Lecture 35 review:

e.g. $\mu_{g_i} = \mu_i^{(0)} + RT\ln C_i + v_i P_i + z_i V_i + \ldots$

$\rightarrow J_i = -U_c \frac{d\mu_g}{dx}$; plus $\left\{ \frac{\partial c}{\partial t} = \frac{-\partial J}{\partial x} \rightarrow = \frac{\partial}{\partial x}\left(U_c \frac{\partial \mu_g}{\partial x}\right) \right.$

$D = URT = \frac{RT}{\gamma}$

Our last 3 lectures & last 3 topics to derive:

Using integrated flux

1. Le Chatelier's principle
2. Microscopic reversability
3. Transition state theory, rate $= e^{\frac{-E}{KT}}$

Lecture 36: Integrated Flux & Le Chatlier

Assume: $J =$ constant $\neq 0$ (steady state)

$T =$ constant

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

(explicitly show only concentration dependance)

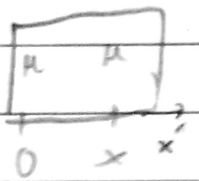
Take eq. for J, and replace concentration C by μ: $C = e^{(\mu_g(x) - \mu^{(0)}(x))/RT}$

$\rightarrow J = -U e^{(\mu_g(x) - \mu^{(0)}(x))/RT} \frac{d\mu_g}{dx}$

$J = -RTU e^{(\mu_g(x) - \mu^{(0)}(x))/RT} \frac{d\left(\frac{\mu_g}{RT}\right)}{dx}$

$\rightarrow J \frac{e^{\mu^{(0)}/RT}}{RT\mu} dx = e^{\mu_g(x)/RT} d\left(\frac{\mu_g}{RT}\right)$

$\rightarrow J \int_0^x \frac{e^{\mu^{(0)}/RT}}{RT\mu} dx' = \left(e^{\mu_g(x)/RT} - e^{\mu_g(0)/RT}\right)$



$$J = \frac{-\left(e^{\mu_g(x)/RT} - e^{\mu_g(0)/RT}\right)}{\int_0^x dx' \frac{e^{\mu(0)/RT}}{RT\mu}}$$

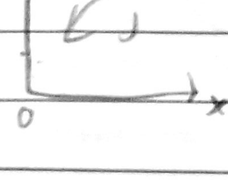
Always positive, since $U > 0, R > 0, T > 0$

Thus if

$\mu_g(x) > \mu_g(0)$, $J < 0$

$\mu_g(x) = \mu_g(0)$, $J = 0$

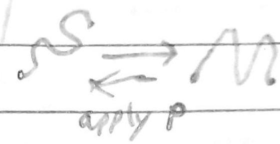
$\mu_g(x) < \mu_g(0)$, $J > 0$



Le Châtelier:

When a system experiences a difference in chemical potential (i.e. goes out of equilibrium), the flux will be in the direction that opposes that change in chemical potential (i.e in the direction that restores equilibrium)

Thought Expt., pg 11.



If I ↑ pressure, protein will unfold.

Conjugate variable of P is V

So $v_U < v_F$

(Radius of U might be larger, but water can fill gaps in U that it can't in F, leading to a lower V)

Microscopic Reversability

constant

In the equation for flux, assume $RTU = D$, $\mu_g = \mu^0 + RT\ln C$

$\rightarrow e^{\mu_g/RT} = e^{\frac{\mu^{(0)} + RT\ln C}{RT}} = C e^{\mu^0/RT}$

$$J = \frac{-D}{x} \frac{C(x) e^{\mu^{(0)}(x)/RT} - C(0) e^{\mu^0(0)/RT}}{\frac{1}{x}\int_0^x dx' e^{\mu^0(x')/RT}}$$

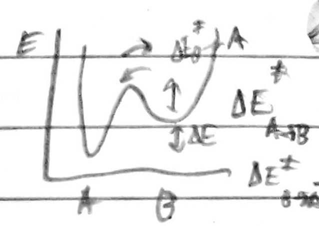
$P_i = \frac{e^{-E_i/RT}}{\sum e^{-E/RT}}$

$$J = \frac{-D}{x}\left\{ C(x) \frac{e^{\frac{\mu^0(x)}{RT}}}{\frac{1}{x}\int_0^x dx' e^{\mu^0/RT}} - C(0) \frac{e^{\mu^0(0)/RT}}{\frac{1}{x}\int_0^x dx' e^{\mu^0/RT}} \right\}$$

$$J = \frac{-D}{x}\left\{ C(x) P(0|x) - C(0) P(x|0) \right\}$$

backward rxn. forward rxn.

Microscopic reversability



$\Delta E^{\ddagger}_{A \to B} = \Delta E^{\ddagger}_{B \to A} + \Delta E$