

Chapter 13

Chemical Equilibrium

Section 13.1

The Equilibrium Condition



Chemical Equilibrium

- Describes reactions that do not go to completion.

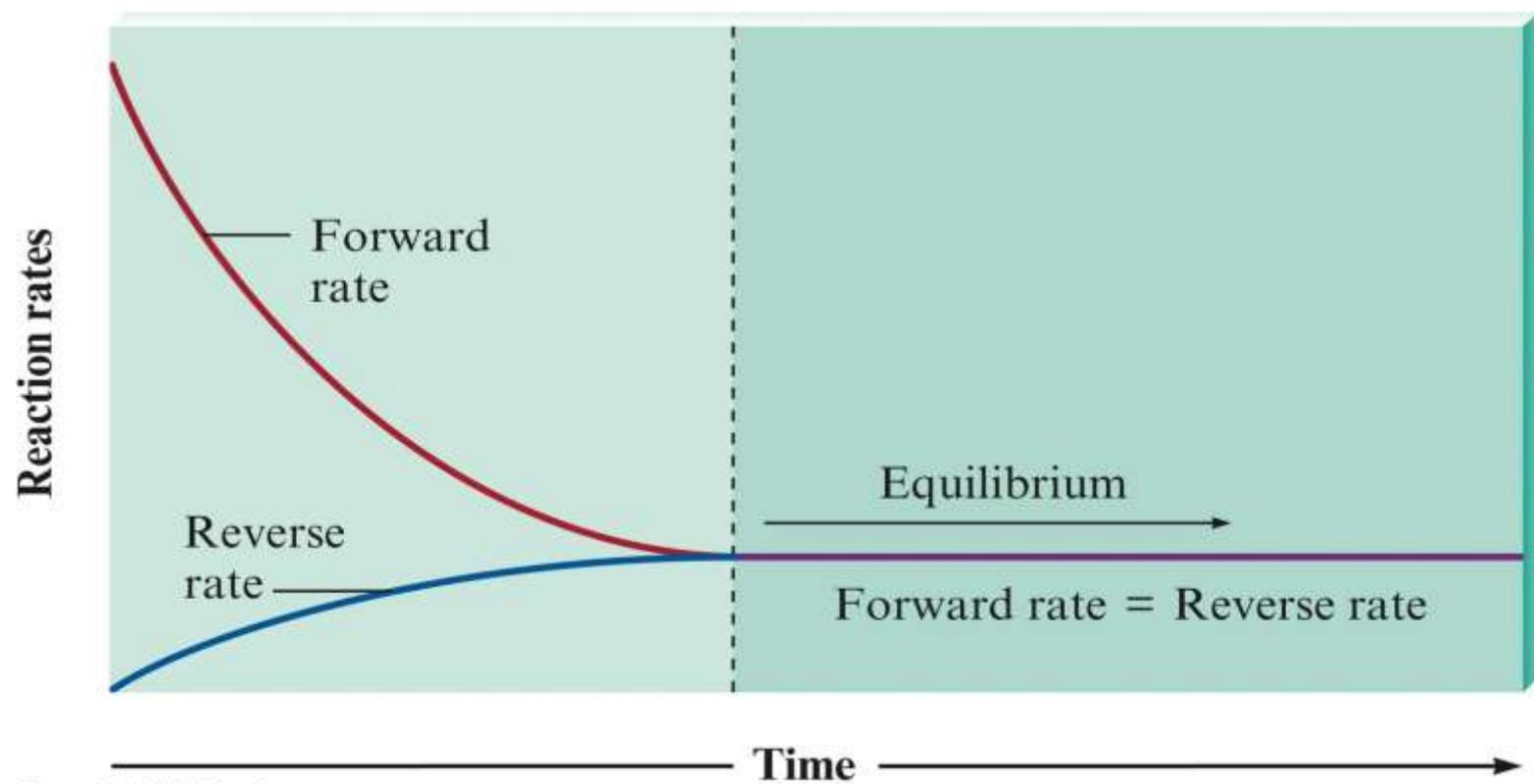


- After equilibrium is reached, none of the reactants or products has a concentration of zero.
- Forward Reaction \rightarrow
- Reverse Reaction \leftarrow
- $\text{HCl} + \text{NaOH} \quad \times$
- $\text{NaCl} + \text{AgNO}_3 \quad \times$

Section 13.1

The Equilibrium Condition

The Changes with Time in the Rates of Forward and Reverse Reactions



Section 13.1

The Equilibrium Condition

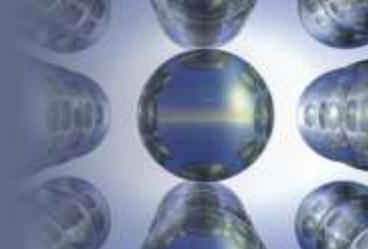


Chemical Equilibrium

- A state of the system where the concentrations of all reactants and products remain constant with time.
- Forward and reverse reactions have the same speed.
- The equilibrium is dynamic.

Section 13.1

The Equilibrium Condition



Chemical Equilibrium (The Equilibrium is Dynamic)

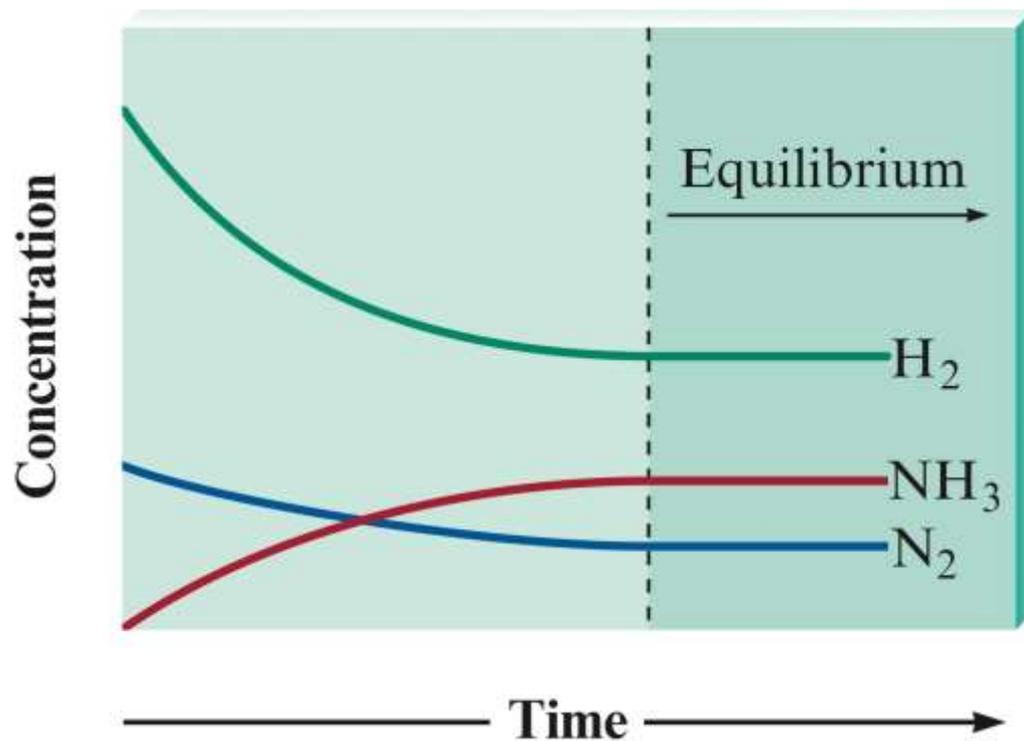
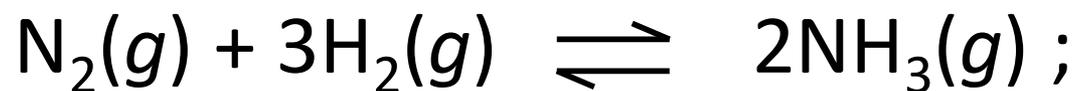
- Concentrations reach levels where the rate of the forward reaction equals the rate of the reverse reaction.

Section 13.1

The Equilibrium Condition



Changes in Concentration with time:



Section 13.2

The Equilibrium Constant

Consider the following reaction at equilibrium:



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

Section 13.1

The Equilibrium Condition

Consider the following equilibria:



$$K' = K^2 \quad (\text{concentrations doubled})$$

$$K'' = (1/K) \quad (\text{reversing the reaction})$$

Section 13.2

The Equilibrium Constant



Conclusions About the Equilibrium Expression

- Equilibrium expression for a reaction is the reciprocal of that for the reverse reaction. $K' = 1/K$
- When the balanced equation for a reaction is multiplied by a factor of n , the equilibrium expression for the new reaction is the original expression raised to the n -th power; thus $K_{\text{new}} = (K_{\text{original}})^n$.
- K values are usually written without units.

Section 13.2

The Equilibrium Constant



- K - always has the same value at a given temperature regardless of the amounts of reactants or products that are initially present.

Section 13.3

Equilibrium Expressions Involving Pressures

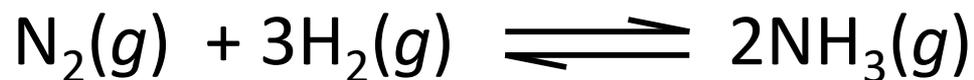


- K is the equilibrium expression in terms of concentrations.
- K_p is the equilibrium expression in terms of the partial pressures of the gaseous constituents of the reaction.
- $PV = nRT$
- Concentration, $[] = n/V = P/RT$
- The concentration can be calculated if we know the pressure and the temperature of the gas.
- $P = [] RT$

Section 13.3

Equilibrium Expressions Involving Pressures

Example



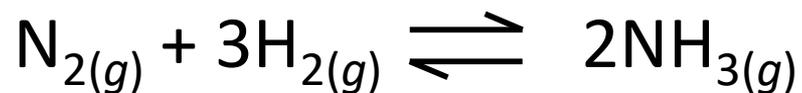
$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3}$$

Section 13.3

Equilibrium Expressions Involving Pressures

Example



Equilibrium partial pressures at a certain temperature:

$$P_{\text{NH}_3} = 2.9 \times 10^{-2} \text{ atm}$$

$$P_{\text{N}_2} = 8.9 \times 10^{-1} \text{ atm}$$

$$P_{\text{H}_2} = 2.9 \times 10^{-3} \text{ atm}$$

Section 13.3

Equilibrium Expressions Involving Pressures

Example: Calculate K_p for the reaction?



$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3}$$

$$K_p = \frac{(2.9 \times 10^{-2})^2}{(8.9 \times 10^{-1})(2.9 \times 10^{-3})^3}$$

$$K_p = 3.9 \times 10^4$$

Section 13.3

Equilibrium Expressions Involving Pressures

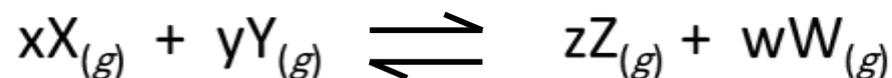
- $P = [] RT$ OR $[] = P/RT$
- When concentrations are replaced by P/RT in the equilibrium constant expression K , a new equilibrium constant in terms of partial pressures is obtained, K_p . Specific relation between K and K_p , that depends on the temperature and the constant R will be obtained. This relation is found to depend on the change in the number of moles of the gaseous substances that appear in the reaction, Δn_g .

Section 13.3

Equilibrium Expressions Involving Pressures

■ K and K_p :

$P = [] RT$, consider the general reaction:



$$K_p = \frac{P_w^w P_z^z}{P_x^x P_y^y} \quad \text{and} \quad K = \frac{[W]^w [Z]^z}{[X]^x [Y]^y}$$

Put the partial pressures of x, y, w and z in terms of concentration,

$$K_p = \frac{[W]^w [Z]^z}{[X]^x [Y]^y} (RT)^{w+z-x-y}$$

$$\Delta n_g = n_p - n_r = w + z - (x + y) = w + z - x - y$$

$$K_p = K (RT)^{\Delta n_g}$$

Section 13.3

Equilibrium Expressions Involving Pressures



The Relationship Between K and K_p

$$K_p = K(RT)^{\Delta n_g}$$

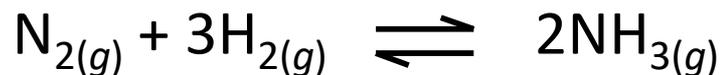
- Δn_g = sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants.
- $R = 0.08206 \text{ L}\cdot\text{atm.}/\text{mol}\cdot\text{K}$
- T = temperature (in Kelvin)
- $\Delta n_g = n_g (\text{P}) - n_g (\text{R})$

Section 13.3

Equilibrium Expressions Involving Pressures



Example



Using the value of K_p (3.9×10^4) from the previous example, calculate the value of K at 35°C .

$$K_p = K(RT)^{\Delta n_g}$$

$$3.9 \times 10^4 = K(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K} \times 308\text{K})^{2-4}$$

$$K = 2.5 \times 10^7$$

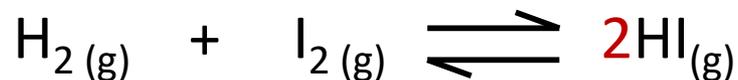
Note: $K_p < K$ (Δn_g is negative)

Section 13.3

Equilibrium Expressions Involving Pressures

- $K_p = K (RT)^{\Delta n_g}$; $\Delta n_g = n_g(P) - n_g(R)$

- $K_p = K$ when $\Delta n_g = 0$



- $K_p > K$ when $\Delta n_g > 0$; $\text{N}_2\text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{2(g)}$
(increase in n of gaseous products)

- $K_p < K$,when $\Delta n_g < 0$; $2\text{NO}_{(g)} + \text{Cl}_{2(g)} \rightleftharpoons 2\text{NOCl}_{(g)}$
(decrease in the n of the gaseous products)

Section 13.4

Heterogeneous Equilibria



Homogeneous Equilibria

- Homogeneous equilibria – involve the same phase:



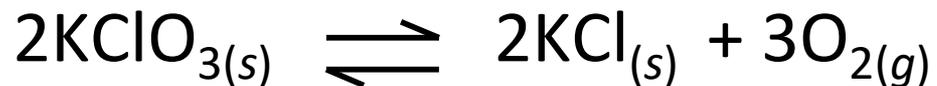
Section 13.4

Heterogeneous Equilibria



Heterogeneous Equilibria

- Heterogeneous equilibria – involve more than one phase:



Section 13.4

Heterogeneous Equilibria



- The position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present because their concentrations are constant.



$$K_p = P^3(\text{O}_2) \quad ; \quad K_p > K \quad ; \quad \Delta n_g = 3 > 0$$

$$K = [\text{O}_2]^3$$

Section 13.5

Applications of the Equilibrium Constant



The Extent of a Reaction

- A value of K much larger than 1 means that at equilibrium the reaction system consists of mostly products. OR The equilibrium lies to the right.
- A very small value of K means that the system at equilibrium consists of mostly reactants. OR The equilibrium position is far to the left. The Reaction does not occur to any significant extent.

Section 13.5

Applications of the Equilibrium Constant



CONCEPT CHECK!

- If the equilibrium lies to the **right (toward the products)**, the value for K is **Larger than 1**.
- If the equilibrium lies to the **left (towards the reactants)**, the value for K is **Smaller than 1**.

Section 13.5

Applications of the Equilibrium Constant

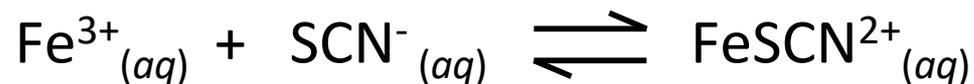


Numerical problems on equilibrium:

Numerical problems come in two different ways:

(I) The initial concentrations and the equilibrium concentration of one of the reactants or products are known. Asks to calculate K.

Consider the reaction represented by the equation:

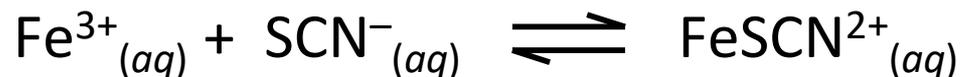


6.00 M $\text{Fe}^{3+}_{(aq)}$ and 10.0 M $\text{SCN}^{-}_{(aq)}$ are mixed at a certain temperature and at equilibrium the concentration of $\text{FeSCN}^{2+}_{(aq)}$ is 4.00 M.

Calculate the value for the equilibrium constant, K, for this reaction?

Section 13.5

Applications of the Equilibrium Constant



Initially: 6.00 10.00 0.00

Change: - 4.00 - 4.00 + 4.00

Equilibrium: 2.00 6.00 4.00

$$K = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^{-}]} = \frac{[4.00 \text{ M}]}{[2.00 \text{ M}][6.00 \text{ M}]}$$

$$K = 1/3 = 0.3333$$

Section 13.5

Applications of the Equilibrium Constant



At equilibrium: $[C] = 3.0M$



■ Initially: 8 10 0

■ Change: -3 -6 +3

■ **At equilibrium:** 5 4 3

■ $K = \frac{[C]}{[B]2[A]} = \frac{3}{4^2 \cdot 5} = 0.0375$

■ Calculate K_p at 25 °C?

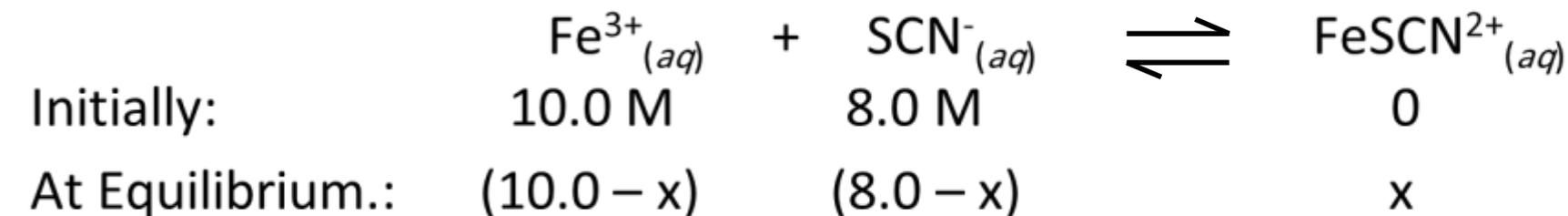
Section 13.5

Applications of the Equilibrium Constant

(II) The initial concentrations of the reactants and the value of the equilibrium constant, asks to calculate equilibrium concentrations.

If the Initial concentrations are: 10.0 M $\text{Fe}^{3+}_{(aq)}$ and 8.00 M $\text{SCN}^{-}_{(aq)}$.
What is the equilibrium concentration of FeSCN^{2+} ? ($K=0.33333$)

The equilibrium reaction is shown below:



$$K = \frac{x}{(8.0-x)(10.0-x)} = 0.33333 \quad 5.00 \text{ M FeSCN}^{2+}$$

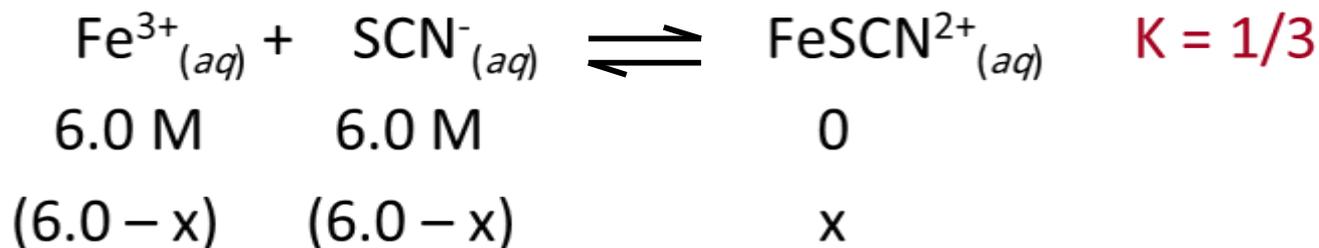
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Section 13.5

Applications of the Equilibrium Constant

Example :

Consider the reaction below where the initial concentrations are 6.0 M for each of the reactants:



Calculate the equilibrium concentration of $\text{FeSCN}^{2+}_{(aq)}$?

$$K = \frac{1}{3} = \frac{x}{(6.0 - x)(6.0 - x)}$$

$$x^2 - 15x + 36 = 0 \quad \text{so,} \quad (x - 3)(x + 12) = 0$$

Answer: $x = 3.00 \text{ M} = [\text{FeSCN}^{2+}]$

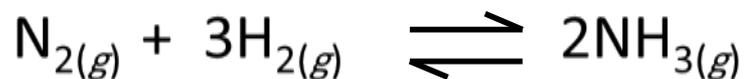
Section 13.5

Applications of the Equilibrium Constant



Reaction Quotient, Q

- Used when all of the initial concentrations are non-zero.
- Apply the law of mass action using initial concentrations instead of equilibrium concentrations.



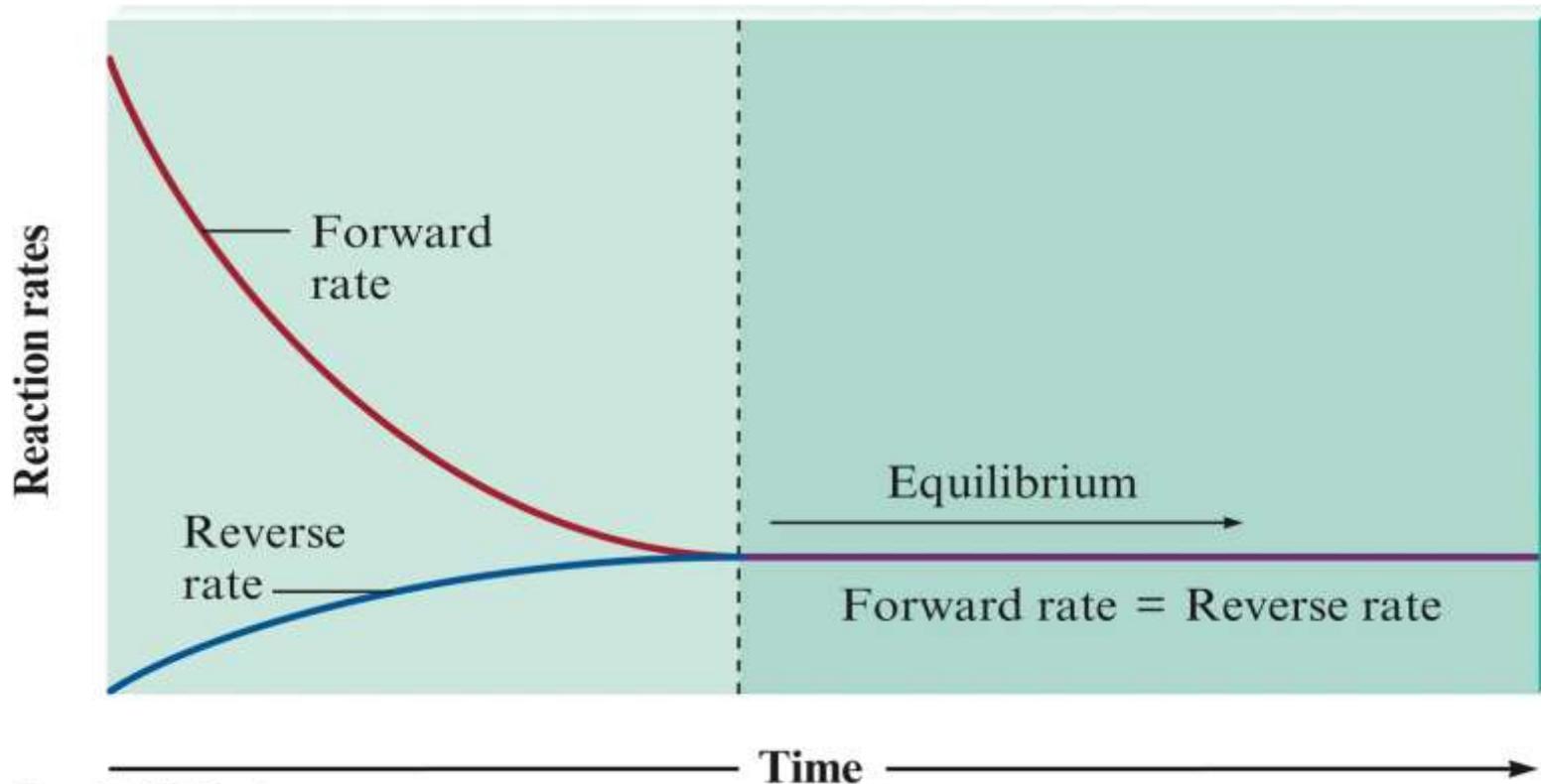
$$Q = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]}$$

- “ Q ” Can be written at any time of the reaction
- $Q = K$ (at equilibrium)

Section 13.5

Applications of the Equilibrium Constant

The Changes with Time in the Rates of Forward and Reverse Reactions



Section 13.5

Applications of the Equilibrium Constant



Reaction Quotient, Q

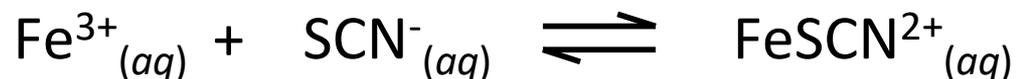
- $Q = K$; The system is at equilibrium. No shift will occur.
- $Q > K$; The system shifts to the **left**. After equilibrium ←
 - Consuming products and forming reactants, until equilibrium is achieved.
- $Q < K$; The system shifts to the **right**. Before equilibrium
- Consuming reactants and forming products, to attain equilibrium. →

Section 13.6

Solving Equilibrium Problems

Q and K:

Consider the reaction represented by the equation:



Consider the following initial concentrations:

| | Fe^{3+} | SCN^{-} | FeSCN^{2+} | Q |
|-----|------------------|------------------|---------------------|--------|
| Q1: | 9.00 M | 5.00 M | 1.00 M | 0.0222 |
| Q2: | 3.00 M | 2.00 M | 5.00 M | 0.8333 |
| Q3: | 2.00 M | 9.00 M | 6.00 M | 0.3333 |

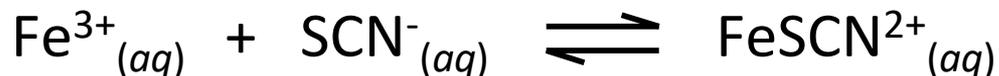
$$K = 0.3333$$

Find the equilibrium concentrations for all species.

Section 13.6

Solving Equilibrium Problems

Consider Q2: $Q > K$, \leftarrow



$$\text{Init.: } 3.00 \quad 2.0 \quad 5.0$$

$$\text{At eq.: } (3.0 + x) \quad (2.0 + x) \quad (5.0 - x)$$

$$K = 1/3 = (5.0 - x)/(3.0 + x)(2.0 + x)$$

$$3(5.0 - x) = (3.0 + x)(2.0 + x)$$

$$x^2 + 8x - 9 = 0$$

$(x + 9)(x - 1) = 0$; $x = -9$ (*neglect*) or $+1$ (*take this*). So:

□ The equilibrium concentrations are:

$$\text{Fe}^{3+} = (3.0 + x) = 4.0 \text{ M} \quad ; \quad \text{SCN}^{-} = (2.0 + x) = 3.0 \text{ M} \quad ;$$

$$\text{FeSCN}^{2+} = (5.0 - x) = 4.0 \text{ M}$$

Section 13.6

Solving Equilibrium Problems



EXERCISE!

Answers

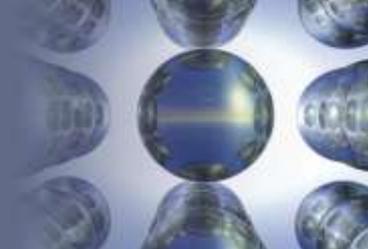
Q1: $[\text{Fe}^{3+}] = 6.00 \text{ M}$; $[\text{SCN}^-] = 2.00 \text{ M}$; $[\text{FeSCN}^{2+}] = 4.00 \text{ M}$

Q2: $[\text{Fe}^{3+}] = 4.00 \text{ M}$; $[\text{SCN}^-] = 3.00 \text{ M}$; $[\text{FeSCN}^{2+}] = 4.00 \text{ M}$

Q3: $[\text{Fe}^{3+}] = 2.00 \text{ M}$; $[\text{SCN}^-] = 9.00 \text{ M}$; $[\text{FeSCN}^{2+}] = 6.00 \text{ M}$

Section 13.7

Le Châtelier's Principle



- If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that reduces that change.

Section 13.7

Le Châtelier's Principle



Effects of Changes on the System

1. Concentration: The system will shift away upon addition of any component that is a part of the system. If a component is removed, the opposite effect occurs.



(Explain the effect of increasing or decreasing a reactant or product on the position of the equilibrium).

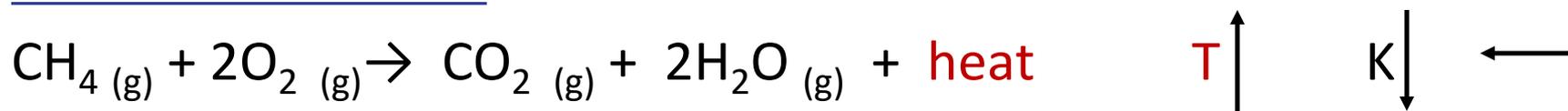
No change in the value of K

Section 13.7

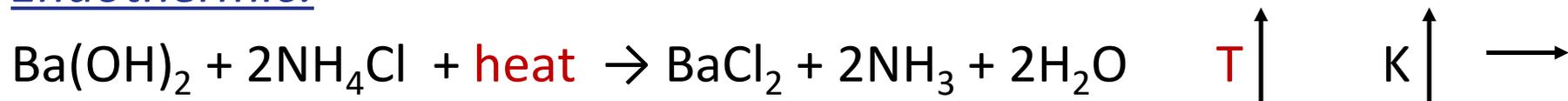
Le Châtelier's Principle

2. Temperature: K will change depending upon the temperature.
(endothermic – energy is a reactant; exothermic – energy is a product).

Exothermic reaction:



Endothermic:



(Explain the effect of increasing or decreasing the temperature on the position of equilibrium)

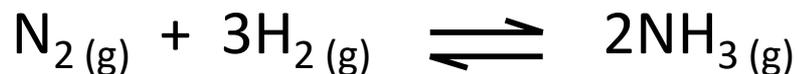
Section 13.7

Le Châtelier's Principle



Effects of Changes on the System

3. Pressure effect at constant temperature, pressure that is due to a volume change (volume pressure):



(Explain the effect of change in volume on the position of equilibrium)

4. Addition of inert gas does not affect the equilibrium position.
If “Ne” gas is added to any of the equilibria above,

$K = [\text{CO}_2][\text{H}_2]/[\text{CO}][\text{H}_2\text{O}]$, will not be affected.