Last time = physicochemical mechanics (PC)

Thermo (derived from P1 & P2 of stat mech)

P1 : E is conserved (isolated sys.)
P2 : $\Delta S \geq 0$ (isolated sys.)
P3 : $S \to 0$ as $E \to$ minimum.

$$\left.\begin{matrix} \\ \\ \end{matrix}\right\} \to \begin{aligned} &G(T,P\dots) \\ &= E - TS + PV \\ &= \sum_i \mu_i (T, P \dots) n_i + \cdots \\ &\quad \uparrow \frac{\partial G}{\partial n_i} \end{aligned}$$

PC : 2 more postulates (also derived from stat mech)

P1 : $\mu_i(T, P, \cdots) \to \mu_{gi}(T, P, \cdots, x)$ can be made position dependent.

P2 : $J = -\mu c \frac{\partial \mu_{gi}}{\partial x}$ give flux of molecules out of equilibrium

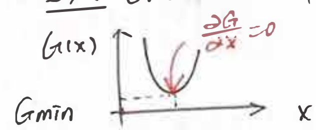
Continuity relation : $\frac{\partial c}{\partial t} + \frac{\partial J}{\partial x} = 0$

①

Today: equilibrium, steady state & transport:

The "progress variable" = "x" could be a position, number of moles in a reaction, density of a substance or anything that allows us to chart the progress of $G(x)$ to equilibrium.

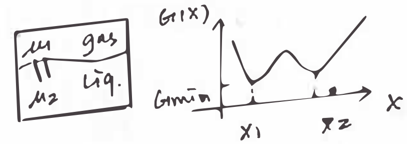
ex: chemical equil



Two equilibrium conditions

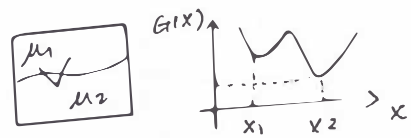
$$\left.\begin{aligned} &1)\ \frac{\partial G}{\partial x} \equiv \Delta G = \sum_i \mu_i \nu_i = 0 \\ &2)\ \frac{\partial^2 G}{\partial x^2} > 0 \quad (\hat{=}\ \delta^2 G > 0) \end{aligned}\right\} \begin{aligned} &\frac{\partial G}{\partial x} = 0 \\ &J = 0 \end{aligned}$$

ex: phases out of equilibrium



x = density

[exactly at 100°C, 1 atm ...]



$T < 100°C$

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ex = steady state

cell

} $\mu_{Mg^{2+}}$ larger

} $\mu_{Mg^{2+}}$ smaller.

RNA

"i" → Mg^{2+}

Using PC P2: $J = 0 \sim \frac{\partial \mu_i}{\partial x} = \frac{\partial \mu_i^{(0)}}{\partial x} + RT \frac{\partial \ln(c_i)}{\partial x}$

(because $\mu_i \approx \mu_i^{(0)} + RT\ln(c)$)

$d\mu_i = d\mu_i^{(0)} + RT\, d\ln c_i = 0$.

$\int \rightarrow \quad \mu_i^{(0)} + RT \ln c_i + \text{constant} = 0$

solving for concentration c_i,

$$c_i(x) = c_i^{(0)} \underbrace{e^{-\frac{\mu_i^{(0)}(x)}{RT}}}_{\text{Boltzmann factor}}$$

②

ex = transport equation

simplest case:

- only one component in solution
- $\mu^{(0)}$ = const everywhere.
- T, p = const
- $\varepsilon = 0$, etc... - D = constant

1) Get Mg_i

$\mu = \mu^{(0)} + RT \ln c(x)$

$$\Rightarrow \frac{\partial \mu}{\partial x} = \underbrace{0}_{\mu^{(0)} = \text{const}} + RT \frac{\partial \ln c(x)}{\partial x}$$

$J = -RT \cancel{\partial x}\, uc \frac{\partial \ln c}{\partial x}$; using the chain rule $\frac{\partial \ln y(x)}{\partial x} = \frac{\partial \ln y}{\partial y} \cdot \frac{\partial y}{\partial x} = \frac{1}{y} \cdot \frac{\partial y}{\partial x}$

$= -RT uc \frac{1}{c} \frac{\partial c}{\partial x} \quad (u = \frac{1}{\gamma},\ D = \frac{RT}{\gamma})$

$= -D \frac{\partial c}{\partial x}$ (Fick's ~~law~~ 1st law)

$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x}$ using Fick's 1st law

$\Rightarrow \frac{\partial J}{\partial x} = -D \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}$.

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

④