

Chapter 13 - Chemical Equilibrium

Intro

A. Chemical Equilibrium

1. The state where the concentrations of all reactants and products remain constant with time
2. All reactions carried out in a closed vessel will reach equilibrium
 - a. If little product is formed, equilibrium lies far to the left
 - b. If little reactant remains, equilibrium lies far to the right

13.1 The Equilibrium Condition

A. Static Equilibrium does not occur in chemical systems

1. No reaction is taking place
2. All product molecules will remain product
3. All unused reactant molecules will remain unreacted

B. Dynamic Equilibrium

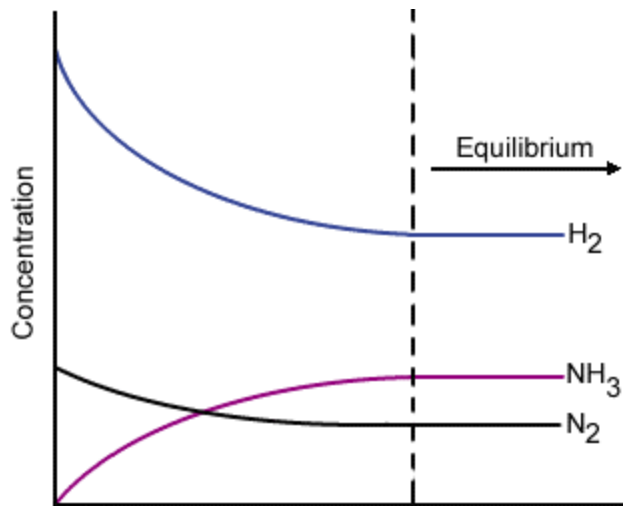
1. Reactions continue to take place
2. Reactant molecules continue to be converted to product
3. Product continues to be converted to reactant (reverse reaction)
4. Forward and reverse reactions take place at the same rate at equilibrium

C. Causes of Equilibrium

1. Beginning of reaction
 - a. Only reactant molecules exist, so only reactant molecules may collide
2. Middle
 - a. As product concentration increases, collisions may take place that lead to the reverse reaction
3. At equilibrium
 - a. Rates of forward and reverse reactions are identical

D. Example - The Haber Process

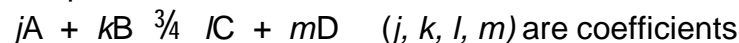
1. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 - a. hydrogen is consumed at 3x the rate of nitrogen
 - b. ammonia is formed at 2x the rate at which nitrogen is consumed



13.2 The Equilibrium Constant

A. The Law of Mass Action

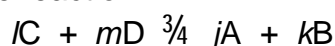
1. For the balanced equation:



The law of mass action is represented by the equilibrium expression:

$$K = \frac{[C]^l [D]^m}{[A]^j [B]^k}$$

- a. K is a constant called the equilibrium constant
 - (1) K varies depending on temperature and upon the coefficients of the balanced equation
 - b. [X] represents concentration of chemical species at equilibrium
2. For the reverse reaction



The law of mass action is represented by the equilibrium expression:

$$K' = \frac{[A]^j [B]^k}{[C]^l [D]^m} = \frac{1}{K}$$

B. Equilibrium Position

1. A set of equilibrium concentrations
2. There is only one value of K for a reaction at a given temperature, but an infinite number of possibilities for equilibrium positions

C. Summary of the Equilibrium Expression

1. The equilibrium expression for a reaction is the reciprocal of that for the reaction written in reverse
2. When the balanced equation for a reaction is multiplied by a factor n , the equilibrium expression for the new reaction is the original expression raised to the n th power

$$K_{new} = (K_{original})^n$$

3. For a particular reaction at a given temperature, the value of K is constant regardless of the amounts of gases that are mixed together (homogeneous rxn system)

13.3 Equilibrium Expressions Involving Pressure

A. Derivation of Equilibrium Gas Laws

1. $PV = nRT$ therefore... $P = \left(\frac{n}{V}\right)RT$

n/V is the molar concentration of the gas, represented by C

$$P = CRT$$

2. For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$\text{In terms of concentrations } K_c = \frac{C_{NH_3}^2}{(C_{N_2})(C_{H_2}^3)}$$

$$\text{In terms of partial pressures } K_p = \frac{P_{NH_3}^2}{(P_{N_2})(P_{H_2}^3)}$$

B. Relationship between K and K_p

1. $K_p = K(RT)^{\Delta n}$

- a. $\Delta n = (l + m) - (j + k)$ the difference in the sums of the coefficients for the gaseous products and reactants

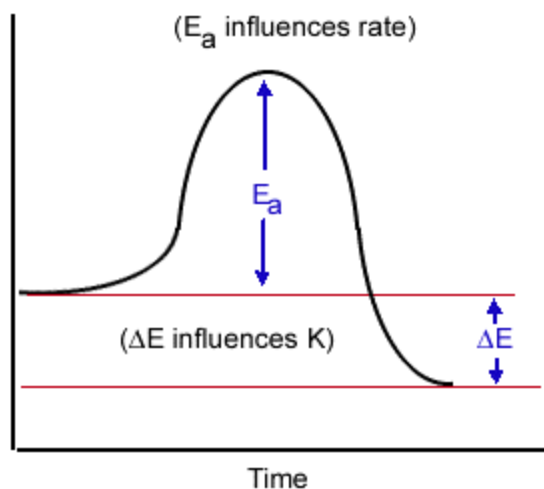
13.4 Heterogeneous Equilibria

- A. The position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present
- B. If pure solids or liquids are involved in a chemical reaction, their concentrations are not included in the equilibrium expression for the reaction
- C. Pure liquids are not the same as solutions, whose concentration can change

13.5 Applications of the Equilibrium Constant

A. Extent of a Reaction

1. Reactions with large equilibrium constants ($K \gg 1$) go essentially to completion
- a. Equilibrium position is far to the right
- a. Generally large, negative ΔE
2. Reactions with small equilibrium constants ($K \ll 1$) consist of mostly reactants
- a. Equilibrium position is far to the left
3. Time required to achieve equilibrium
- a. Related to reaction rate and activation energy
- b. Not related to the magnitude of K



B. Reaction Quotient (Q)

1. Apply the law of mass action to initial concentrations in order to determine what direction the rxn must move in order to achieve equilibrium

$$Q = \frac{[NH_3]_0^3}{[N_2]_0[H_2]_0^3}$$

the subscript zero indicates initial concentrations

2. IF Q is equal to K
- a. The system is at equilibrium, no shift will occur
3. IF Q is greater than K
- a. The system shifts to the left, consuming products and forming reactants to reach equilibrium
4. IF Q is less than K
- a. The system shifts to the right, consuming reactants and forming products until equilibrium is reached

13.6 Solving Equilibrium Problems

A. Procedure for Solving Equilibrium Problems

1. Write the balanced equation for the reaction
2. Write the equilibrium expression using the law of mass action
3. List the initial concentrations
4. Calculate Q, and determine the direction of the shift to equilibrium
5. Define the change needed to reach equilibrium, and define the equilibrium concentrations by applying the change to the initial concentration
6. Substitute the equilibrium concentrations into the equilibrium expression, and solve for the unknown
7. Check you calculated equilibrium concentrations by making sure they give the correct value of K

B. Treating Systems That Have Small Equilibrium Constants

1. The small value of K and the resulting small shift to the right to reach equilibrium allows for simplification of the math

13.7 Le Chatelier's Principle

A. Statement of Le Chatelier's Principle (very important!)

1. If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change

B. The Effect of Change in Concentration

1. If a reactant or product is added to a system at equilibrium, the system will shift away from the added component (it will attempt to "use up" the added component)
2. If a reactant or product is removed from a system at equilibrium, the system will shift toward the removed component (it will attempt to "replace" the removed component)

C. The Effect of a Change in Pressure

1. Ways to change pressure

- a. Add or remove a gaseous reactant or product

(1) covered above ↑

- b. Add an inert gas (one not involved in the reaction)

(1) An inert gas increases the total pressure but has no effect on the concentrations or partial pressures of the reactants or products

- c. Change the volume of the container

(1) When the volume of the container holding a gaseous system is reduced, the system responds by reducing its own volume. This is done by decreasing the total number of gaseous molecules in the system

$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ shifts to the right to decrease the total molecules of gas present

(2) When the container volume is increased, the system will shift so as to increase its volume

$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ shifts to the left to increase the total number of molecules of gas present

D. The Effect of a Change in Temperature

1. An increase in temperature increases the energy of the system. Le Chatelier's principle predicts that the system will shift in the direction that consumes the energy
 - a. For an exothermic rxn, energy is a product. The rxn will shift to the left to use up the excess energy
 - b. For an endothermic rxn, energy is a reactant. The rxn will shift to the right to use up the energy
2. A decrease in temperature will cause a system shift in the direction that "replaces" the lost energy