Lecture 25: ΔG_{toeq}, ICE Tables, Le Chatlier Principle

Correction Lecture 23: Connecting Gibbs to Equilibrium

$$\Delta G_{\text{rxn}} = \Delta G^\circ + RT \ln K$$

At equilibrium, $\Delta G_{\text{rxn}} = 0$:

$$0 = \Delta G^\circ + RT \ln K$$

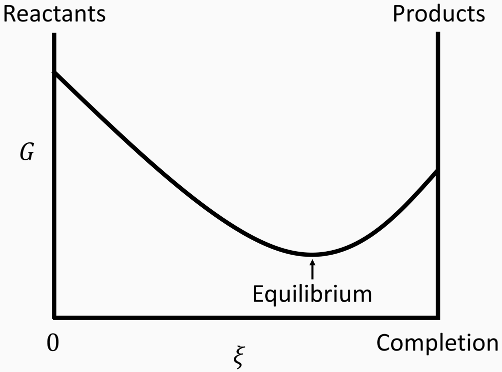
$$\boxed{\Delta G^\circ = -RT \ln K}$$

Relating Gibbs to Equilibrium

$$\Delta G^\circ = -RT \ln K$$

ΔG°	K	Favored
< 0	> 1	Products favored
$= 0$	$= 1$	Equally Favored
> 0	< 1	Reactants favored

ΔG_{toeq}



Q vs K	$Q < K$	$Q = K$	$Q > K$
Shift	$\rightarrow$	At EQ	$\leftarrow$
ΔG_{toeq}	< 0	$= 0$	> 0

$$\Delta G_{toeq} = \Delta G^\circ + RT \ln Q$$
$$\Delta G^\circ = -RT \ln K$$
$$\Delta G_{toeq} = RT \ln \frac{Q}{K}$$

ΔG_{toeq}

Free energy required to reach equilibrium

$$\Delta G_{toeq} = 0 \quad \text{(at EQ)}$$
$$\Delta G_{toeq} = \Delta G^\circ + RT \ln Q$$
$$\Delta G_{toeq} = RT \ln \frac{Q}{K}$$

ICE - Calculating K

At a certain temperature, the initial concentrations are:

$$[\mathrm{PCl_5}] = 1.0\ \mathrm{M} \quad [\mathrm{PCl_3}] = 0.5\ \mathrm{M} \quad [\mathrm{Cl_2}] = 0.5\ \mathrm{M}$$

$$\mathrm{PCl_5(g)} \rightleftharpoons \mathrm{PCl_3(g)} + \mathrm{Cl_2(g)}$$

At equilibrium, $[\mathrm{Cl_2}] = 0.243$ M. Calculate K_c.

	PCl_5	PCl_3	Cl_2
Initial (M)	1.0	0.5	0.5
Change	$+x$	$-x$	$-x$
Equilibrium	$1 + x$	$0.5 - x$	0.243

$$0.5 - x = 0.243 \implies x = 0.5 - 0.243 = 0.257$$

$$K_c = \frac{[\mathrm{PCl_3}][\mathrm{Cl_2}]}{[\mathrm{PCl_5}]} = \frac{0.243 \cdot 0.243}{1.0 - 0.257} = 0.053$$

ICE - Calculating Equilibrium Concentrations

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g) \quad K = 25$$

If hydrogen gas ($P_{H_2} = 1$ bar) is mixed with iodine ($P_{I_2} = 1$ bar) and HI ($P_{HI} = 2$ bar), what are the equilibrium pressures?

$$Q = \frac{(P_{HI})^2}{P_{H_2} P_{I_2}} = \frac{2^2}{1 \cdot 1} = 4 < K$$

	H_2	I_2	$2\,HI$
Initial (bar)	1	1	2
Change	$-x$	$-x$	$+2x$
Equilibrium	$1-x$	$1-x$	$2+2x$

$$K = 25 = \frac{(2+2x)^2}{(1-x)^2}$$

$$5 = \frac{2+2x}{1-x}$$

$$5 - 5x = 2 + 2x \implies x = \frac{3}{7}$$

Remember quadratic formula for some problems with harder K's

Le Chatelier's Principle

Le Chatelier's Principle

If a system at equilibrium is stressed, the system will shift to undo the stressor

Adding a Reactant or Product

If a system at equilibrium is stressed by the addition of moles, the system will shift to consume the added species.

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

$$Q = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

Stressor: adding $CH_3COOH(aq)$

Before adding mol: $Q = K$
Immediately after: $Q < K$
At new equilibrium: $Q = K$

Adding $CH_3COOH(aq)$ means the reaction shifts to the right to consume the additional reactant

Note: Adding solid or liquid has no impact on equilibrium since they are not in Q unless it is a solvent (H_2O).

Changing Temperature

If a system at equilibrium is stressed by changing temperature, the system will shift the equilibrium to oppose the temperature change.

$$2\,\mathrm{NO_2(g)} \rightleftharpoons \mathrm{N_2O_4(g)} \quad \Delta H^\circ_{\mathrm{rxn}} = -24.02\ \mathrm{kJ}$$

$$Q = \frac{P_{\mathrm{N_2O_4}}}{(P_{\mathrm{NO_2}})^2}$$

Stressor: increasing T

Immediately, no effect on Q, but K changes

$$\ln\frac{K_2}{K_1} = -\frac{\Delta H^\circ_{\mathrm{rxn}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

K decreases, Q goes to new K

Heat is product, adding T means the reaction shifts to the left to consume the heat

Changing Volume of Gas

If a system at equilibrium is compressed, the system shifts toward the side with fewer moles of gas to oppose the increase in pressure.

$$I_2(g) \rightleftharpoons 2\,I(g)$$

$$Q = \frac{(P_I)^2}{P_{I_2}}$$

Stressor: decreasing volume, increasing pressure

Q changes immediately

$Q > K \implies$ shift toward reactants

System responds by shifting to the side with fewer moles of gas, towards reactants.

Changing Volume of Aqueous Solution

When a solution is diluted (volume increases), the system shifts toward the side with more dissolved particles to oppose the decrease in concentration.

$$\mathrm{CoCl_2}^{2-}(\mathrm{aq}) + 6\,\mathrm{H_2O} \rightleftharpoons \mathrm{Co(H_2O)_6}^{2+}(\mathrm{aq}) + 4\,\mathrm{Cl}^{-}(\mathrm{aq})$$

$$Q = \frac{[\mathrm{Co(H_2O)_6}^{2+}][\mathrm{Cl}^{-}]^4}{[\mathrm{CoCl_2}^{2-}]}$$

Stressor: Adding water, concentrations decrease

Q changes immediately

$Q < K \implies$ shift toward products

With dilution, shift towards side with more mols of solute, so products

Adding of Inert Gas

Adding an inert gas does not affect equilibrium unless it changes the volume.

Stressor: Adding Xe(g)

$$3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g)$$

Constant Volume Container:
Adding inert gas does not affect partial pressures.

Constant Pressure Container:
Volume increases $\implies$ partial pressures decrease. Shift towards side with more mols of gas

Example: Le Chatlier's Principle

Identify the stressor and compare the following quantities at EQ1 vs EQ2.

- K
- Q
- ΔG_{toeq}
- mol CO
- [CO]
- mol Cl_2
- mol $COCl_2$
- $[COCl_2]$

$\boxed{\text{Magnitude Stressor} > \text{Response}}$

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$