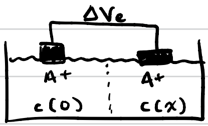
Lecture 35

Last time: Steady State $J = 0 \Rightarrow \frac{d\mu_g}{dx} = 0$



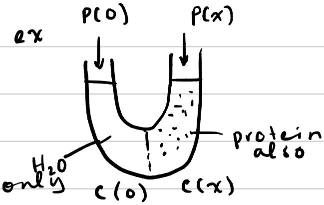
$$\mu_g = \mu^{(0)} + RT \ln c(x) + zV_e$$

$$\Rightarrow V_e(x) - V_e(0) = \Delta V_e = \frac{-RT}{z} \ln \frac{c(x)}{c(0)}$$

The nernst equation

$c(0)$ often chosen as 1 M

ex



$$\mu_g = \mu^{(0)} + RT \ln c(x) + \underbrace{\nu}_{\text{molar volume}} P$$

$$\Rightarrow P(x) - P(0) = \Delta P = \frac{-RT}{\nu} \ln \frac{c(x)}{c(0)}$$

or, if we use $\ln(1+x) \approx x$

$$\Delta P = -RT \Delta c$$

Recipe: simply include the terms, such as $S \cdot T$, $\nu \cdot P$, $RT \ln c$, $L \cdot f$, etc relevant for the particular problem in μ_g

Today: integrated flux in steady state and the Le Châtelier principle.

a) The integrated flux:

Let's do the case for a simple system

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

again, the boltzmann factor

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

assume that T is constant

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

$\Rightarrow$ J is constant (independent of x)

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

$$\Rightarrow \quad J = - \frac{e^{\mu_g(x)/RT} - e^{\mu_g(0)/RT}}{\underbrace{\int_0^x dx' \, \frac{e^{\mu(0)/RT}}{uRT}}_{\text{always } > 0}}$$

As a consequence,

if $\mu_g(x) < \mu_g(0) \iff J > 0$

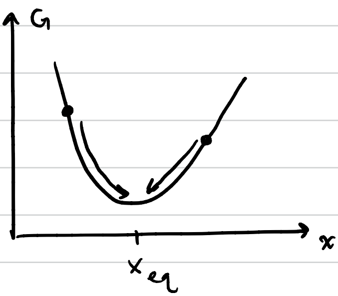
if $\mu_g(x) > \mu_g(0) \iff J < 0$

if $\mu_g(x) = \mu_g(0) \iff J = 0$

Le Chatelier:

"When a system experiences a difference in chemical potential, then the flux will be in the direction that equalizes the chemical potential."

ex:



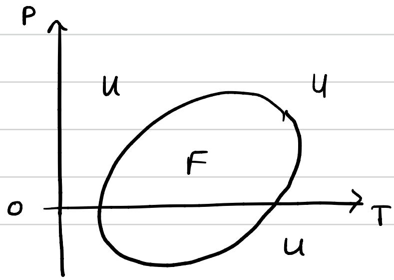
Thought Experiment

$U \rightleftharpoons F$

$W_U >> W_F$

$\downarrow \ln$

$S_U > S_F$



- $F \rightarrow U$ at high temp bc U has higher entropy than F
- $F \rightarrow U$ at high pressure bc U has smaller volume than F