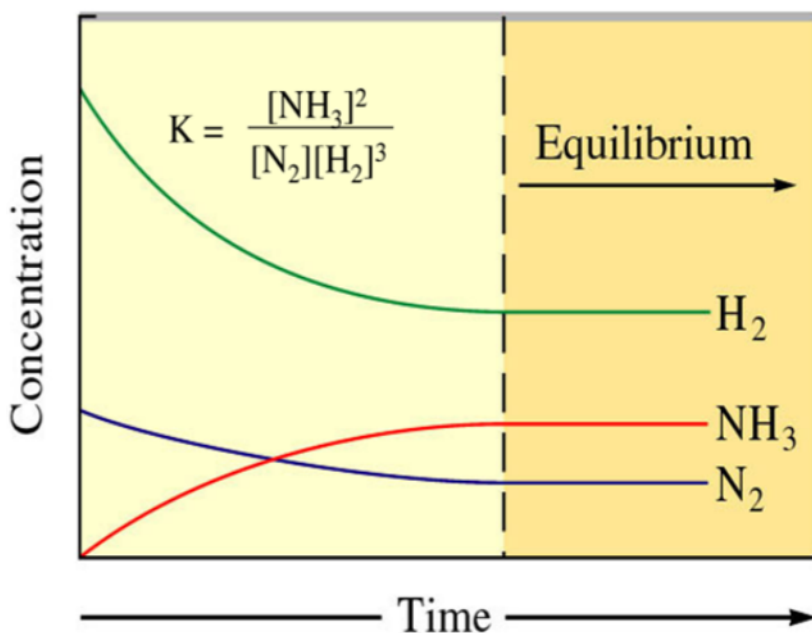# CHEM 20B Week 6

Aidan Jan
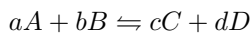
February 23, 2024

Chemical Equilibrium

- In principle, every chemical reaction is reversible... capable of moving in the forward of backward reaction

- At equilibrium the two opposing reactions occur at the same rate.

- Concentrations of chemical species do not change once equilibrium is established.

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

The Empirical Law of Mass Action

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

- A and B are reactants, C and D are products.

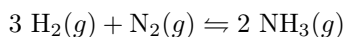- K, the ratio at equilibrium, is always the same. It is a constant and depends only on the temperature.

$$K_C = \frac{[C]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b}$$

$$K_P = \frac{(P_C)_{eq}^c (P_D)_{eq}^d}{(P_A)_{eq}^a (P_B)_{eq}^b}$$

- K_C is for concentration in aqueous reactions, K_P is for pressure in gaseous reactions.

- Essentially,

$$K = \frac{\text{Products}}{\text{Reactants}}$$

Example

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

$$K_P = \frac{(P^2_{\mathrm{NH_3}})_{eq}}{(P^3_{\mathrm{H_2}})(P_{\mathrm{N_2}})}$$

Law of Mass Action for Reactions involving Pure Substances and Multiple Phases

For example: $\mathrm{Zn}(s) + 2\,\mathrm{H_2O^+}(aq) \rightleftharpoons \mathrm{Zn^{2+}}(aq) + \mathrm{H_2}(g) + 2\,\mathrm{H_2O}(l)$

$$K = \frac{([\mathrm{Zn^{2+}}])_{eq}(P_{\mathrm{H_2}})_{eq}}{([\mathrm{H_3O^+}])^2_{eq}}$$

- (s) = pure solid

- (aq) = dissolved species (aqueous)

- (g) = gas

- (l) = pure liquid

General Rules for writing the mass action law:

1. Gases enter the equilibrium expression as partial pressures, measured in atm.

2. Dissolved species enter as concentrations, in Molarity.

3. Pure solids and pure liquids do not appear in equilibrium expressions.

4. Products appear in the numerator and reactants appear in the denominator; each raised to a power equal its coefficient in the balanced chemical equation.

5. K is dimensionless.

Thermodynamics Description of the Equilibrium State

In a reaction among ideal gases, the gas pressure is changing $P_1 \rightarrow P_2$ at a constant temperature.

- $\Delta T = 0$

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right) \qquad \text{isothermal, ideal gas}$$

$$G = H - TS$$

$$\Delta G = \Delta(H - TS) = \Delta H - T\Delta S = -T\Delta S = -nRT \ln\left(\frac{V_2}{V_1}\right) = nRT \ln\left(\frac{P_2}{P_1}\right)$$
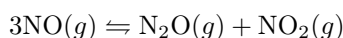
Importantly,

$$\Delta G = nRT \ln\left(\frac{P_2}{P_1}\right) = nRT \ln\left(\frac{P}{P_{ref}}\right)$$

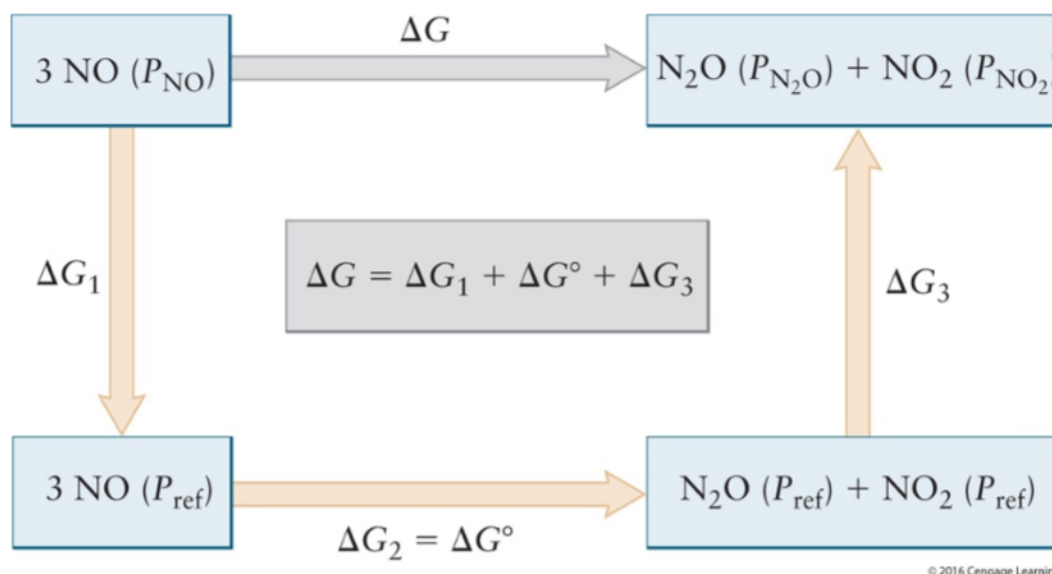Since usually the beginning pressure $P_1 = 1$ atm, $P_{ref} = 1$ atm. Thus,

$$\Delta G = nRT \ln P$$

The Equilibrium Expression for Reactions in the Gas Phase:

$$3NO(g) \rightleftharpoons N_2O(g) + NO_2(g)$$

Derive ΔG

$$\Delta G_1 = nRT\ln\left(\frac{P_2}{P_1}\right) = 3RT\ln\left(\frac{P_{ref}}{P_{NO}}\right) = RT\ln\left(\frac{P_{ref}}{P_{NO}}\right)^3$$

$$\Delta G_2 = \Delta G^0$$

$$\Delta G_3 = RT\ln\left(\frac{P_{N_2O}}{P_{ref}}\right) + RT\ln\left(\frac{P_{NO_2}}{P_{ref}}\right) = RT\ln\left[\left(\frac{P_{N_2O}}{P_{ref}}\right)\left(\frac{P_{NO_2}}{P_{ref}}\right)\right]$$

$$\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3$$
$$= RT\ln\left(\frac{P_{ref}}{P_{NO}}\right)^3 + \Delta G^0 + RT\ln\left[\left(\frac{P_{N_2O}}{P_{ref}}\right)\left(\frac{P_{NO_2}}{P_{ref}}\right)\right]$$
$$= -RT\ln\left(\frac{P_{NO}}{P_{ref}}\right)^3 + \Delta G^0 + RT\ln\left[\left(\frac{P_{N_2O}}{P_{ref}}\right)\left(\frac{P_{NO_2}}{P_{ref}}\right)\right]$$
$$= \Delta G^0 + RT\ln\left[\frac{\left(\frac{P_{N_2O}}{P_{ref}}\right)\left(\frac{P_{NO_2}}{P_{ref}}\right)}{\left(\frac{P_{NO}}{P_{ref}}\right)^3}\right]$$
$$= \Delta G^0 + RT\ln Q$$

When the reaction arrives at equilibrium, $\Delta G = 0$ and $Q = K$ $\Delta G^0 = -RT\ln K$

Reactions in Ideal Solutions

ΔG for n moles of solute, as ideal (dilute) solution changes in concentration form c_1 to c_2 mol/L, is

$$\Delta G = nRT\ln\left(\frac{c_2}{c_1} =\right) = nRT\ln\left(\frac{c}{c_{ref}}\right) = nRT\ln c$$

$$c_{ref} = 1M$$

$$\Delta G = \Delta G^0 + RT \ln \left[\frac{\left(\frac{[C]}{c_{ref}}\right)^c \left(\frac{[D]}{c_{ref}}\right)^d}{\left(\frac{[A]}{c_{ref}}\right)^a \left(\frac{[B]}{c_{ref}}\right)^b} \right]$$

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

When the reaction arrives at equilibrium, $\Delta G = 0$ and $Q = K$.

$$\Delta G^0 = -RT \ln K$$

$$K = \left[\frac{[C]^c [D]^d}{[A]^a [B]^b} \right]$$

Properties of K

Consider the reaction:

$$aA + bB \rightleftharpoons cC$$

- The reverse reaction: Invert K. $K' = 1/K$

- A balanced chemical equation is multiplied by a constant: Raise K to a power equal to that constant. $K' = K^C$, where C is the constant multiplied.

- When two reactions are added, the K-values multiply. $K' = K_A \cdot K_B$, where K_A and K_B are the K-values of the two reactions.

The Reaction Quotient:

$$Q = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

Where the partial pressures are the actual values measured at any point during the reactions, not just at equilibrium.

- $Q < K$: reaction moves to the right

- $Q = K$: system at equilibrium, no reaction

- $Q > K$: reaction moves to the left

(a) (b)

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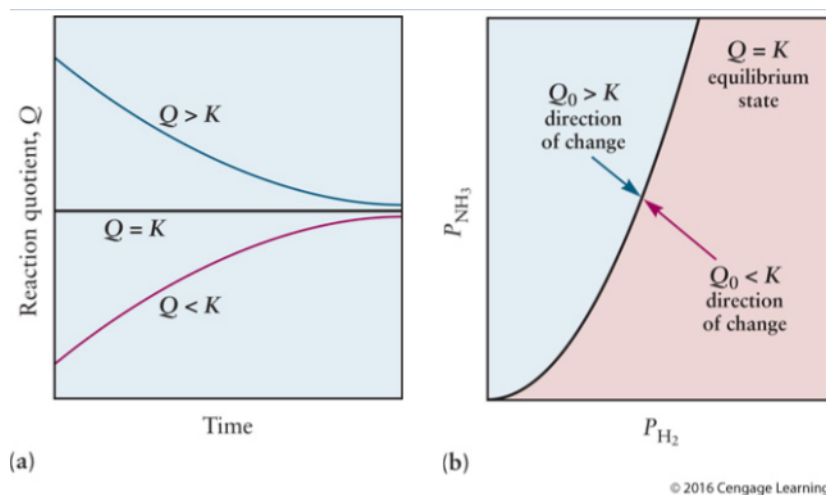
Le Chatelier's Principle

- A system in equilibrium that is subjected to a stress will react in a way that tends to counteract the stress. **System rearranges to mitigate change.**

- Effects of changing the concentration of a reactant or product:

    - Stress: Increase the concentration or pressure of species A
    - Response: The reaction will move in the appropriate direction to decrease A

- Effects of Changing the Volume

    - Stress: Increase pressure or decrease Volume
    - Response: The reaction will move in the direction to produce fewer gaseous molecules to decrease the pressure

- Effects of Changing the temperature

    - Stress: Increase temperature
    - Response: The reaction will move in the appropriate direction to absorb heat and decrease the temperature.

The Effect of a Temperature Change on the Equilibrium Constant

The values of K at two different temperatures are related by van't Hoff equation:

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^0}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

K increases with temperature increase for endothermic reactions and decreases with temperature increase for exothermic reactions.