

Chapter 7 Equilibrium

Equilibrium Constant KP Formula Chemical

Equilibrium state- When rate of formation of a product in a process is in competition with rate of formation of reactants, the state is then named as "Equilibrium state".

Equilibrium in physical processes:

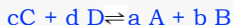
solid \rightleftharpoons liquid \rightleftharpoons gas. $\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{O}_{(g)}$
Law of chemical equilibrium: At a given temperature, the product

of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the Equilibrium Law or Law of Chemical Equilibrium.



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

Chemical equation



Equilibrium constant

$$K$$

$$K' = 1/K$$

$$K'' = (K)^n$$

Concentrations or partial pressure of pure solids or liquids do not appear in the expression of the

equilibrium constant. In the reaction, $K_c = \frac{2\text{AgNO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})}{\text{Ag}_2\text{O}(\text{s}) + 2\text{HNO}_3(\text{aq})}$ $\Rightarrow \frac{[\text{AgNO}_3]^2}{[\text{HNO}_3]^2}$

If $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse reaction). If $Q_c < K_c$, the reaction will proceed in the direction of the products (forward reaction)

K_p is equilibrium constant in terms of partial pressure of gaseous reactants and products.

K_c is equilibrium constant in terms of molar concentration of gaseous reactants and products

$K_p = K_c (RT)^{\Delta n}$ here **R** is gas constant, **T** is temperature at which the process is carried out & Δn is no. of moles of gaseous product minus no. of moles of gaseous reactants.

If $K_c > 10^3$; K_c is very high i.e. the reaction proceeds nearly to completion.

If $K_c < 10^{-3}$; K_c is very small i.e. the reaction proceeds rarely.

If K_c is ranging in the range of 10^3 to 10^{-3} ; i.e. reactants and products are just in equilibrium.

$$\Delta G^\circ = -RT \ln K \quad \text{or} \quad \Delta G^\circ = -2.303RT \log K$$

Factors affecting equilibrium constant :- temperature, pressure, catalyst and molar concentration of reactants and products.

Le Chatelier's principle :- It states that a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.

Arrhenius acids are the substances that ionize in water to form H^+ .

Arrhenius bases are the substances that ionize in water to form OH^- .

Lewis acids are lone pair (of e.) accepters while Lewis bases are lone pair donors.

Proton donor are acids while proton accepters are bases (Bronsted-Lowry concept).

The acid-base pair that differs only by one proton is called a **conjugate acid-base pair**. If Brønsted acid is a strong acid then **its conjugate base is a weak base and vice versa**.

Ionic product of water. $K_w = [\text{H}^+][\text{OH}^-]$

$\text{pH} = -\log [\text{H}^+]$; here $[\text{H}^+]$ is molar concentration of hydrogen ion.

$\text{pH} + \text{pOH} = 14$

$\text{pK}_a + \text{pK}_b = 14$

$K_a \times K_b = K_w = \text{ionic product of water} = 1 \times 10^{-14}$

Buffer solution : The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.

common ion effect: It can be defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium.

Hydrolysis of Salts: process of interaction between water and cations an ions or both of salts is called hydrolysis.

The cations (e.g., Na^+ , K^+ , Ca^{2+} , Ba^{2+} , etc.) of strong bases and anions (e.g., Cl^- , Br^- , NO_3^- , ClO_4^- etc.) of strong acids simply get hydrated but do not hydrolyse, and therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7.

Salts of weak acid and strong base e.g., CH_3COONa are basic in nature.

Salts of strong acid and weak base e.g., NH_4Cl , are acidic

Salts of weak acid and weak base, e.g., $\text{CH}_3\text{COONH}_4$. The pH is determined by the formula $\text{pH} = 7 + \frac{1}{2} (\text{pK}_a - \text{pK}_b)$

Solubility product- product of the molar concentrations of the ions in a saturated solution, each concentration term raised to the power equal to the no. of ions produced.

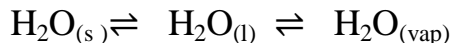
Chapter 7 part -1

CHAPTER-7

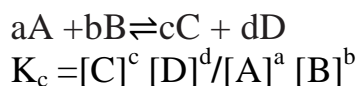
EQUILIBRIUM

➤ Equilibrium state- When rate of formation of a product in a process is in competition with rate of formation of reactants, the state is then named as “Equilibrium state” .

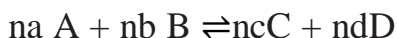
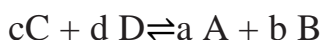
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Chemical equation



Equilibrium constant

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$$K' = (1/K_c)$$

$$K'' = (K_c^n)$$

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➤ If $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse reaction). If $Q_c < K_c$, the reaction will proceed in the direction of the products (forward reaction)

➤ K_p is equilibrium constant in terms of partial pressure of gaseous reactants and products.

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➤ $\Delta G^0 = -RT \ln K$ or $\Delta G^0 = -2.303RT \log K$

➤ Factors affecting equilibrium constant:- temperature, pressure, catalyst and molar concentration of reactants and products.

- **Le Chatelier's principle:-** It states that a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.
- Arrhenius acids are the substances that ionize in water to form H^+ .
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- **Ionic product of water.** $K_w = [\text{H}^+][\text{OH}^-]$
- **pH = $-\log [\text{H}^+]$; here $[\text{H}^+]$ is molar concentration of hydrogen ion.**
- **pH + pOH = 14**
- **pKa + pKb = 14**
- **Ka x Kb = Kw = ionic product of water = 1×10^{-14}**
- **Buffer solution :** The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.
- **common ion effect:** It can be defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium.
- **Hydrolysis of Salts:** process of interaction between water and cations/anions or both of salts is called hydrolysis.
- The cations (e.g., Na^+ , K^+ , Ca^{2+} , Ba^{2+} , etc.) of strong bases and anions (e.g., Cl^- , Br^- , NO_3^- , ClO_4^- etc.) of strong acids simply get hydrated but do not hydrolyse, and therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7.
- Salts of weak acid and strong base e.g., CH_3COONa are basic in nature.
- Salts of strong acid and weak base e.g., NH_4Cl , are acidic
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- **Solubility product-** product of the molar concentrations of the ions in a saturated solution, each concentration term raised to the power equal to the no. of ions produced.

ONE MARK QUESTIONS

Q.1. Mention the factors that affect equilibrium constant.

Ans. Temperature, pressure, catalyst and molar concentration of reactants and products.

Q.2. What are ionic products of water?

Ans. $K_w = [H^+][OH^-]$

Q.3. Write conjugate acids of H_2O & NH_3 .

Ans. H_3O^+ & NH_4^+ .

Q.4. Define Arrhenius acids.

Ans. Arrhenius acids are the substances that ionize in water to form H^+ .

Q.5. Define the term degree of ionization.

Ans. Extent up to which an acid/base/salt ionize to form ions.

Q.6. What are Buffer solutions?

Ans. The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.

Q.7. Write K_c for the gaseous reaction- $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Ans. $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

Q.8. Out of H_2O & H_3O^+ which is stronger acid?

Ans. H_3O^+ .

Q.9. What is common ion effect?

Ans. Shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium.

Q.10. Write relationship between K_p and K_c for the gaseous reaction - $N_2 + O_2 \rightleftharpoons 2NO$

Ans. $K_p = K_c$ as Δn is zero for the above said reaction.

TWO MARKS QUESTIONS

1. What is effect of catalyst on equilibrium constant 'Kc'?

Ans. A catalyst does not affect equilibrium constant because it speeds up both forward and backward reactions to the same extent.

2. State Le Chatelier's principle.

Ans. It states that a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.

3. What is meant by conjugate acid-base pairs? Explain.

Ans:- $H_2O + HCl \rightleftharpoons H_3O^+ + Cl^-$
base acid conjugate acid conjugate base

4. Classify the following bases as strong and weak bases: NaHCO_3 , NaOH , KOH , Ca(OH)_2 , Mg(OH)_2 .

Ans:-strong base NaOH , KOH ; weak bases NaHCO_3 , Ca(OH)_2 , Mg(OH)_2 .

5. The concentration of hydrogen ion in a sample of soft drink is $3.8 \times 10^{-3}\text{M}$. What is its pH ?

Ans:- $\text{pH} = -\log[3.8 \times 10^{-3}]$

$= -\{\log[3.8] + \log[10^{-3}]\}$

$= -\{(0.58) + (-3.0)\} = -\{-2.42\} = 2.42$

Therefore, the pH of the soft drink is 2.42 and it is acidic.

6. The species: H_2O , HCO_3^- , HSO_4^- and NH_3 can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and conjugate base.

Ans:-

Species	Conjugate acid	Conjugate base
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{2-}
HSO_4^-	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	NH_2^-

7. Explain Lewis acids and bases with suitable examples.

Ans:-Lewis acids are lone pair (of e^-) accepters while Lewis bases are lone pair donators.

AlCl_3 is a Lewis acid while NH_3 is a Lewis base.

8. What is difference between alkali and bases? Give examples.

Ans:- An alkali is a water soluble base. All the alkalis are bases but all the bases are not alkali. Ex- NaOH is an alkali/base.

Ca(OH)_2 is a base but not an alkali.

9. Explain homogeneous and heterogeneous equilibrium giving examples.

Ans:- If all the reactants and products present in an equilibrium mixture are in same phase \rightarrow homogeneous equilibrium.

If all the reactants and products present in an equilibrium mixture are in different phase \rightarrow heterogeneous equilibrium.

$\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$ homogeneous equilibrium

$\text{CaCO}_{3(s)} \rightleftharpoons \text{CaO}_{(s)} + \text{CO}_{2(g)}$ heterogeneous equilibrium

THREE MARK QUESTIONS

1. The pH of some common substances is given below. Classify the substances as acidic/basic

Name of fluid	pH
Lime water	10
Milk of magnesia	10
Human saliva	6.4
Lemon juice	2.2
Sea water	7.8
Vinegar	3
milk	6.8

Ans.:- acidic-Human saliva, Lemon juice, milk, vinegar

Basic- Lime water, sea water, milk of magnesia.

2. Explain general characteristics of acids and bases.

Ans.:- Most of the acids taste sour. Acids are known to turn blue litmus paper into red and liberate dihydrogen on reacting with some metals.

Bases are known to turn red litmus paper blue, taste bitter and feel soapy.

3. Water is amphoteric in nature. Explain.

Ans.:- Water can react with acid as well as base



4. Describe the effect of :

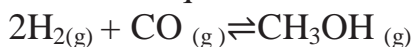
a) addition of H_2

b) addition of CH_3OH

c) removal of CO

d) removal of CH_3OH

on the equilibrium of the reaction:



Ans.:- a) addition of H_2

equilibrium will shift on RHS

b) addition of CH_3OH

equilibrium will shift on LHS

c) removal of CO

equilibrium will shift on LHS

d) removal of CH_3OH

equilibrium will shift on RHS

5. Classify the following species into Lewis acids and Lewis bases and show how these act as such:

(a) HO^- (b) F^- (c) H^+ (d) BCl_3

Solution

(a) Hydroxyl ion is a Lewis base as it can donate an electron lone pair ($:\text{OH}^-$).

(b) Fluoride ion acts as a Lewis base as it can donate any one of its four electron lone pairs.

(c) A proton is a Lewis acid as it can accept a lone pair of electrons from bases like hydroxyl ion and fluoride ion.

(d) BCl_3 acts as a Lewis acid as it can accept a lone pair of electrons from species like ammonia or amine molecules.

6. For the equilibrium, $2\text{NOCl}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g})$ the value of the equilibrium constant, K_c is 3.75×10^{-6} at 1069 K. Calculate the K_p for the reaction at this temperature?

Solution

We know that, $K_p = K_c(RT)^{\Delta n}$

For the above reaction, $\Delta n = (2+1) - 2 = 1$

$$K_p = 3.75 \times 10^{-6} (0.0831 \times 1069)$$

$$K_p = 0.033.$$

7. Hydrolysis of sucrose gives, $\text{Sucrose} + \text{H}_2\text{O} \rightarrow \text{Glucose} + \text{Fructose}$
Equilibrium constant K_c for the reaction is 2×10^{13} at 300K. Calculate ΔG^0 at 300K.

Solution

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

$$\Delta G^0 = -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K} \times \ln(2 \times 10^{13})$$

$$\Delta G^0 = -7.64 \times 10^4 \text{ J mol}^{-1}$$

8. Explain the following :

(i) Common ion effect (ii) solubility products (iii) pH

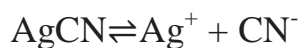
Ans. (i) Suppression of ionization of weak electrolyte by adding a strong electrolyte having an ion common.

(ii) Product of the molar concentrations of the ions in a saturated solution, each concentration term raised to the power equal to the no. of ions produced.

(iii) Negative logarithm of hydrogen ion concentration.

9. The values of K_{sp} of two sparingly soluble salts $\text{Ni}(\text{OH})_2$ and AgCN are 2.0×10^{-15} and 6×10^{-17} respectively. Which salt is more soluble? Explain.

Solution



$$K_{sp} = [\text{Ag}^+][\text{CN}^-] = 6 \times 10^{-17}$$



$$K_{sp} = [\text{Ni}^{2+}][\text{OH}^-]^2 = 2 \times 10^{-15}$$

$$\text{Let } [\text{Ag}^+] = S_1, \text{ then } [\text{CN}^-] = S_1$$

$$\text{Let } [\text{Ni}^{2+}] = S_2, \text{ then } [\text{OH}^-] = 2S_2$$

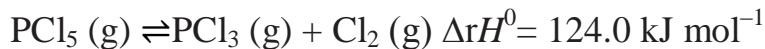
$$S_1^2 = 6 \times 10^{-17}, S_1 = 7.8 \times 10^{-9}$$

$$(S_2)(2S_2)^2 = 2 \times 10^{-15}, S_2 = 0.58 \times 10^{-4}$$

$\text{Ni}(\text{OH})_2$ is more soluble than AgCN .

FIVE MARKS QUESTIONS

1. At 473 K, equilibrium constant K_c for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3} . If decomposition is depicted as,



a) Write an expression for K_c for the reaction.

b) What is the value of K_c for the reverse reaction at the same temperature?

c) what would be the effect on K_c if (i) more PCl_5 is added (ii) pressure is increased (iii) the temperature is increased?

Ans: (a) $K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$

(b) 120.48

(c) (i) equilibrium will shift on RHS

(ii) equilibrium will shift on LHS

(iii) equilibrium will shift on RHS

2. Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction: $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$

(a) Write an expression for K_p for the above reaction.

(b) How will the values of K_p and composition of equilibrium mixture be affected by (i) increasing the pressure (ii) increasing the temperature (iii) using a catalyst?

Ans. (a) $K_p = \frac{p(\text{CO}) \cdot p(\text{H}_2)^3}{p(\text{CH}_4) \cdot p(\text{H}_2\text{O})}$

(b) (i) value of K_p will not change, equilibrium will shift in backward direction.

(ii) Value of K_p will increase and reaction will proceed in forward direction.

(iii) no effect.

3. What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species: HNO_2 , CN^- , HClO_4 , F^- , OH^- , CO_3^{2-} , and S^{2-}

Ans. The acid-base pair that differs only by one proton is called a conjugate acid-base pair

Species	Conjugate acid/base
HNO_2	NO_2^-
CN^-	HCN
HClO_4	ClO_4^-
F^-	HF
OH^-	H_2O
CO_3^{2-}	HCO_3^{2-}

S^{2-}	HS^-
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HOTS QUESTIONS

1. The value of K_c for the reaction $2A \rightleftharpoons B + C$ is 2×10^{-3} . At a given time, the composition of reaction mixture is $[A] = [B] = [C] = 3 \times 10^{-4}$ M. In which direction the reaction will proceed?

Solution

For the reaction the reaction quotient Q_c is given by, $Q_c = [B][C] / [A]^2$

as $[A] = [B] = [C] = 3 \times 10^{-4}$ M

$$Q_c = (3 \times 10^{-4})(3 \times 10^{-4}) / (3 \times 10^{-4})^2 = 1$$

as $Q_c > K_c$ so the reaction will proceed in the reverse direction.

2. PCl_5 , PCl_3 and Cl_2 are at equilibrium at 500 K and having concentration 1.59 M PCl_3 , 1.59 M Cl_2 and 1.41 M PCl_5 . Calculate K_c for the reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Solution

The equilibrium constant K_c for the above reaction can be written as,

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= (1.59)^2 / 1.41 = 1.79$$

3. Why is ammonia termed as a base though it does not contain OH^- ions?

Ans. ammonia is termed as a base on the basis of Lewis concept it can donate a lone pair of electrons.

SUMMARY

7 .Equilibrium

Some Important Points and Terms of the Chapter

1. **Equilibrium** represents the state of a process in which the properties like temperature, pressure etc do not show any change with the passage of time
2. **Chemical equilibrium:** When the rates of the forward and reverse reactions become equal, the concentrations of the reactants and the products remain constant. This is the stage of chemical equilibrium. This equilibrium is *dynamic* in nature as it consists of a *forward* reaction in which the reactants give product(s) and *reverse* reaction in which product(s) gives the original reactants. Equilibrium is possible only in a closed system at a given temperature. A mixture of reactants and products in the equilibrium state is called an equilibrium mixture.
3. In a **Homogeneous system**, all the reactants and products are in the same phase. For example, in the gaseous reaction, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$, reactants and products are in the homogeneous phase.
4. Equilibrium in a system having more than one phase is called **heterogeneous equilibrium**. The equilibrium between water vapor and liquid water in a closed container is an example of heterogeneous equilibrium. $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$

calculated by substituting the concentration terms in mol/L and for K_p partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same. For the reactions (i) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}$, K_c and K_p have no unit. (ii) $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$, K_c has unit mol/L and K_p has unit bar

9. Characteristics Of Equilibrium Constant

- Equilibrium constant is applicable only when concentrations of the reactants and products have attained their equilibrium state.
- The value of equilibrium constant is independent of initial concentrations of the reactants and products.
- Equilibrium constant is temperature dependent having one unique value for a particular reaction represented by a balanced equation at a given temperature.
- The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction.
- The equilibrium constant K for a reaction is related to the equilibrium constant of the corresponding reaction, whose equation is obtained by multiplying or dividing the equation for the original reaction by a small integer.

10. Applications of equilibrium constant :

- Predict the extent of a reaction on the basis of its magnitude.

whereas H_2 is consumed i.e more of H_2 and I_2 react to form HI and finally the equilibrium shifts in forward direction.

- **Effect of change of pressure:** When the pressure is increased the equilibrium shifts in the direction in which the number of moles of the gas decreases.

Consider the reaction, $\text{CO (g)} + 3\text{H}_2 \text{(g)} \rightleftharpoons \text{CH}_4 \text{(g)} + \text{H}_2\text{O (g)}$ Here, 4 mol of gaseous reactants ($\text{CO} + 3\text{H}_2$) become 2 mol of gaseous products ($\text{CH}_4 \text{(g)} + \text{H}_2\text{O}$). so by Le Chatelier's principle. The increase in pressure will shift the equilibrium in the forward direction, a direction in which the number of moles of the gas or pressure decreases.

- **Effect of change of Temperature:** When a change in temperature occurs, the value of equilibrium constant changes. In general, the temperature dependence of the equilibrium constant depends on the sign of ΔH for the reaction. The equilibrium constant for an exothermic reaction (-ve ΔH) decreases as the temperature increases. The equilibrium constant for an endothermic reaction (+ve ΔH) increases as the temperature increases. When the Temperature is increased the equilibrium shifts in the direction in of endothermic reaction.

Consider a reaction $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$ $\Delta H = -92.38\text{Kj/mol}$

According to Le Chatelier's principle, raising the temperature shifts the equilibrium to left (backward direction i.e direction of endothermic reaction) and decreases the equilibrium concentration of ammonia.

amount. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression.

Summary of Le Chatelier's Principle

Type of Effect or Change	Direction of Equilibrium
Addition of more reactants	Forward direction
Addition of more products	Backward direction
Increase in temperature	Towards endothermic reaction
Decrease in temperature	Towards exothermic reaction
Addition of Catalyst	No effect
Increase in Pressure	where the no. of gaseous moles are less
Decrease in Pressure	where the no. of gaseous moles are more

