

## Chapter 08

### Chemical Equilibrium



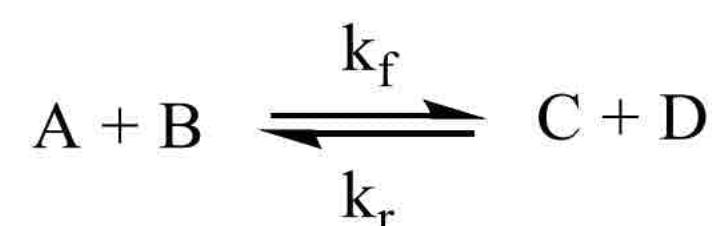
#### Law of Mass Action

##### Statement

The rate at which the reaction proceeds is directly proportional to the product of the active masses of the reactants.

##### General reaction

Consider a general reaction in which A and B are the reactants and C and D are the products.



The equilibrium concentrations, called active mass, of A, B, C and D are represented in square brackets like [A], [B], [C] and [D] respectively and they are expressed in moles dm<sup>-3</sup>.

##### Rate of forward reaction

According to the law of mass action, the rate of the forward reaction, is proportional to the product of molar concentrations of A and B.

$$\text{Rate of forward reaction (R}_f\text{)} \propto [A][B]$$

OR

$$R_f = k_f [A][B]$$

k<sub>f</sub> = proportionality constant and is called rate constant for forward reaction.

R<sub>f</sub> = rate of forward reaction.

##### Rate of reverse reaction

The rate of reverse reaction (R<sub>r</sub>) is given by:

$$\text{Rate of reverse reaction (R}_r\text{)} \propto [C][D]$$

$$R_r = k_r [C][D]$$

k<sub>r</sub> = proportionality constant and is called the rate constant for backward reaction.

##### At equilibrium

$$\text{Rate of forward reaction} = \text{Rate of reverse reaction}$$

$$R_f = R_r$$

Putting the values

$$k_f [A][B] = k_r [C][D]$$

Rearrangement

$$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

$$\frac{k_f}{k_r} = K_c$$

$$K_c = \frac{[C][D]}{[A][B]}$$

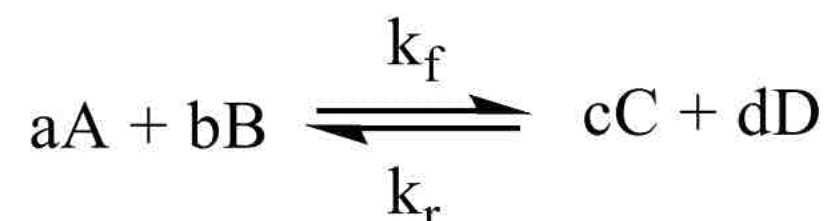
$$K_c = \frac{[\text{products}]}{[\text{reactants}]}$$



$$K_c = \frac{\text{rate constant for forward step}}{\text{rate constant for reverse step}}$$

$K_c$  = equilibrium constant

### General reaction



Where a, b, c and d are the coefficients of balanced chemical equation.

### Equilibrium constant

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

### Applications of Equilibrium Constant

Following are the applications of equilibrium constant:

1. Direction of reaction
2. Extent of reaction
3. Effect of various factors on equilibrium constant and equilibrium position

#### 1. Direction of reaction

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

The direction of a chemical reaction at any particular time can be predicted by means of [products] / [reactants] ratio, calculated before the reaction attains equilibrium.

#### Possibilities

The value of [product] / [reactants] ratio leads to one of the following three possibilities:

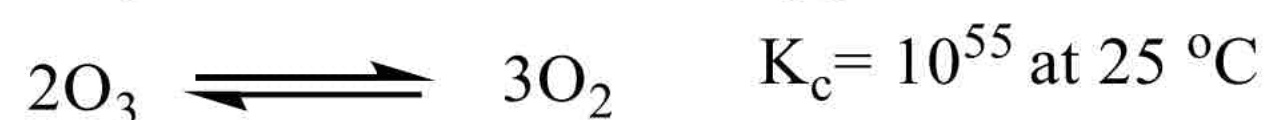
- (a) The ratio is less than  $K_c$ . The reaction will proceed in the forward direction.
- (b) The ratio is greater than  $K_c$ . The reaction will proceed in the reverse direction.
- (c) The ratio is equal to  $K_c$ . The reaction is at equilibrium.

#### 2. Extent of reaction

- (a) If the equilibrium constant is very large, this indicates that the reaction is almost complete.
- (b) If the value of  $K_c$  is small, it reflects that the reaction does not proceed appreciably in the forward direction.
- (c) If the value of  $K_c$  is very small, this shows a very little forward reaction.

#### Examples

1. Equilibrium constant for the decomposition of ozone to oxygen is  $10^{55}$  at  $25^\circ\text{C}$ .



This reaction is almost complete.

2. The value of equilibrium constant for the decomposition of HF at  $2000^\circ\text{C}$  is  $10^{-13}$ .



It indicates high stability and slow decomposition of HF even at  $2000^\circ\text{C}$ .

#### 3. The Effect of Conditions on the Position of Equilibrium



Equilibrium constant and position of equilibrium are two different entities.

### **Difference between equilibrium constant and equilibrium position**

$K_c$  is equilibrium constant and has constant value at a particular temperature whereas the ratio of products to reactants in equilibrium mixture is described as the position of equilibrium

### **Change of equilibrium position**

Equilibrium position can change if the external conditions e.g. temperature, pressure and concentrations are altered.

### **Value of $K_c$ and equilibrium position**

For a reversible reaction:

If  $K_c$  is large the position of equilibrium lies on the right.

If  $K_c$  is small the position of equilibrium lies on the left.

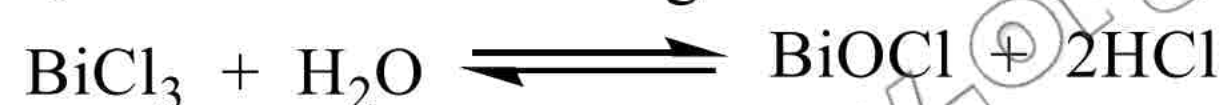
## **The Le-Chatelier's Principle**

### **Statement**

If a stress is applied to a system at equilibrium the system acts in such a way so as to nullify, as far as possible, the effect of that stress.

### **(a) Effect of Change in Concentration**

Consider the reaction in which  $\text{BiCl}_3$  reacts with water to give a white insoluble compound  $\text{BiOCl}$ .



### **Equilibrium constant**

$$K_c = \frac{[\text{BiOCl}][\text{HCl}]^2}{[\text{BiCl}_3][\text{H}_2\text{O}]}$$

Aqueous solution of  $\text{BiCl}_3$  is cloudy because of hydrolysis and formation of  $\text{BiOCl}$ .

### **Addition of HCl**

If a small amount of  $\text{HCl}$  is added to this solution, it will disturb the equilibrium and force the system to move in such a way so that effect of addition of  $\text{HCl}$  is minimized. The reaction will move in the backward direction to restore the equilibrium again and a clear solution will be obtained.

### **Addition of $\text{H}_2\text{O}$**

However, if water is added to the above solution the system will move in the forward direction and the solution will again become cloudy.

The shifting of reaction to forward and backward direction by disturbing the concentration is just according to Le-Chatelier's principle.

### **Conclusion**

Addition of a substance among the reactants or the removal of a substance among the products at equilibrium stage disturbs the equilibrium position and reaction is shifted to forward direction. The addition of a substance among the products or the removal of a substance among the reactants will derive the equilibrium towards the backward direction. Removing one of the products formed can increase the yield of a reversible reaction. The value of  $K_c$  remains constant.

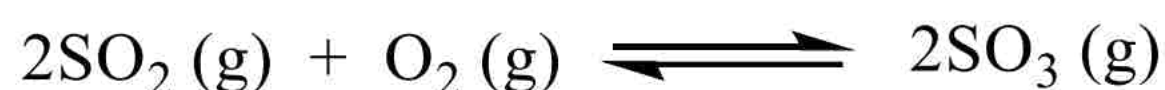
### **(b) Effect of Change in Pressure or Volume**

The change in pressure or volume is important only for the reversible gaseous reactions where the number of moles of reactants and products are not equal.

### **Example**

Take the example of formation of  $\text{SO}_3$  gas from  $\text{SO}_2$  gas and  $\text{O}_2$  gas.





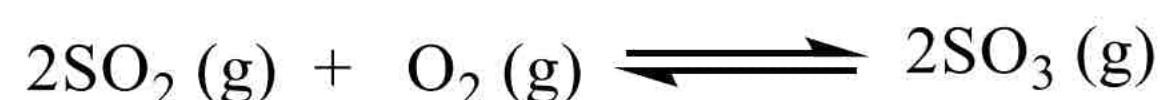
This gas phase reaction proceeds with the decrease in the number of moles and hence decreases in volume at equilibrium stage.

#### Effect of pressure/volume change at equilibrium

When the reaction approaches the equilibrium stage the volume of the equilibrium mixture is less than the volume of reactants taken initially. If one decreases the volume further at equilibrium stage the reaction is disturbed. It will move to the forward direction to minimize the effect of disturbance. It establishes a new equilibrium position while  $K_c$  remains constant. The reverse happens when the volume is increased or pressure is decreased at equilibrium stage.

#### (c) Quantitative Effect of Volume on Equilibrium Position

The quantitative effect of change of volume or pressure can be inferred from the mathematical expression of  $K_c$  for  $\text{SO}_3$  (g) synthesis.



#### Equilibrium constant expression

$$K_c = \frac{4x V}{(a-2x)(b-x)}$$

$V$  = volume of reaction mixture at equilibrium stage

$a$  and  $b$  = the number of moles of  $\text{SO}_2$  and  $\text{O}_2$  present initially

$Y$  = the number of moles of oxygen which has reacted at equilibrium.

#### Effect of volume change at equilibrium

According to the above equation, when volume is increased, then ' $x$ ' has to be decreased to keep  $K_c$  constant. The decrease of  $x$  means that reaction is pushed to the backward direction. From the amount of the increase in volume, we can calculate the amount of  $x$  which has to be decreased to keep  $K_c$  constant.

#### Effect of pressure change at equilibrium

Increasing the pressure on the above reaction at equilibrium will decrease the volume and the value of  $K_c$  will increase. In order to keep the value of  $K_c$  constant the reaction will move in the forward direction.

#### Dissociation of $\text{PCl}_5$

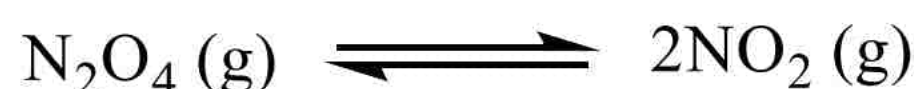
$\text{PCl}_5$  dissociates to give  $\text{PCl}_3$  and  $\text{Cl}_2$



#### Equilibrium constant

$$K_c = \frac{x^2}{V(a-x)}$$

#### Dissociation of $\text{N}_2\text{O}_4$



#### Equilibrium constant

$$K_c = \frac{4x^2}{V(a-x)}$$

Both these reactions have the factor of volume present in the denominator.

#### Reason



The reason is that numbers of moles of products are greater than those of reactants. So, increase in pressure will decrease  $x$  to keep the value of  $K_c$  constant and the reaction will be pushed to the backward direction.

### Effect on $K_c$ and equilibrium position

The equilibrium position is disturbed but not the  $K_c$  value.

### Reactions not affected by pressure/volume change

Those gaseous reactions, in which number of moles of reactants and products are same, are not affected by change in pressure or volume. Same is the case for reactions in which the participating substances are either liquids or solids.

### (d) Effect of Change in Temperature

Most of the reversible chemical reactions are disturbed by change in temperature. A temperature increase favours the endothermic reactions and a temperature decrease favours the exothermic reactions.

### Change of equilibrium constant

The equilibrium constant changes by the change of temperature because the equilibrium position shifts without any substance being added or removed.

#### Example 1

Consider the following exothermic reaction in gas phase at equilibrium taking place at a known temperature.



### Temperature change at equilibrium

At equilibrium stage, if we take out heat and keep the system at this new lower temperature, the system will readjust itself, so as to compensate the loss of heat energy. More of  $\text{CO}$  and  $\text{H}_2\text{O}$  molecules will react to form  $\text{CO}_2$  and  $\text{H}_2$  molecules, thereby, liberating heat because reaction is exothermic in the forward direction. It means by decreasing temperature, we shift the initial equilibrium position to the right until a new equilibrium position is established. Heating the reaction at equilibrium will shift the reaction to the backward direction because the backward reaction is endothermic.

#### Example 2

Consider a salt such as  $\text{KI}$ . It dissolves in water and absorbs heat.



Let us have a saturated solution of  $\text{KI}$  in water at a given temperature at equilibrium.

### Effect of temperature on equilibrium

A rise in temperature at equilibrium favours more dissolution of the salt. Equilibrium is shifted to the forward direction. Cooling will favour crystallization of salt.

### Zero heat of solution

For some salts the heat of solution is close to zero. The solubility of these salts in water is not affected by the change in temperature.

#### Example

Formation of aqueous solution of  $\text{NaCl}$  is an example of such a salt.

### Negative heat of solution

Those substances, whose heats of solutions are negative (exothermic), decrease their solubilities by increasing temperature, as  $\text{LiCl}$  and  $\text{Li}_2\text{CO}_3$  etc.

### (e) Effect of Catalyst on Equilibrium Constant

In most of the reversible reactions the equilibrium is not always reached within a suitable short time. So, an appropriate catalyst is added.

### Role of catalyst

#### 1. Time to attain equilibrium lowered

A catalyst does not affect the equilibrium position of the reaction. It increases the rates of both forward and backward reactions and this reduces the time to attain the state of equilibrium.

#### 2. Energy of activation lowered



A catalyst lowers the energy of activation of both forward and reverse steps by giving new path to the reaction.

### Applications of Chemical Equilibrium in Industry

Concept of chemical equilibrium is widely applicable for preparation of certain materials on industrial scale.

#### **1. Synthesis of Ammonia by Haber's Process**

The process of ammonia synthesis was developed by German chemist F. Haber and first used in 1933.

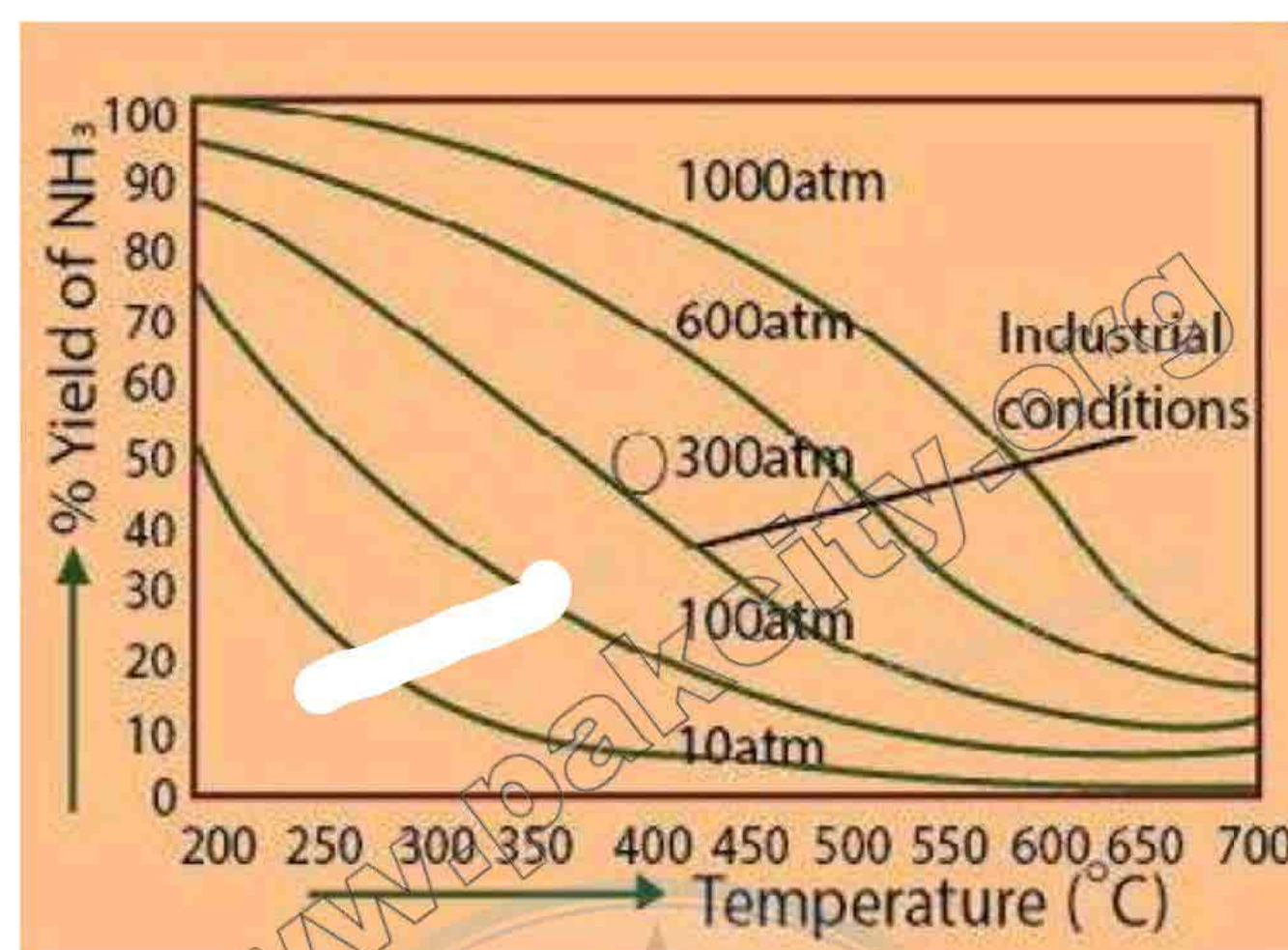
##### **Chemical equation**



##### **Ways to maximize yield**

- (i) By continual withdrawal of ammonia after intervals the equilibrium will shift to forward direction.
- ii) Increase the pressure to decrease the volume of the reaction vessel. Four moles of the reactants combine to give two moles of the products. High pressure will shift the equilibrium position to right to give more and more ammonia.
- (iii) Decreasing the temperature will shift it to the forward direction.

##### **Graphical representation**



At very high pressure and low temperature the yield of NH<sub>3</sub> is high but the rate of formation is low.

##### **Industrial conditions**

Industrial conditions denoted by circle are between 200 and 300 atmospheres at about 400 °C.

##### **Low temperature yield**

The yield of NH<sub>3</sub> is favoured at low temperature, but the rate of its formation does not remain favourable.

##### **Optimum conditions**

The optimum conditions are the pressure of 200-300 atm and temperature around 673 K (400 °C). The catalyst is the pieces of iron crystals embedded in a fused mixture of MgO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>.

##### **Equilibrium mixture**

The equilibrium mixture has 35% by volume of ammonia.

##### **Cooling of equilibrium mixture**

The mixture is cooled by refrigeration coils until ammonia condenses (B.P = -33.4 °C) and is removed.

##### **Recycling of gases**

Boiling points of nitrogen and hydrogen are very low they remain in the gaseous state and are recycled by pumps back into the reaction chamber.

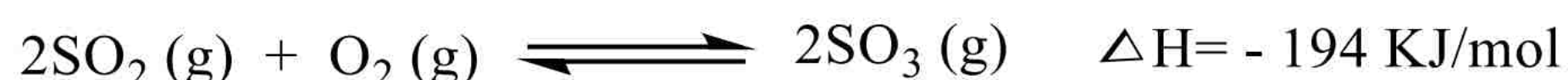
##### **Advantages of Haber's process**

Nearly 13% of all nitrogen fixation on earth is accomplished industrially through Haber's process. This process synthesizes approximately 110 million tons of ammonia in the world. About 80% of this is used for the production of fertilizers and some is used in manufacture of explosives or the production of nylon and other polymers.

#### **1. Preparation of Sulphur Trioxide**



In the contact process for manufacture of  $\text{H}_2\text{SO}_4$  the conversion of  $\text{SO}_2$  to  $\text{SO}_3$  is achieved in a reversible reaction.



### Low temperature

At low temperature, the equilibrium constant for formation of  $\text{SO}_3$  is large but equilibrium is reached very slowly.

### High temperature

As the temperature is raised the rate increases but the yield of  $\text{SO}_3$  drops off according to Le-Chatelier's principle.

### High pressure

High pressure tends to increase yield of  $\text{SO}_3$ .

### High oxygen level

The concentration of  $\text{O}_2$  (air) is increased to increase the yield of  $\text{SO}_3$ . During the process pressure is kept at one atmosphere.

### Optimum conditions

Effect of temperature reasonable time, a mixture of  $\text{SO}_2$  and  $\text{O}_2$  (air) at 1 atm pressure is passed over a solid catalyst at  $650^\circ\text{C}$ . The equilibrium mixture is then recycled at lower temperature, 400 to  $500^\circ\text{C}$ , to increase the yield of  $\text{SO}_3$ . The most effective catalysts are  $\text{V}_2\text{O}_5$  and finely divided platinum.

### Oleum and sulphuric acid

$\text{SO}_3$  is dissolved in  $\text{H}_2\text{SO}_4$  to get oleum which is diluted to get  $\text{H}_2\text{SO}_4$ .  $\text{H}_2\text{SO}_4$  is the king of chemicals.

## Common Ion Effect

### Definition

The addition of a common ion to the solution of a less soluble electrolyte suppresses its ionization and the concentration of unionized species increases, which may come out as a precipitate.

### Examples

#### 1. Purification of sodium chloride

Pass hydrogen chloride gas through saturated brine. Sodium chloride is fully ionized in the solution.



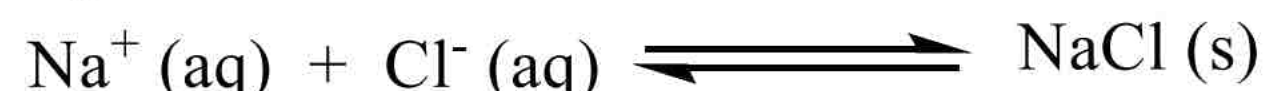
Equilibrium constant expression for this process can be written as follows:

$$K_c = \frac{[\text{Na}^+][\text{Cl}^-]}{[\text{NaCl}]}$$

HCl ionizes in solution



On passing HCl gas, concentration of  $\text{Cl}^-$  ions is increased, therefore NaCl crystallizes out of the solution to maintain the constant value of the equilibrium constant.



#### 2. Suppression of $\text{KClO}_3$ ionization

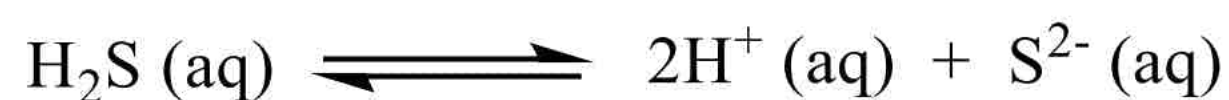
The solubility of a less soluble salt  $\text{KClO}_3$  in water is suppressed by the addition of a more soluble salt KCl by common ion effect.  $\text{K}^+$  is a common ion.



#### 3. Suppression of $\text{H}_2\text{S}$ dissociation

The dissociation of a weak acid  $\text{H}_2\text{S}$  in water can be suppressed by the addition of stronger acid HCl.  $\text{H}^+$  is a common ion.





### Application

This low concentration of  $\text{S}^{2-}$  ions helps to do the precipitation of radicals of second group basic radicals during salt analysis.

### 4. Suppression of $\text{NH}_4\text{OH}$ ionization

An addition of  $\text{NH}_4\text{Cl}$  in  $\text{NH}_4\text{OH}$  solution suppresses the concentration of  $\text{OH}^- \text{ (aq)}$  due to the presence of a large excess of  $\text{NH}_4^+$  from  $\text{NH}_4\text{Cl}$ . Actually,  $\text{NH}_4\text{Cl}$  is a strong electrolyte.



### Application

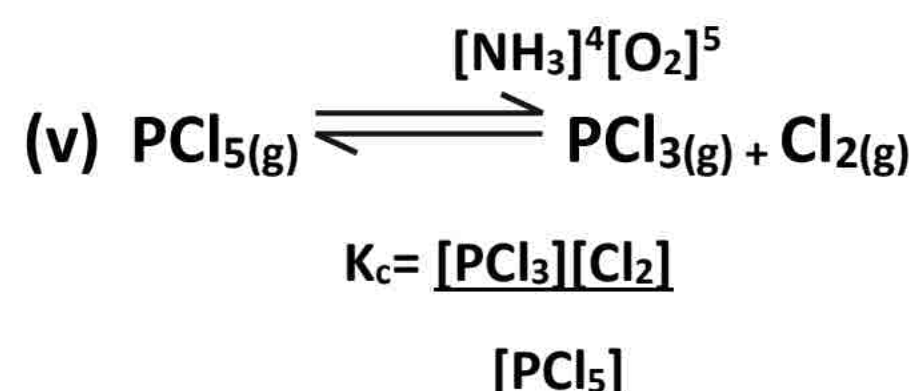
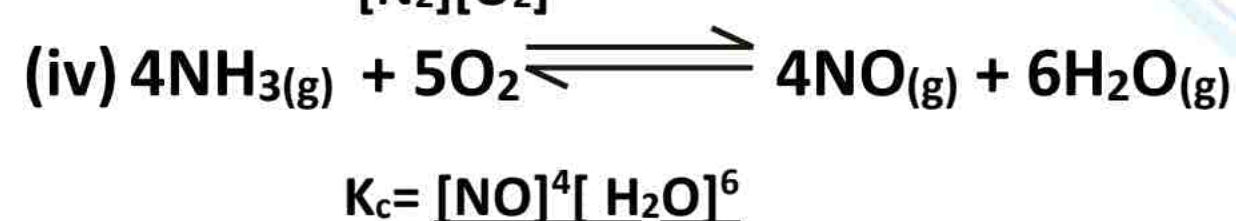
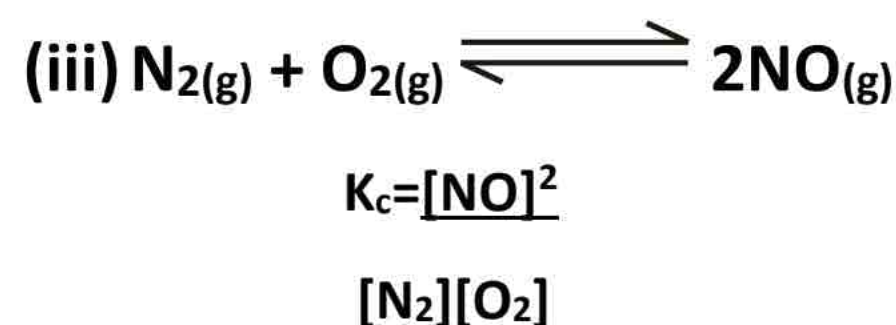
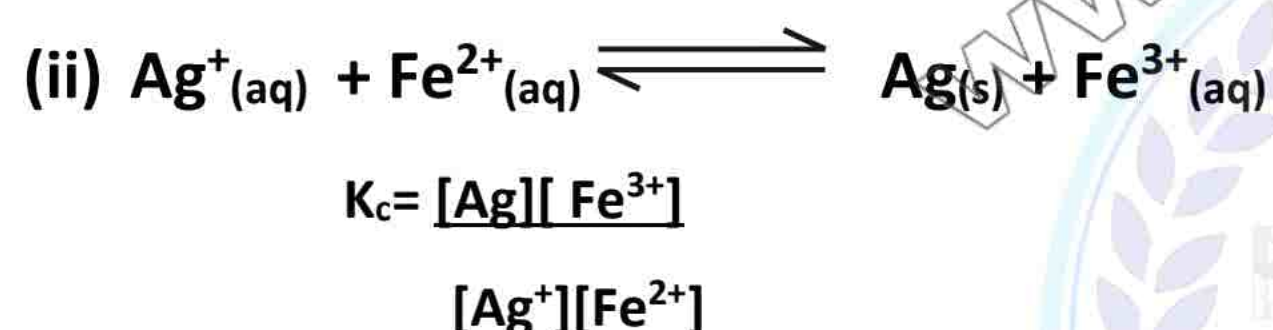
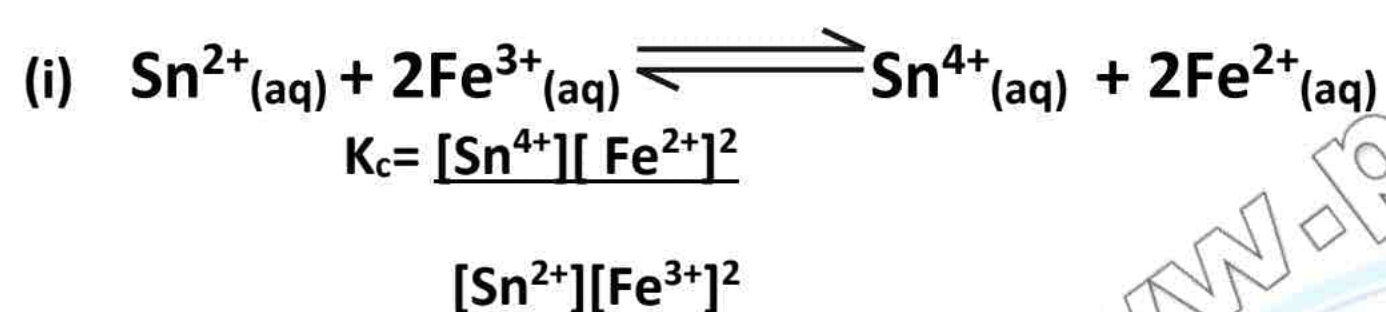
The combination of these two substances is used as a group reagent in third group basic radicals.

### 5. Qualitative analysis and buffer preparation

Common ion effect finds extensive applications in the qualitative analysis and the preparation of buffers.

### Numericals

4. Write  $K_c$  for the following reactions.



11. How would you prove that at  $25^\circ\text{C}$ ,  $1\text{dm}^3$  of water contains  $10^{-7}$  moles of  $\text{H}_3\text{O}^+$  and  $10^{-7}$  moles of  $\text{OH}^-$

Ans: In neutral water, at  $25^\circ\text{C}$ , The product of  $[\text{H}^+][\text{OH}^-]$  is equal to  $10^{-14}$

$$\text{As} \quad [\text{H}^+] = [\text{OH}^-]$$



$$\begin{aligned}
 \text{or} \quad [H^+][H^+] &= 10^{-14} \\
 [H^+]^2 &= 10^{-14} \\
 [H^+] &= 10^{-7} \text{ mol dm}^{-3} \\
 \text{and} \quad [OH^-] &= 10^{-7} \text{ mol dm}^{-3}
 \end{aligned}$$

19.  $K_c$  for the following reaction is 0.016 at 520°C



The equilibrium mixture contains  $[HI] = 0.08 \text{ M}$ ,  $[H_2] = 0.01 \text{ M}$  and  $[I_2] = 0.01 \text{ M}$ . To this mixture more HI is added so that its new concentration is 0.096 M. What will be the concentrations of HI,  $H_2$  and  $I_2$  when equilibrium is re-established?

Data:

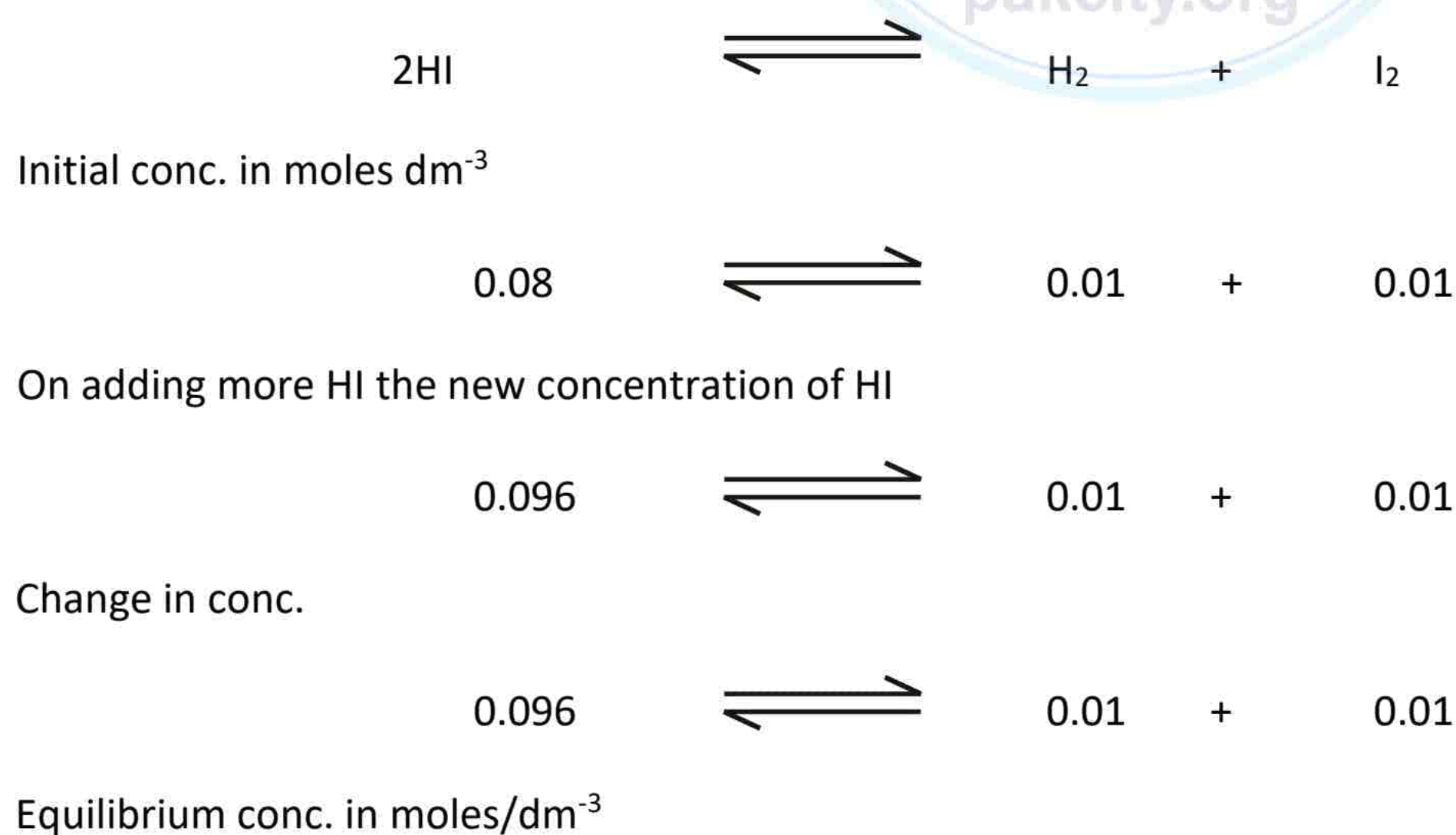
$$\begin{aligned}
 [HI] &= 0.08 \text{ M} \\
 [H_2] &= 0.01 \text{ M and} \\
 [I_2] &= 0.01 \text{ M} \\
 K_c &= 0.0016
 \end{aligned}$$

To Find:

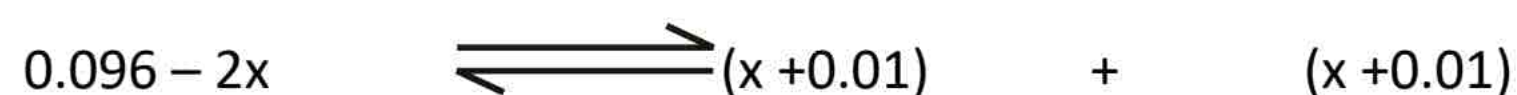
At equilibrium

$$\begin{aligned}
 [HI] &= ? \\
 [H_2] &= ? \\
 [I_2] &= ?
 \end{aligned}$$

Calculation and Result:







The equilibrium expression for the reaction can be written as:

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

On substituting the values we get

$$0.016 = \frac{(0.01 + x) \times (0.01 + x)}{(0.096 - 2x)^2}$$

$$0.016 = \frac{(0.01 + x)^2}{(0.096 - 2x)^2}$$

Taking square root on both sides

$$\sqrt{0.016} = \sqrt{\frac{(0.01 + x)^2}{(0.096 - 2x)^2}}$$

$$0.126 = \frac{0.01 + x}{0.096 - 2x}$$

$$0.126 (0.096 - 2x) = 0.01 + x$$

$$0.012 - 0.252x = 0.01 + x$$

$$0.012 - 0.01 = 0.252x + x$$

$$1.252x = 0.002$$

$$x = \frac{0.002}{1.252}$$

$$= 0.0016 \text{ mol dm}^{-3} = [I_2] = [H_2]$$

Conc. of HI at equilibrium =  $0.096 - 0.0016 = 0.095 \text{ mol dm}^{-3}$

**20. The equilibrium constant for the reaction between acetic acid and ethyl alcohol is 4.0. A mixture of 3 moles of acetic acid and 1 mole of  $C_2H_5OH$  (ethyl alcohol) is allowed to come to equilibrium. Calculate the amount of ethyl acetate present at equilibrium state in number of moles and grams. Also calculate the masses of reactants left behind.**

**Data:**

$$\text{Equilibrium constant } K_c = 4$$

$$\text{Initial conc. of acetic acid, } (CH_3COOH) = 3$$

$$\text{Initial conc. of ethyl alcohol } C_2H_5OH = 1 \text{ mol}$$

**To Find:**

$$\text{Amount of ethyl acetate present at equilibrium} = ?$$

Let the number of moles of ethyl acetate at equilibrium = x moles



**Chemical Equation:**

Initial conc. in moles:

Equilibrium conc. in moles  $\text{dm}^{-3}$ **Formula:**

Equilibrium constant expression for the reaction can be written as:

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

Substituting the values

$$4 = \frac{(x)(x)}{(3-x)(1-x)}$$

$$4 = \frac{x^2}{x^2 - 4x + 3}$$

By cross multiplying

$$4(x^2 - 4x + 3) = x^2$$

$$4x^2 - 16x + 12 = x^2$$

$$3x^2 - 16x + 12 = 0$$

To find out the values of x, since

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

Here a = 3, b = -16 and c = 12

Putting these values

$$x = \frac{+16 \pm \sqrt{(-16)^2 - 4(3)(12)}}{2(3)}$$

$$= \frac{+16 \pm \sqrt{256 - 144}}{6}$$

$$= \frac{+16 \pm \sqrt{116}}{6}$$

$$= 4.43 \text{ or } 0.9 \text{ mol}$$

The values, x = 4.43 moles is not possible as it is greater than the concentrations of the reactant. Thus 0.9 mole of ethyl acetate is present at equilibrium.

Number of moles of ethyl acetate at equilibrium = 0.9 moles



Molar mass of ethyl acetate =  $88 \text{ g mol}^{-1}$

Mass of ethyl acetate =  $0.9 \times 88 = 79.46 \text{ g}$

Number of moles of water produced = 0.9 moles

Molar mass of water =  $18 \text{ g mol}^{-1}$

Mass of water produced =  $0.9 \times 18 = 16.2 \text{ g}$

Moles of acetic acid left behind =  $3 - x = 3 - 0.9 = 2.1$  moles

Molar mass of acetic acid =  $60 \text{ g mol}^{-1}$

Mass of alcohol left behind =  $2.1 \times 60 = 126 \text{ g}$

Moles of alcohol left behind =  $1.0 - 0.9 = 0.1$

Molar mass of ethyl alcohol =  $46 \text{ g mol}^{-1}$

Mass of alcohol left behind =  $0.1 \times 46 = 4.6 \text{ g}$

## 21. Study the equilibrium



(a) Write an expression of  $K_p$

(b) When 1.00 mole of steam and 1.00 mole of carbon monoxide are allowed to reach equilibrium, 33.3% of the equilibrium mixture is hydrogen. Calculate the value of  $K_p$ . State the unit of  $K_p$ .

Solution (a):

$$(a) \quad K_p = \frac{P_{\text{H}_2} P_{\text{CO}_2}}{P_{\text{H}_2\text{O}} P_{\text{CO}}}$$

Solution(b):

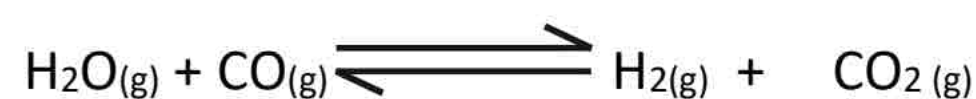
Data:

Moles of steam	=	1.00
Moles of $\text{CO}_2$	=	1.00
Conc. Of $\text{H}_2$ in equilibrium mixture	=	33.3%

To Find:

Value and units of  $K_p$  = ?

Calculation and Result:



Initial conc.    1 mole    1 mole    0 mole    0 mole



Eq. Conc.	1 - X	1 - X moles	x moles	x moles
Total moles of reactants and products	=	(1 - x) + (1 - x) + x + x		
Total moles at equilibrium	=	2 moles		
Conc. of H <sub>2</sub> at equilibrium	=	33%		
	=	$\frac{33}{100} \times 2 = 0.66$ mole		
	X	=	0.66	
K <sub>c</sub>	=	$\frac{[H_2][CO_2]}{[H_2O][CO]}$		
	=	$\frac{(x)(x)}{(1-x)(1-x)}$		
	=	$\frac{(0.66)(0.66)}{(1-0.66)(1-0.66)}$		
	=	$\frac{(0.66)(0.66)}{(0.33)(0.33)}$		
K <sub>c</sub>	=	4		

Since  $K_p = K_c(RT)^{\Delta n}$

$\Delta n = n_{\text{products}} - n_{\text{reactants}} = 2 - 2 = 0$

As number of moles of reactants are equal to that of products so  $K_p = K_c = 4$

## 22. Calculate the pH of following:

### (a) $10^{-4} \text{ mol dm}^{-3}$ of HCl

HCl ionizes as



Since HCl is strong acid and it is 100% dissociated. Hence  $10^{-4} \text{ mol/dm}^3$  of HCl produces  $10^{-4} \text{ mol/dm}^3$  of H<sup>+</sup> ions

Thus,

$$[H^+] = 10^{-4} \text{ mol/dm}^3$$

$$pH = -\log [H^+]$$

$$pH = -\log [10^{-4}]$$

$$pH = 4$$

### (b) $10^{-4} \text{ mol dm}^{-3}$ of Ba(OH)<sub>2</sub>

Ba(OH)<sub>2</sub> ionizes as



Since Ba(OH)<sub>2</sub> is strong base and it is 100% dissociated. Hence  $2 \times 10^{-4} \text{ mol/dm}^3$  of Ba(OH)<sub>2</sub> produces  $10^{-4} \text{ mol/dm}^3$  of OH<sup>-</sup> ions

$$[OH^-] = 10^{-4} \text{ mol/dm}^3$$

$$pOH = -\log [OH^-]$$

$$pOH = -\log (2 \times 10^{-4})$$

$$pOH = 3.699$$

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

$$pH = 14 - pOH$$

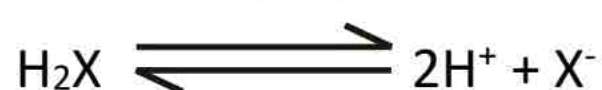


$$\text{pH} = 14 - 3.699$$

$$\text{pH} = 10.301$$

**(c) 1 mol dm<sup>-3</sup> of H<sub>2</sub>X, which is 50% dissociated**

H<sub>2</sub>X ionizes as



1 mole of H<sub>2</sub>X produces 2 moles of H<sup>+</sup> ions if 100% dissociated

However, since H<sub>2</sub>X is 50% dissociated therefore 1 mole of H<sub>2</sub>X produce 1 mole of H<sup>+</sup> ion

Thus,

$$[\text{H}^+] = 1 \text{ mol/dm}^3$$

$$\text{pH} = -\log [1]$$

$$\text{pH} = 0$$

**(d) 1 mol/dm<sup>3</sup> of NH<sub>4</sub>OH that is 1% dissociated**

NH<sub>4</sub>OH ionizes as



It shows that 1mole of NH<sub>4</sub>OH produces 1 mole of OH<sup>-</sup> ions. NH<sub>4</sub>OH is only 1% dissociated

Hence

$$\% \text{ dissociation} = \frac{\text{mol of OH}^-}{\text{Total moles of NH}_4\text{OH}} \times 100$$

$$1 = \frac{\text{mol of OH}^-}{1} \times 100$$

$$\text{mol of OH}^- = \frac{1}{100} \times 1$$

$$\text{OH}^- = 0.01 \text{ mol dm}^{-3}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{pOH} = -\log [0.01]$$

$$\text{pOH} = 2$$

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

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

$$\text{pH} = 14 - 2$$

$$\text{pH} = 12$$

**23. (a) Benzoic acid, C<sub>6</sub>H<sub>5</sub>COOH, is a weak non-basic (K<sub>a</sub> = 6.4 × 10<sup>-5</sup> mol dm<sup>-3</sup>). What is the pH of a solution containing 7.2g of sodium benzoate in one dm<sup>3</sup> of 0.02 mole dm<sup>-3</sup> of benzoic acid?**

**Data:**

$$\text{K}_a \text{ of Benzoic acid} = 6.4 \times 10^{-5}$$

$$\text{Mass of sodium benzoate, C}_6\text{H}_5\text{COONa} = 7.2 \text{ g}$$

$$\text{Moles of benzoic acid} = 0.02 \text{ moles}$$

**To Find:**

$$\text{pH of the Solution} = ?$$

**Calculation and Result:**

$$\text{Molar mass of C}_6\text{H}_5\text{COONa} = 144 \text{ g/mole}$$

$$\text{Moles of C}_6\text{H}_5\text{COONa} = \frac{7.2}{144}$$



$$\begin{aligned} &= 0.05 \text{ moles} \\ \text{Moles of benzoic acid} &= 0.02 \text{ moles} \end{aligned}$$

$$\begin{aligned} \text{pH} &= \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ &= -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ &= -\log (6.4 \times 10^{-5}) + \log \frac{[0.05]}{[0.02]} \\ &= -(0.80 - 5) + \log 2.5 \\ &= 5 - 0.80 + 0.39 \\ \text{pH} &= 4.59 \end{aligned}$$

**(b) A buffer solution has been prepared by mixing 0.2 M CH<sub>3</sub>COONa and 0.5 M CH<sub>3</sub>COOH in 1 dm<sup>3</sup> of solution. Calculate the pH of solution. pK<sub>a</sub> of acid=4.74 at 25°C. How the value of pH will change by adding 0.1 mole of NaOH and 0.1 mole of HCl.**

**Data:**

$$[\text{CH}_3\text{COOH}] = 0.5 \text{ M} \quad [\text{CH}_3\text{COONa}] = 0.2 \text{ M}$$

$$\text{pK}_a = 4.74$$

**To Find:**

$$\text{pH} = ?$$

**Calculation and Result:**

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

$$\text{pH} = 4.74 + \log \frac{0.2}{0.5}$$

$$\text{pH} = 4.74 + \log 0.4$$

$$\text{pH} = 4.74 - 0.4 \text{ or } \text{pH} = 4.34$$

By adding 0.1 M NaOH, concentration of CH<sub>3</sub>COOH decreases to 0.4 M and that of CH<sub>3</sub>COONa increases 0.3 M, thus new concentrations are

$$[\text{CH}_3\text{COOH}] = 0.4 \text{ M} \quad [\text{CH}_3\text{COONa}] = 0.3 \text{ M}$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$



$$\text{pH} = 4.74 + \log \frac{0.3}{0.4}$$

$$\text{pH} = 4.74 + \log (0.75)$$

$$\text{pH} = 4.74 - 0.12 = \mathbf{4.62}$$

By adding 0.1 m HCl, concentration of  $\text{CH}_3\text{COONa}$  decreases from 0.2 M to 0.1 M and that of  $\text{CH}_3\text{COOH}$  increases from 0.5 M to 0.6 M.

$$[\text{CH}_3\text{COOH}] = 0.6 \text{ M} [\text{CH}_3\text{COONa}] = 0.1 \text{ M}$$

$$\text{pH} = \text{pka} + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

$$\text{pH} = 4.74 + \log \left( \frac{0.1}{0.6} \right)$$

$$\text{pH} = 4.74 - 0.78 = \mathbf{3.96}$$

**24. The solubility of  $\text{CaF}_2$  in water at  $25^\circ\text{C}$  is found to be  $2.05 \times 10^{-4} \text{ mol dm}^{-3}$ . What is the value of  $K_{\text{sp}}$  at this temperature?**

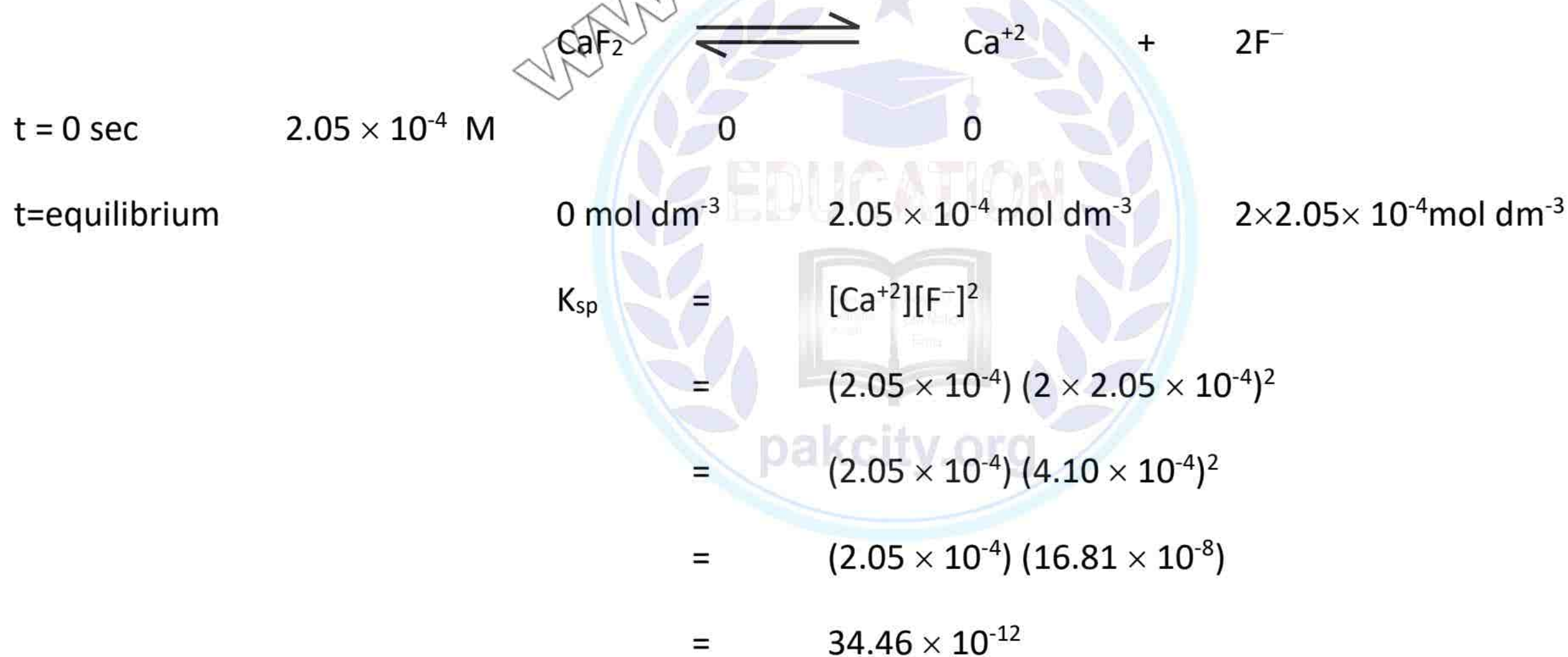
**Data:**

$$\text{Solubility or concentration of } \text{CaF}_2 = 2.05 \times 10^{-4} \text{ mol dm}^{-3}$$

**To Find:**

Value of  $K_{\text{sp}}$

**Calculation and Result:**



$$K_{\text{sp}} = \mathbf{3.446 \times 10^{-11} \text{ mol}^3 \text{dm}^{-9}}$$

**25. The solubility product of  $\text{Ag}_2\text{CrO}_4$  is  $2.6 \times 10^{-2}$  at  $25^\circ\text{C}$ . Calculate the solubility of the compound.**

**Data:**

$$\text{Solubility product of } \text{Ag}_2\text{CrO}_4 = K_{\text{sp}} = 2.6 \times 10^{-2}$$

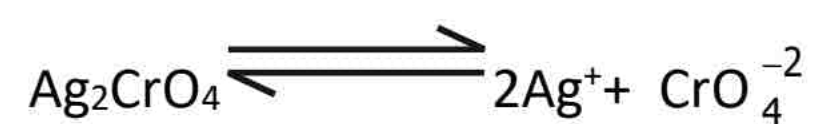
**To Find:**



Solubility of  $\text{Ag}_2\text{CrO}_4$  = ?

**Calculation and Result:**

Let solubility of  $\text{Ag}_2\text{CrO}_4$  be 'S'



Initial stage                      S                      0                      0

Equilibrium stage                S                      2S                      S

$$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{-2}]$$

$$2.6 \times 10^{-2} = (2S)^2(S)$$

$$2.6 \times 10^{-2} = 4S^3$$

$$\text{Or } S^3 = \frac{2.6 \times 10^{-2}}{4}$$

$$= 0.0065$$

$$S = \sqrt[3]{0.0065}$$

$$S = 0.1866 \text{ mol dm}^{-3}$$

**Important long questions from past papers**

17. Example# 2, 4, 5, 6, 7

18. Exercise Q. 23 (a, b), 24, 25

19. Write a note on synthesis of ammonia by Haber's process keeping in mind the applications of chemical equilibrium in industry.

20. State le-Chatelier's principle. Describe the effect of change in temperature of a system in equilibrium by this Principle.

21. State le-Chatelier's principle. How is this principle used to explain the effect of change in concentration on equilibrium constant of a reaction?

22. What is common ion effect? Explain it.