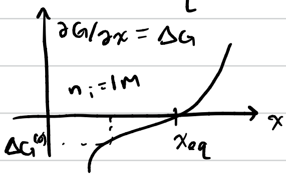
Lecture 29

Last Time: $\Delta S_{tot} \geq 0 \Rightarrow \Delta G \leq 0$ (const T, P)



Rxn:

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$$

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

$$\Delta G^{(0)} = \sum \mu_i^{(0)} \nu_i$$

$$= \Delta H^{(0)} - T^{(0)} S^{(0)}$$

(298 K)

$$Q = \prod c_i^{\nu_i} = \frac{[C]^{\nu_C}[D]^{\nu_D}}{[A]^{\nu_A}[B]^{\nu_B}}$$

At equilibrium, $\Delta G = 0 \Rightarrow Q = K_{eq}$

$$= e^{-\Delta G^{(0)}/RT}$$

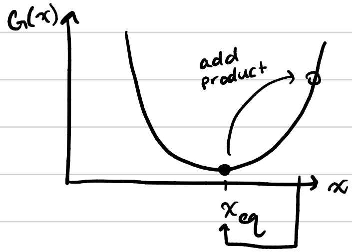
$$= e^{-\Delta H^{\circ}/RT + \Delta S^{\circ}/R}$$

when all $c_i = 1\,M \Rightarrow Q = 1$

$$\Rightarrow \Delta G = \Delta G^{(0)}$$

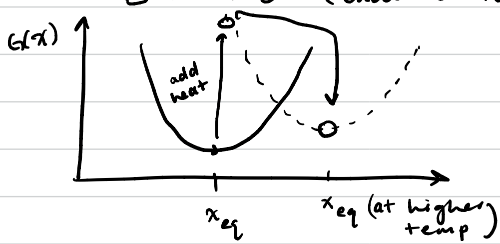
Today: Le Chatelier, and how to calculate $\Delta G^{(0)}$ or K_{eq}

ex of L.C.



- if you add product then the rxn runs backwards

ex: add heat, assume $\Delta H^{(0)} > 0$ (endothermic)



- the rxn makes more product to remove the heat.

K_{eq} , $\Delta G^{(0)}$; 3 steps from postulates 1 & 2:

1) P1: $H\Psi_j = E_j \Psi_j \Rightarrow$ use to calculate E_j and W_j

ex: H-atom

$j=2$ — — — — $E_2 = -R_y/2^2$; $W_2 = 4$

$j=1$ — $E_1 = -\frac{R_y}{1^2}$; $W_1 = 1$

2) P2: Calculate z_i for chemical "i" =

$z_i = \sum W_i \, e^{-E_j/RT}$ for all chemicals in the rxn

$$Z_i = \frac{z_i^{N_i}}{N_i!} \Rightarrow Z = \prod Z_i$$

3) Calculate $\mu_j^{(0)} = -RT \left.\frac{\partial \ln Z}{\partial n_i}\right|_{\substack{STP \\ 298K \\ 1\,atm}}$

$$\Delta G = \sum \mu_i \nu_i$$

$$\Delta G^{(0)} = \sum \mu_i \nu_i$$

$$K_{eq} = e^{-\Delta G^{(0)}/RT}$$

Where did the formula in (3) come from?

$$\mu_i^{(0)} = -RT \left.\frac{\partial \ln Z}{\partial n_i}\right|_{STP}$$

$$Z = \sum W_j \, e^{-E_i/RT} = e^{-F/RT}$$

$$\Rightarrow F = -RT \ln Z$$

$$F(T) = E - TS = -PV + \sum_i \mu_i n_i$$

$E(S)$

$$\frac{\partial F}{\partial n_i} = \mu_i \Rightarrow \left.\frac{\partial F}{\partial n_i}\right|_{STP} = \mu_i^{(0)} \Rightarrow -RT \left.\frac{\partial \ln Z}{\partial n_i}\right|_{STP} = \mu_i^{(0)}$$