10.F.2. Fick's Law for Diffusion

Consider a solution with water as the solvent. Let  $\rho_w$  &  $\rho_s$  be the density of water & solute, respectively. The density of the solution is therefore

$$\rho = \rho_w + \rho_s \quad (10.181a)$$

For Brownian motion,

$$\tilde{\chi} = \frac{\rho_s}{\rho_w} \ll 1 \quad (10.181b)$$

For the sake of simplicity, we assume the absence of any chemical reactions, and  $P$  &  $T$  to be uniform throughout the solution. The entropy production (10.180) reduces to

$$\begin{aligned} T \sigma &= - \sum_{j=w,s} \tilde{\mathbf{J}}_j \cdot (\nabla_r \tilde{\mu}_j)_{T,P} \\ &= -\tilde{\mathbf{J}}_w \cdot (\nabla_r \tilde{\mu}_w)_{T,P} - \tilde{\mathbf{J}}_s \cdot (\nabla_r \tilde{\mu}_s)_{T,P} \end{aligned} \quad (10.181)$$

Similarly, the Gibbs-Duhem equation (10.180b) becomes

$$\begin{aligned} \sum_{j=w,s} \rho_j (d \tilde{\mu}_j)_{T,P} &= 0 \\ \rightarrow \rho_w (\nabla_r \tilde{\mu}_w)_{T,P} + \rho_s (\nabla_r \tilde{\mu}_s)_{T,P} &= 0 \end{aligned}$$

Also, since  $\mathbf{v} = 0$ , we have [see (10.171a)]

$$\tilde{\mathbf{J}}_w + \tilde{\mathbf{J}}_s = 0$$

(10.181) thus becomes

$$T \sigma = \left( \frac{\rho_s}{\rho_w} \tilde{\mathbf{J}}_w - \tilde{\mathbf{J}}_s \right) \cdot (\nabla_r \tilde{\mu}_s)_{T,P} \quad (10.182)$$

$$\begin{aligned} &= - \left( \frac{\rho_s}{\rho_w} + 1 \right) \tilde{\mathbf{J}}_s \cdot (\nabla_r \tilde{\mu}_s)_{T,P} \\ &= -\tilde{\mathbf{J}}_s^D \cdot (\nabla_r \tilde{\mu}_s)_{T,P} \end{aligned} \quad (10.183)$$

where

$$\tilde{\mathbf{J}}_s^D = \left( \frac{\rho_s}{\rho_w} + 1 \right) \tilde{\mathbf{J}}_s = \tilde{\mathbf{J}}_s - \frac{\rho_s}{\rho_w} \tilde{\mathbf{J}}_w \quad (10.183a)$$

Writing

$$\tilde{\mathbf{J}}_w = \rho_w \mathbf{v}_w \quad \tilde{\mathbf{J}}_s = \rho_s \mathbf{v}_s$$

(10.183a) becomes

$$\tilde{\mathbf{J}}_s^D = \rho_s (\mathbf{v}_s - \mathbf{v}_w) = \text{mass flux of the solute relative to water.}$$

Comparing (10.183) with (10.81) of §10.D.1, we make the following assignment:

$$\begin{aligned} \mathcal{J} &= \frac{d \alpha}{d t} \rightarrow \tilde{\mathbf{J}}_s^D \\ \chi &\rightarrow (\nabla_r \tilde{\mu}_s)_{T,P} \end{aligned}$$

so that (10.96) becomes [  $\mathbb{L}$  is now a scalar ]

$$\tilde{\mathbf{J}}_s^D = -\tilde{L}_s (\nabla_r \tilde{\mu}_s)_{T,P}$$

$$= -\tilde{L}_s \left( \frac{\partial \tilde{\mu}_s}{\partial x_s} \right)_{T,P} \nabla_r x_s \quad (10.184)$$

where we have made use of the functional dependence [ see (10.179b) ]

$$\tilde{\mu}_s = \tilde{\mu}_s(T, P, x_s) \quad x_s = \frac{n_s}{n_s + n_w} = \frac{n_s}{n} = \frac{c_s}{c}$$

Taking the gradient, we have

$$\nabla_r x_s = \frac{\nabla_r c_s}{c} - \frac{c_s \nabla_r c}{c^2} = \frac{\nabla_r c_s}{c} - \frac{c_s (\nabla_r c_s + \nabla_r c_w)}{c^2} = \frac{c_w \nabla_r c_s - c_s \nabla_r c_w}{c^2} \quad (10.184a)$$

For an ideal gas mixture [see (2.242)]

$$\tilde{\mu}_s = \tilde{\mu}_s^0 + \frac{RT}{m_s} \ln x_s \quad R = \text{ideal gas constant}$$

$$\rightarrow \left( \frac{\partial \tilde{\mu}_s}{\partial x_s} \right)_{T,P} = \frac{RT}{m_s x_s}$$

In a dilute solution,

$$c_s \ll c_w < c \quad \frac{c_w}{c} = \frac{c - c_s}{c} \approx 1$$

so that (10.184a) becomes

$$\nabla_r x_s \approx \frac{c_w \nabla_r c_s}{c^2} \approx \frac{\nabla_r c_s}{c} \quad (10.184b)$$

Thus, for a dilute ideal-gas-like solution, (10.184) simplifies to

$$\tilde{J}_s^D = -\frac{RT}{m_s c_s} \tilde{L}_s \nabla_r c_s \quad (10.184c)$$

Thus, we arrive at the **Fick's law of diffusion** for the **particle flux** of the solute:

$$\begin{aligned} \mathbf{J}_s^D &= \frac{\tilde{J}_s^D}{m_s} \approx -\frac{RT}{m_s^2 c_s} \tilde{L}_s \nabla_r c_s \\ &= -D \nabla_r c_s \end{aligned} \quad (10.185)$$

where

$$D = \frac{RT}{m_s^2 c_s} \tilde{L}_s = \text{diffusion coefficient} \quad (10.185a)$$

Recall now the **Einstein's diffusion coefficient** [see §5.E.1]

$$D = \frac{k_B T}{\gamma} = \frac{RT}{6 \pi \eta a N_A} \quad (10.185b)$$

where

$N_A$  = Avogadro's number,

$k_B = \frac{R}{N_A}$  = Boltzmann constant

$\gamma = 6 \pi \eta a$

$\eta$  = coefficient of viscosity of solvent (water)

$a$  = radius of solute particles

Comparing (10.185a & b) gives

$$\tilde{L}_s = \frac{m_s^2 c_s}{6 \pi \eta a N_A}$$

Experimental values of  $D$  for various solutes in extremely dilute solutions can be found in Reichl's Table 10.1-2.