Last Time: Transport

Isolated system: $F = ma$

Open system: $F = F_{applied} + F_{random} + F_{friction} = 0$

$r_{rm}^{1/3}$ radius

$\Rightarrow -\frac{d\mu}{dx} + F_{random} - \gamma v = 0$

collision, $\gamma = 6\pi\eta \cdot r$

$\Rightarrow -\frac{d\mu}{dx} = \gamma v$ if we neglect the random force

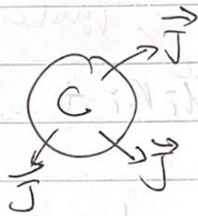
viscosity

ex: $V_{drift} = \frac{\varepsilon \cdot Q}{\gamma}$ for protein on gel.

Flux: $J\left(\frac{mole}{m^2 \cdot s}\right) = v \cdot c = -\frac{1}{\gamma}\frac{d\mu}{dx} \cdot c$
$= -U \cdot c \cdot \frac{d\mu}{dx}$.

Also: p.531 always true

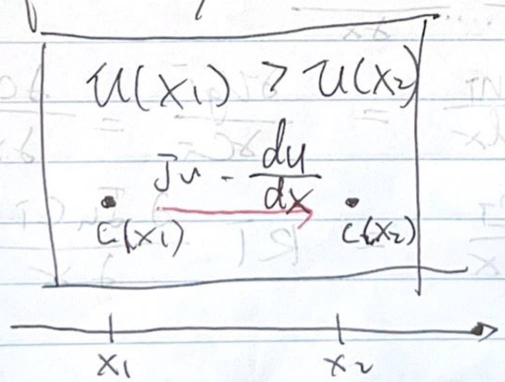
$-\frac{dJ}{dx} = \frac{dc}{dt}$, reason:



$\vec{\nabla} \cdot \vec{J} > 0$

or $\frac{dJ}{dx} > 0$.

Today: Postulate of physichemical mechanics, or "How do molecule move in an open system?"



Flux moves particle to lower chemical potential.

For ideal solutions, $u = u^{(0)} + RT \ln C$

$C(x_2)$ increase

$\Rightarrow$ $C(x_1)$ decrease until $u(x_1) = u(x_2)$

e.g. $-3 \cdot \mathcal{E} \cdot x$

P1: $u_i(T, P, n_i, \dots) \rightarrow u_{gi}(T, P, n_i, \dots, x)$

Assumed: we only talk about volume δV large enough so $N >> \sqrt{N}$.

P2: $J_{xi} = - u_i C_i \frac{d u_{gi}}{dx}$

"Flux" "molar force"

P1 $\Rightarrow$ $\frac{d u_{gi}}{dx} = \frac{\partial u_{gi}}{\partial x} + \underbrace{\frac{\partial u_{gi}}{\partial T}}_{-S_i} \frac{dT}{dx} + \underbrace{\frac{\partial u_{gi}}{\partial P}}_{V_i} \frac{dP}{dx}$

$+ \frac{\partial u_{gi}}{\partial n_i} \frac{d n_i}{dx}$

molar free energy

$G = \sum u_i n_i + \dots$

We can also simplify the 1st & last term in this eq.

Assume an ideal system:

$$u_{gi} = u_{i(x)}^{(0)} + RT \ln C$$

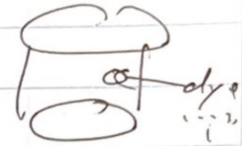
$$\Rightarrow \frac{\partial u_{gi}}{\partial x} = \frac{\partial u_{i(x)}^{(0)}}{\partial x}$$

$$\Rightarrow \frac{\partial u_{gi}}{\partial n_i} \frac{d n_i}{dx} = \frac{\partial u_{gi}}{\partial C_i} = \frac{\partial C_i}{\partial x}.$$

$$= \frac{RT}{C_i} \frac{\partial C_i}{\partial x} = RT \frac{\partial \ln C_i}{\partial x}$$

$$\Rightarrow \frac{\partial \mu_{gi}}{\partial x} = \frac{\partial \mu_i^{(0)}}{\partial x} - S_i \frac{dT}{dx} + V_i \frac{dP}{dx}$$

$$+ RT \frac{\partial \ln C_i}{\partial x}$$



Example of deriving a "law"

Let $\mu_g(x) = \mu_i^{(0)} + RT \ln C(x)$; dye concentration

one component, only concentration depends on x.

$\gamma = \frac{1}{U} = \frac{RT}{D}$

$$\Rightarrow \frac{d\mu_g}{dx} = RT \frac{\partial \ln c}{\partial x} = \frac{RT}{c} \frac{\partial c}{\partial x}$$

$$J = -Uc \frac{d\mu_g}{dx} = -URT \frac{\partial c}{\partial x}$$

$$= -D \frac{\partial c}{\partial x}$$

$$\Rightarrow -\frac{dJ}{dx} = D \frac{\partial^2 c}{\partial x^2}$$

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

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$ Fick's law.