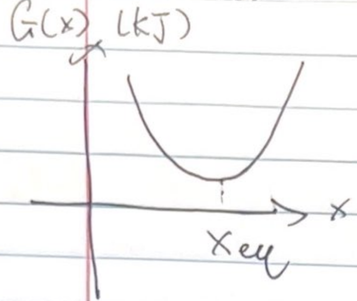
Last Time: $\Delta G = \frac{\partial G}{\partial x} = \Delta G^\circ + RT \ln Q$

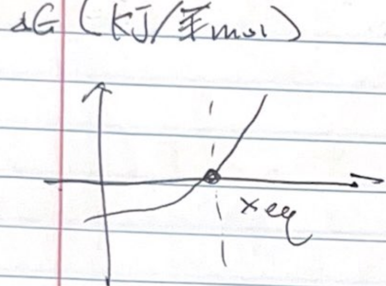


ex: $aA + bB \rightleftharpoons cC + dD$

$Q = \prod c_i^{\nu_i} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

At equilibrium $\Delta G = 0$

$\Rightarrow Q = K_{eq} = e^{-\Delta G^\circ / RT}$



When all $c_i = 1$

$Q = 1 \Rightarrow \ln Q = 0$

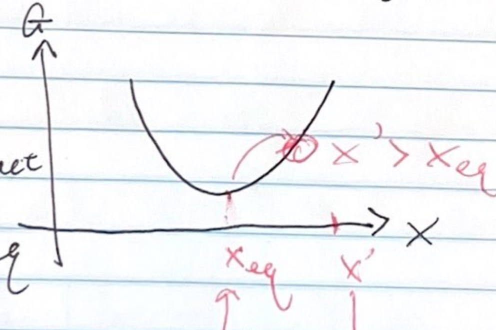
$\Rightarrow \Delta G = \Delta G^\circ$ (standard condition).

Today: Le Châtelier; computing Keq.

LC: ex: I.

add product

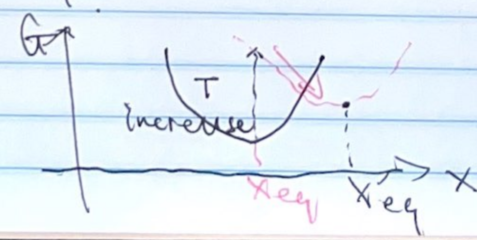
$x \to x' > x_{eq}$



If concentration is increased, the rx. runs backward to decrease conc.

ex:2 $\Delta H^\circ > 0$ ("endothermic")

Increase T.



$K_{eq} = e^{-\frac{\Delta G^\circ}{RT}}$

$= e^{-\frac{\Delta H^\circ - T\Delta S^\circ}{RT}}$

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

$\Rightarrow$ if $\Delta H^\circ > 0$ & T increases
The exponent becomes a smaller negative number.

$\Rightarrow$ K_{eq} will increase
$\Rightarrow$ X_{eq} increases
$\Rightarrow$ rx makes more product, which absorbs that was added to raise T.

K_{eq} = ? ; 3 steps from postulate 1 & 2 of stat. mech and postulate 1...4 of QM.

1) Use $H\Psi_j = E_j \Psi_j \Rightarrow$ Calculate E_j, W_j.
For each reactant & product atom or molecule.

2) Calculate $Z_i = \sum W_j e^{-\beta E_j}$ for each molecule "i"
Partition functions are multiplicative, so for N_i molecules "i"

$$\Rightarrow Z_T = \frac{Z_i^{N_i}}{N_i!} \qquad Z = \prod_i Z_i$$

Avogadro constant

$(n_i A)$

$$\frac{Z_i}{n_i A}$$

$$\Delta G^\circ = \sum_i u_i^\circ \nu_i$$

3) Calculate $u_i^\circ = -RT \left.\frac{\partial \ln Z}{\partial n_i}\right|_{STP}$ $\begin{cases} T = 298K \\ P = 1 atm \end{cases}$

$$\hookrightarrow \Delta G^\circ = -RT \sum_i \left.\frac{\partial \ln Z}{\partial n_i}\right|_{STP} \cdot \nu_i$$

$$\Rightarrow K_{eq} = e^{-\Delta G^\circ / RT}$$

where did the eq in (3) come from?

$Z = e^{-\frac{F}{RT}}$ $(F = E - TS)$, $E = TS - PV + \sum_i u_i n_i$

$\Rightarrow F = -RT \ln Z = -PV + \sum_i u_i n_i$

$\frac{\partial F}{\partial n_i} = u_i \Rightarrow \frac{\partial F}{\partial n_i}\Big|_{STP} = u_i^{0}$

$\Rightarrow -RT \frac{\partial \ln Z}{\partial n_i} = u_i$