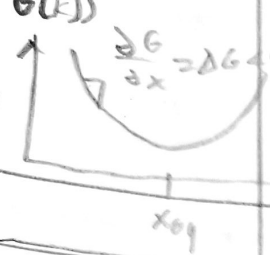


Lecture 28

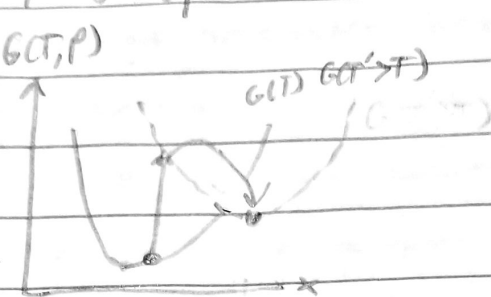
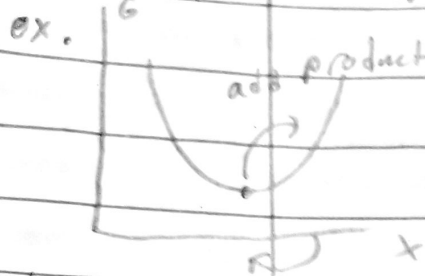


review: $\Delta G = \Delta G^0 + RT \ln Q$
 $aA + bB \rightleftharpoons cC + dD$
 $Q = \prod_i c_i^{v_i} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

Mass Action Law
 Derivation: $G = \sum_i \mu_i n_i = \sum_i (h_i - TS_i) (n_i^{(0)} + v_i x)$
 $S_i = S_i^{(0)} - RT \ln c_i$

Equilibrium: $\Delta G = 0$
 $\rightarrow Q = K_{eq} = e^{-\Delta G^0 / RT}$

Lecture 29: Le Chatelier & computing K_{eq}



now rx. runs backward to restore equilibrium

ex. makes more product to absorb heat

K_{eq} : steps from postulates 1+2:

1. Use $H\psi_j = E_j \psi_j$ to calculate E_j and w_j
2. Calculate $z_j = \sum w_j e^{-\beta E_j}$ for each molecule in the reactor; $Z_j = \frac{z_j}{N_j!}$, $Z = \prod_j Z_j$

3. Calculate $\mu_j^{(0)} = -RT \frac{\partial \ln Z}{\partial n_j}$

$$\Delta G^{(0)} = \sum_j \mu_j^{(0)} \nu_j$$

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

Origin:

$$Z = e^{-\beta F} \rightarrow F = -RT \ln Z = E - TS$$

$$= -PV + \sum_j \mu_j n_j$$

$$\rightarrow \left. \frac{\partial F}{\partial n_j} \right|_{\text{standard conditions}} = \mu_j^{(0)}$$

$$\rightarrow -RT \ln \left. \frac{\partial Z}{\partial n_j} \right|_{\text{standard conditions}} = \mu_j^{(0)}$$