

Module 4: Multicomponent Transport

Lecture 35: Thermal, Forced and Pressure Diffusion

(I) Thermal Diffusion

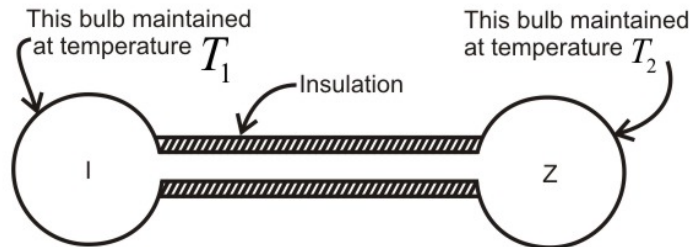


Figure showing steady-state binary thermal diffusion in a bulb apparatus. The mixture of gases A and B tends to separate under the influence of the thermal gradient.

The temperature gradient will cause a mass flux given by (see Eq. 3.7.16)

$$j_{Az}^{(T)} = -\frac{C^2}{\rho} M_A M_B D_{AB} \frac{k_T}{T} \frac{dT}{dz} \quad (3.7.26)$$

This mass flux will tend to develop a concentration gradient which in turn will yield a (ordinary) diffusion flux equal to:

$$j_{Az}^{(x)} = -\frac{C^2}{\rho} M_A M_B D_{AB} \frac{dx_A}{dz} \quad (3.7.27)$$

At steady state the net mass flux will be zero.

$$j_{Az}^{(T)} + j_{Az}^{(x)} = 0 \Rightarrow \frac{dx_A}{dz} = -\frac{k_T}{T} \frac{dT}{dz}$$

$$\Rightarrow x_{A2} - x_{A1} = -\int_{T_1}^{T_2} \frac{k_T}{T} dT \approx -k_T \ln \frac{T_2}{T_1}$$

$$\text{Or, } x_{A2} - x_{A1} = -k_T \ln \frac{T_2}{T_1}, \quad (3.7.28)$$

Where k_T is evaluated at a “mean” temperature T_m

Recommended mean temperature:

$$T_m = \frac{T_1 T_2}{T_2 - T_1} \ln \frac{T_2}{T_1}$$

Equation (3.7.28) is useful for estimating the order of magnitude of thermal diffusion (Soret) effects.

(II) Pressure Diffusion

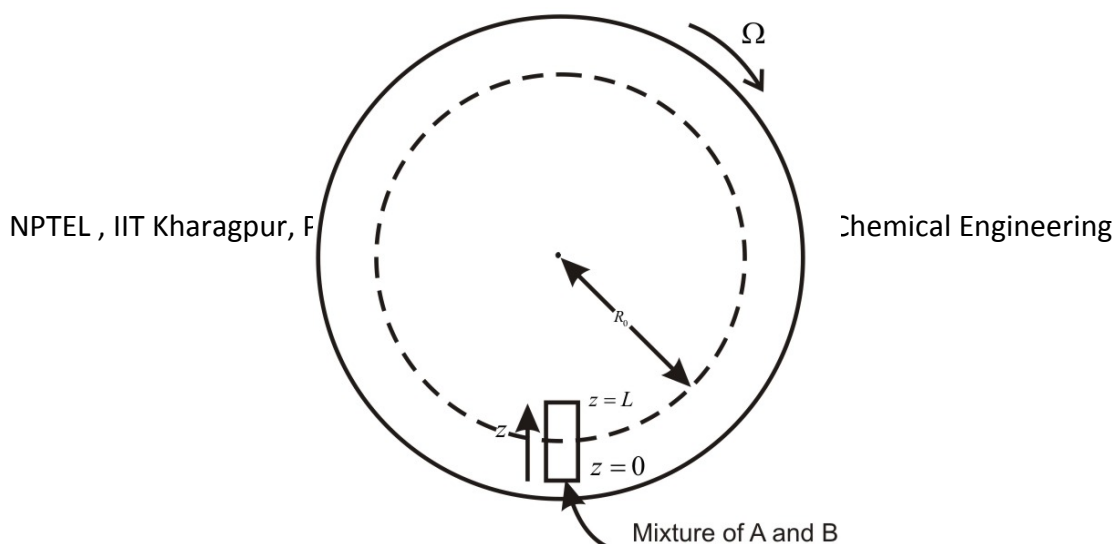


Figure showing steady-state pressure diffusion in a centrifuge. The mixture of A and B tends to separate by virtue of the pressure gradient produced in the centrifuge.

Pressure gradient in centrifuge $\frac{dp}{dz} = -\rho g_{\Omega} = -\rho \Omega^2 R_0,$

Where Ω is the angular velocity.

At steady-state the net mass flux \dot{j}_{Az} is zero.

Equation (3.7.16) yields

$$\frac{d}{dz} \ln x_A = - \left(\frac{g_{\Omega}}{RT} \right) (M_A - \rho \bar{V}_A).$$

Integration of the above equation yields

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$$\left(\frac{X_A}{X_{A0}}\right)^{\bar{V}_B} \left(\frac{X_{B0}}{X_B}\right)^{\bar{V}_A} = \exp \left[\left(\bar{V}_A M_B - \bar{V}_B M_A \right) \frac{g_{\Omega} z}{RT} \right] \quad (3.7.29)$$

Where \bar{V}_A, \bar{V}_B are assumed to be constants independent of composition

(III) Forced Diffusion

Electrolytic Cell

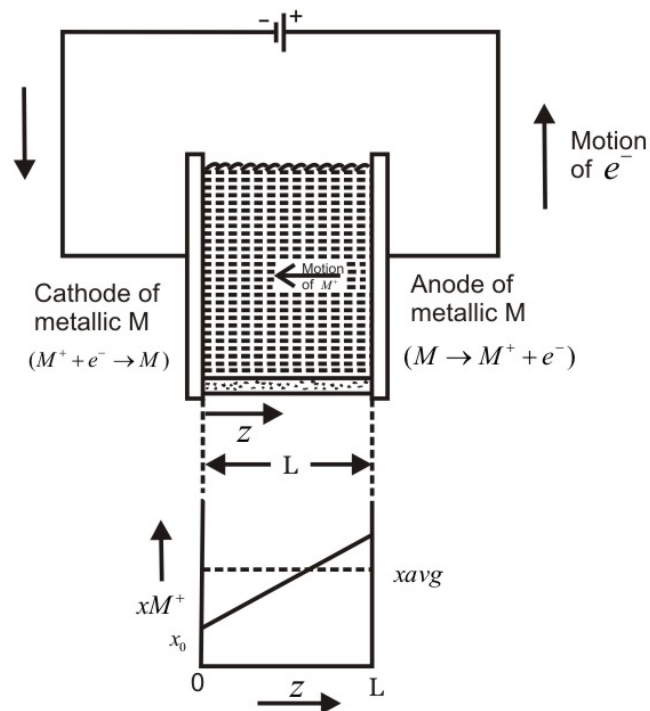


Figure showing Concentration Polarization

Assumptions:

- a) Ions M^+ (i.e., Ag^+) and X^- (i.e., Cl^-) diffuse in water independently of one another (dilute solution)
- b) Activity coefficient of ions is unity

Because of dilute and quiescent solution assumption:

$$N_i \approx J_i^* \quad (\text{i.e., } v_i^* = 0)$$

Cell current is given by

$$\underline{I} = \underline{N}_{M^+} = \underline{J}_{M^+}^{*(x)} \text{ (ordinary diffusion)} + \underline{J}_{M^+}^{*(g)} \text{ (forced diffusion)} \quad (3.7.30)$$

$$0 = \underline{N}_{X^-} = \underline{J}_{X^-}^{*(x)} + \underline{J}_{X^-}^{*(g)} \quad (3.7.31)$$

Assumption (b) implies that $d\bar{G}_i = RT(d \ln x_i)$

$$g_{iz} = \frac{\varepsilon_i}{m_i} \left(-\frac{d\phi}{dz} \right),$$

Also we have:

where ε_i is the charge and ϕ is the potential.

$$\text{So we have: } J_{iz}^* = -cD_{iw} \left(\frac{dx_i}{dz} + \frac{x_i \varepsilon_i}{kT} \frac{d\phi}{dz} \right) \quad (3.7.32)$$

Combining, we get

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$$I_z = -cD_{M^+w} \left(\frac{dx_{M^+}}{dz} + \frac{x_{M^+} |\varepsilon_i|}{kT} \frac{d\phi}{dz} \right),$$

$$0 = -cD_{X^-w} \left(\frac{dx_{X^-}}{dz} - \frac{x_{X^-} |\varepsilon_i|}{kT} \frac{d\phi}{dz} \right).$$

Summing up and taking into account that $x_{M^+} = x_{X^-}$ (electro-neutrality), we get

$$I_z = -2cD_{M^+w} \frac{dx_{M^+}}{dz},$$

Which on integration yields

$$\frac{x_{M^+} - x_0}{z} = -\frac{I_z}{2cD_{M^+w}}, \quad (3.7.33)$$

where x_0 is the mole fraction at the cathode.

This shows a linear concentration gradient and that the maximum current that can be drawn is found by setting $x_0=0$.

$$I_{\max} = -\frac{2cD_{M^+w} x_{M^+}}{L}. \quad (3.7.34)$$

This equation shows that there is a limit to the rate at which metal can be deposited on the cathode.

This is set by mass transfer.