Lecture 35

Last time: ↙here means voltage

- Nernst equ $\underset{(V_e)}{\mathcal{E}} = \underset{(V_e^\circ)}{\mathcal{E}^\circ} - \frac{RT}{q_i \mathcal{F}} \ln\left(\frac{c_i}{c_{io}}\right)$ usually set to 1M (typically standard tabulated data)

- Osmosis: $\Delta P = -RT\Delta C$ ← solvent

- Others: Fick's law, Ohm's Law, Faraday's Law $\left(v_{drift} = \frac{z_i \cdot \mathcal{E}}{\gamma}\right)$ gravity, etc.

① $-\frac{d\mu_{gi}}{dx}$ = Sum over driving force for your system

② $J = -uc\frac{d\mu_{gi}}{dx}$; at equilibrium $J=0$

Today; Integrated constant flux (steady state).

① Le Châtlier

② Flux as Bayesian probability

③ Transition state theory; $k = a \cdot e^{-E^\ddagger/RT}$

First, Integrated flux;

$J = -uc\frac{d\mu_g}{dx}$ ↖ integrate; we'll make some simplifying assumptions

Let $\mu_g(x) = \mu^{(0)} + RT\ln c \Rightarrow c = e^{\frac{\mu_g - \mu^{(0)}}{RT}}$

$\therefore J = -u \cdot e^{\frac{\mu_g - \mu^{(0)}}{RT}} \frac{d\mu_g}{dx}$; T = const., rearranging

$\frac{J \cdot e^{\mu^{(0)}/RT}}{u \cdot RT} = -e^{\mu_g/RT} \frac{d}{dx}\left(\frac{\mu_g}{RT}\right)$; J = constant

$$\Rightarrow J = \left[- \frac{\int_0^x dx' e^{\mu_g/RT} \frac{d}{dx'}\left(\frac{\mu_g}{RT}\right)}{\int_0^x dx' \frac{e^{\mu^{(0)}/RT}}{R \cdot T \cdot u}} \right] \Rightarrow J = - \frac{\left(e^{\mu_g^{(x)}/RT} - e^{\mu_g^{(0)}/RT}\right)}{\int_0^x dx' \frac{e^{\mu^{(0)}/RT}}{u(x) \cdot T \cdot R}}$$

Greater than 0

Now to derive:

① Le Châtlier

As a consequence: If $\mu_g^{(x)} < \mu_g^{(x=0)} \Rightarrow J > 0$

If $\mu_g^{(x)} > \mu_g^{(x=0)} \Rightarrow J < 0$

If $\mu_g^{(x)} = \mu_g^{(x=0)} \Rightarrow J = 0$

"When a system experiences a difference in chemical potential, flux will be in the direction that restores equal chemical potential"

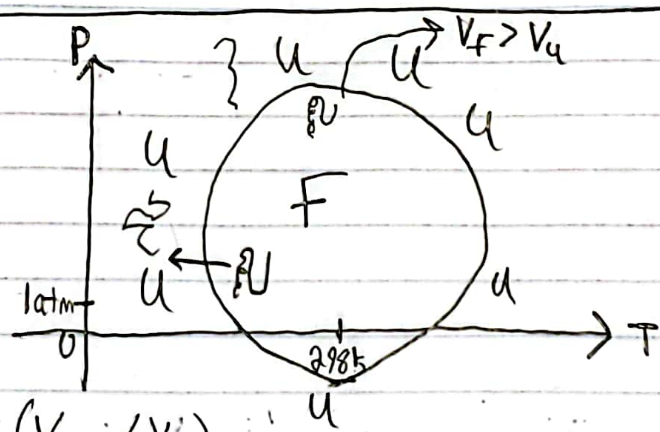
Thought experiment:

$$U \rightleftharpoons F$$

$W_u \gg W_F$

or

$S_u \gg S_f$



$F \to u$ at high P $(V_u < V_f)$

$F \to u$ at high T $(W_u > W_f)$

$F \to u$ at low T as well! cold denature (H_2O entropy)