Lecture 32

Last Time: transport

$\downarrow v_{drift}$

isolated system: $F = ma$

many random collisions

open system: $F_{appl} + F_{rand} + F_{friction} = 0$

$$\text{molar force} = -\frac{\partial E}{\partial n \, \partial x} = -\frac{\partial \mu}{\partial x} \qquad \langle \delta x^2 \rangle = 2Dt \qquad -\gamma \cdot v$$

p. 31: $u = \frac{D}{kT} = \frac{1}{\gamma}$

$$\Rightarrow \quad \frac{\partial \mu}{\partial x} = \gamma v \quad \text{if we neglect } F_{rand}$$

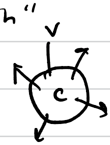
ex: protein on gel $\Rightarrow$ $v_{drift} = \frac{\varepsilon \cdot z}{\gamma}$ $\leftarrow$ $\gamma = 6\pi \eta r$ (viscosity, protein radius)

Flux: $$J\left(\frac{\text{moles}}{m^2 \, s}\right) = v \cdot c = -\frac{1}{\gamma} c \frac{\partial \mu}{\partial x} = -uc \frac{\partial \mu}{\partial x}$$

p. 532 "always true math"

$$-\frac{\partial J}{\partial x} = \frac{\partial c}{\partial t}$$

eg

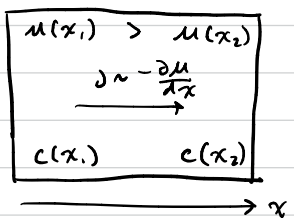


$\nabla \cdot J = \frac{\partial J}{\partial x}$ in 1-D > 0

$\frac{\partial c}{\partial t} < 0$

Today: Physiochemical mechanics postulates:

how to derive "laws" of how molecules move



flux moves particles to lower chemical potential (lower G, higher S_{tot})

Since $\mu = \mu^{(0)} + RT \ln c$ (ideal solution or gas)

$\mu(x_2)$ will go up and $\mu(x_1)$ will go down until $\mu(x_1) = \mu(x_2)$ "equilibrium" postulates: "generalized"

P1: $\mu_{gi} = \mu_i(T, P, n, \ldots, x)$

P2: $J_{xi} = -U_i \cdot c_i \cdot \dfrac{d\mu_{gi}}{dx}$ ✓

$$P1 \Rightarrow \frac{d\mu_{gi}}{dx} = \frac{\partial \mu_i}{\partial x} + \frac{\partial \mu_i}{\partial T}\frac{\partial T}{\partial x} + \frac{\partial \mu_i}{\partial P}\frac{\partial P}{\partial x} + \frac{\partial \mu_i}{\partial n}\cdot\frac{\partial n}{\partial x} + \ldots$$

$$G = \sum \mu_i n_i \Rightarrow \frac{\partial \mu_i}{\partial T} = -S_i \qquad \frac{\partial \mu_i}{\partial P} = V_i$$

simplify the first and last term in $\dfrac{d\mu_{gi}}{dx}$ by assuming an ideal substance:

$$\Rightarrow \mu_i = \mu_i^{(0)} + RT \ln c$$

$$\Rightarrow \frac{\partial \mu_i}{\partial x} = \frac{d\mu_i^{(0)}}{dx}$$

$c_i \sim n_i$

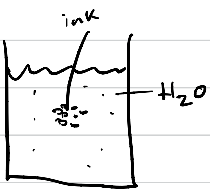
$$\Rightarrow \frac{\partial \mu_i}{\partial n_i}\frac{\partial n_i}{\partial x} = \frac{\partial \mu_i}{\partial c_i}\frac{\partial c_i}{\partial x} = \frac{RT}{c_i}\frac{dc_i}{dx} = RT\frac{d\ln c_i}{dx}$$

$$\Rightarrow \frac{d\mu_{gi}}{dx} = \frac{d\mu_i^{(0)}}{dx} + \frac{\partial \mu_i}{\partial T}\frac{\partial T}{\partial x} + \frac{\partial \mu_i}{\partial P}\frac{\partial P}{\partial x} + RT\frac{d\ln c_i}{dx}$$

Derive transport laws:

1. Get $\mu_i(x)$ for your system (μ_{gi})
2. Calculate $\dfrac{d\mu_i}{dx} \longrightarrow J_i$

ex:



1. $\mu_g(x) = \mu^{(0)} + RT \ln c(x)$
2. $\dfrac{d\mu_g}{dx} = 0 + RT\dfrac{d\ln c(x)}{dx} = \dfrac{RT}{c}\dfrac{dc}{dx}$

$$\Rightarrow J = -Uc\frac{d\mu}{dx} = -\underbrace{URT}_{D}\frac{dc}{dx} = -D\frac{dc}{dx}$$

$$\frac{\partial J}{\partial x} = -\frac{dc}{dt}$$

$$\Rightarrow -\partial J/\partial x = \boxed{D\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}}$$ Fick's law