

Exercise 3.1.

Consider a local concentration of $0,7 \text{ [mol/dm}^3\text{]}$ which drops by 15% over a distance of 1[cm] . Assuming that diffusion coefficient is $7 \cdot 10^{-6} \text{ [cm}^2\text{/s]}$ (typical value for fluids), calculate **atomic and molar** fluxes.

Solution:

atomic flux

$$c_1 = 0,7 \cdot 6,022 \cdot 10^{23} = 4,215 \cdot 10^{23} \left[\frac{\text{atom}}{\text{dm}^3} \right]$$

$$c_2 = 0,85 \cdot 0,7 \cdot 6,022 \cdot 10^{23} = 3,583 \cdot 10^{23} \left[\frac{\text{atom}}{\text{dm}^3} \right]$$

$$\nabla c = \frac{3,583 \cdot 10^{23} - 4,215 \cdot 10^{23}}{0,1} = -6,319 \cdot 10^{23} \left[\frac{\text{atom}}{\text{dm}^4} \right]$$

$$J = -7 \cdot 10^{-8} (-6,319 \cdot 10^{23}) = 4,423 \cdot 10^{16} \left[\frac{\text{atom}}{\text{dm}^2 \text{s}} \right]$$

molar flux

$$\nabla c = \frac{-0,15 \cdot 0,7}{0,1} = -1,05 \left[\frac{\text{mol}}{\text{dm}^4} \right]$$

$$J = -7 \cdot 10^{-8} (-1,05) = 7,35 \cdot 10^{-8} \left[\frac{\text{mol}}{\text{dm}^2 \text{s}} \right]$$

Exercise 3.2. Nernst-Planck equation for diffusion flux has a following form:

$$J_i^{diff} = B_i c_i \vec{F}_i$$

Using Nernst-Einstein relation express diffusion flux in a form analogous to Fick's law (one dimensional case) for:

- a) Ideal solution (activity $f_i=1$)
- b) Non-ideal solution (activity $f_i \neq 1$)

Assume, that the only force is the gradient of chemical potential, which potential could be expressed as:

$$\mu_i = \mu_i^0 + kT \ln f_i n_i$$

- a) ideal solution

$$J_i^{diff} = B_i c_i \vec{F}_i = -B_i c_i \frac{\partial \mu_i}{\partial x} = -\frac{D_i}{kT} c_i \frac{\partial \mu_i}{\partial x} = -\frac{D_i}{kT} c_i kT \frac{\partial \ln n_i}{\partial x} = -\frac{D_i}{kT} c_i kT \frac{1}{n_i} \frac{\partial n_i}{\partial x} = -D \frac{\partial c_i}{\partial x}$$

- b) non-ideal solution

$$J_i^{diff} = B_i c_i \vec{F}_i = -\frac{D_i}{kT} c_i \frac{\partial \mu_i}{\partial x} = -\frac{D_i}{kT} c_i kT \left(\frac{\partial \ln f_i}{\partial x} + \frac{\partial \ln n_i}{\partial x} \right) = -\frac{D_i}{kT} c_i kT \frac{\partial \ln n_i}{\partial x} \left(1 + \frac{\partial \ln f_i}{\partial \ln n_i} \right)$$

$$= -D_i \frac{\partial c_i}{\partial x} \left(1 + \frac{\partial \ln f_i}{\partial \ln n_i} \right) = -D_i \frac{\partial c_i}{\partial x} \left(1 + \frac{\partial \ln f_i}{\partial \ln n_i} \right)$$

Exercise 3.3. Calculate the flux, knowing that potentials are following functions of space (2D: x, y):

$$\mu^{chem} = 2x^3 + \sin yx$$

$$\mu^{mech} = 5xy^{\frac{3}{2}} + \cos 2xy$$

$$\mu^{elec} = 2e^{x^2}$$

Solution:

$$\mu^{diff} = \mu^{chem} + \mu^{mech} + \mu^{elec}$$

$$\nabla \mu^{diff} = \nabla \left(2x^3 + \sin xy + 5xy^{\frac{3}{2}} + \cos 2xy + 2e^{x^2} \right)$$

$$\nabla \mu^{diff} = (6x^2 + y \cos xy + 5y^{\frac{3}{2}} - 2y \cos 2xy + 4xe^{x^2}; x \cos xy + \frac{15}{2}xy^{\frac{1}{2}} - 2x \cos 2xy)$$

$$\vec{J}_i = B_i c_i (6x^2 + y \cos xy + 5y^{\frac{3}{2}} - 2y \cos 2xy + 4xe^{x^2}; x \cos xy + \frac{15}{2}xy^{\frac{1}{2}} - 2x \cos 2xy)$$

Exercise 3.4. Consider a diffusion in a binary A-B system ($n_A + n_B = 1$). Knowing, that the Gibbs-Duhem relation is fulfilled :

$$\sum_i^2 n_i \nabla \mu_i = 0$$

a) write both fluxes as a functions of conjugate forces only ($J_i = J_i(-\nabla \mu_i)$)

b) find the value of diffusion coefficients knowing, that the Fick's 1st law has a form $J_i = -D_i \nabla n_i$ and chemical potential is given by:

$$\mu_i = \mu_i^0 + kT \ln n_i$$

Solution:

a)

$$\begin{pmatrix} J_A \\ J_B \end{pmatrix} = \begin{pmatrix} L_{AA} & L_{AB} \\ L_{AB} & L_{BB} \end{pmatrix} \begin{pmatrix} -\nabla \mu_A \\ -\nabla \mu_B \end{pmatrix}$$

$$n_A \nabla \mu_A = -n_B \nabla \mu_B \Rightarrow \nabla \mu_B = -\frac{n_A}{n_B} \nabla \mu_A$$

$$J_A = \left(L_{AA} - \frac{n_A}{n_B} L_{AB} \right) (-\nabla \mu_A)$$

$$J_A = \left(L_{BB} - \frac{n_B}{n_A} L_{AB} \right) (-\nabla \mu_B)$$

b)

$$\nabla\mu_i = \frac{kT}{n_i} \nabla n_i$$

$$\nabla n_A = -\nabla n_B$$

$$J_A = -L_{AA} \frac{kT}{n_A} \nabla n_A + L_{AB} \frac{kT}{n_B} \nabla n_A = kT \left(\frac{L_{AA}}{n_A} - \frac{L_{AB}}{n_B} \right) (-\nabla n_A)$$

$$J_B = -L_{BB} \frac{kT}{n_B} \nabla n_B + L_{AB} \frac{kT}{n_A} \nabla n_B = kT \left(\frac{L_{BB}}{n_B} - \frac{L_{AB}}{n_A} \right) (-\nabla n_B)$$

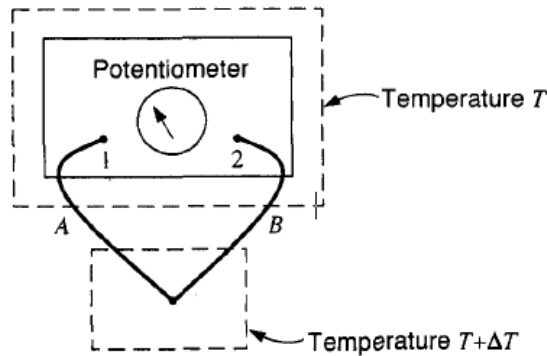
as a result:

$$D_A = kT \left(\frac{L_{AA}}{n_A} - \frac{L_{AB}}{n_B} \right)$$

$$D_B = kT \left(\frac{L_{BB}}{n_B} - \frac{L_{AB}}{n_A} \right)$$

Exercise 3.5. A common device used to measure temperature is the thermocouple. Wires of metals A and B are connected with their common junction at the temperature $T+\Delta T$ and the opposite ends are connected to the terminals of a potentiometer maintained at temperature T . The potentiometer measures voltage across terminals under conditions where no electric current is flowing. This voltage is then a measure of ΔT . Explain this effect (known as Seebeck effect) using Onsager's fluxes. **Hint:**

$$F_Q - \frac{1}{T} \frac{dT}{dx} \text{ and } F_q = -\frac{d\phi}{dx}$$



Solution:

$$\begin{pmatrix} Q \\ j \end{pmatrix} = \begin{pmatrix} L_{QQ} & L_{qQ} \\ L_{qQ} & L_{qq} \end{pmatrix} \begin{pmatrix} F_Q \\ F_q \end{pmatrix}$$

$$\begin{pmatrix} Q \\ j \end{pmatrix} = \begin{pmatrix} L_{QQ} & L_{qQ} \\ L_{qQ} & L_{qq} \end{pmatrix} \begin{pmatrix} -\frac{1}{T} \frac{dT}{dx} \\ -\frac{d\phi}{dx} \end{pmatrix}$$

no electric current means $j=0$:

$$0 = -L_{qQ} \frac{1}{T} \frac{dT}{dx} - L_{qq} \frac{d\phi}{dx}$$

$$\frac{d\phi}{dx} = -\frac{L_{qQ}}{L_{qq}} \frac{1}{T} \frac{dT}{dx}$$

$$\frac{d\phi}{dT} = -\frac{L_{qQ}}{L_{qq}} \frac{1}{T}$$

Since the values of L coefficients are not equal for different materials, the potential generated by the difference of the temperatures will not be the same for A and B - a difference of a potential will be generated.