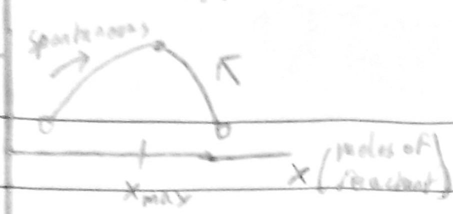
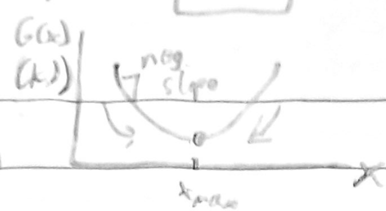
Lecture 27 review: What is ΔG?

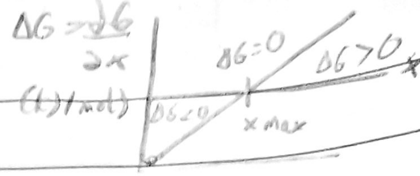
$dS_{tot} > 0 \xrightarrow[T,P]{\text{constant}} -TdS_{tot} = dG < 0$ system

T, P, const.

$dS_{tot} = dS_{sys} + dS_{surr}$ $\swarrow \frac{dH_{sys}}{T}$







Lecture 28: The mass action law: $\Delta G(x) = ?$

- Consider $\nu_A A + \nu_B B + \ldots \rightleftarrows \nu_C C + \nu_D D + \ldots$
- Equivalently, $\sum \nu_i x_i = 0$ $\begin{cases} \nu_i < 0 & \text{for reactants} \\ \nu_i > 0 & \text{for products} \end{cases}$
- Assumptions from stat mech / thermo:

1. Molecules move randomly in container $\rightarrow$

   $S_i = S_i^{(0)} - R \ln c_i$ per mole of substance

2. Enthalpy is constant at given $T \rightarrow$

   $h_i = h_i^{(0)}$

   reasoning: Average distance r is large in dilute solutions.

- Now: $\left.\begin{aligned} E &= TS - PV + \sum_i \mu_i n_i \\ G &= H - TS = E + PV - TS \end{aligned}\right\} \rightarrow G = \sum \mu_i n_i$
- To define x (reaction progress), let $n_i = n_i^{(0)} + \nu_i x$
- $n_i^{(0)}$ is the # of moles at the start of the reaction, and as $x \uparrow$, $n_i \downarrow$ for reactants and $n_i \uparrow$ for products.
- $G(x) = \sum_i \mu_i (n_i^{(0)} + \nu_i x) \rightarrow$
- $\frac{\partial G}{\partial x} = \Delta G = \sum_i \mu_i \nu_i$
- At constant T, since $G = H - TS \rightarrow$

  $\frac{\partial G}{\partial n_i} = \frac{\partial H}{\partial n_i} - T\left(\frac{\partial S}{\partial n_i}\right) = h_i - Ts_i$ ← molar entropy, ← molar enthalpy

- But also, since $G = \sum_i \mu_i n_i \rightarrow$

  $\frac{\partial G}{\partial n_i} = \mu_i(T,P) \rightarrow \mu_i = h_i - Ts_i \rightarrow$

  $\Delta G = \sum_i (h_i - Ts_i) \nu_i$

  $= \sum_i (h_i^{(0)} - Ts_i^{(0)} + RT \ln c_i) \nu_i$ ↘ $a \ln x = \ln x^a$

  $= \sum_i (h_i^{(0)} - Ts_i^{(0)}) \nu_i + RT \ln Q$ ↖ $Q = \prod_i c_i^{\nu_i}$ ↖ product analog of Σ

  $\Delta G = \Delta G^{0} + RT \ln Q$

  ↑ usually tabulated at 1 atm, 298 K

- Thus $\Delta G = 0$ if

  $\Delta G^{(0)} = RT \ln Q$ or $Q = e^{-\frac{\Delta G^{(0)}}{RT}} = K_{eq}$

  in which case Q is the equilibrium constant.

- Next time:
  - Can we calculate K_{eq} from postulate 1 & 2?
  - What happens when T or P or $n_i^{(0)}$ changes? $\rightarrow$ Le Châtelier