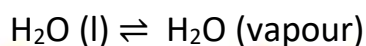


## CLASS XI Chapter 6 Equilibrium

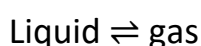
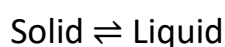
- A state in which reactants and products are present in concentrations which have no further tendency to change with time is known as equilibrium.
- In state of equilibrium the forward reaction take place at the same rate as the reverse reaction.
- There is no change in the concentrations of both the reactants and products.
- It is indicated by double half arrow, which indicates that the processes in both the directions are taking place simultaneously.
- For example: vaporization of water

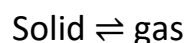


- It can be established not only for physical processes but also for chemical reactions.
- Based on the degree to which the reactions progress to reach the state of chemical equilibrium, these can be classified as follows:
  1. The reactions that reached almost to completion and only negligible concentrations of the reactants are left. In some cases, it might not be even possible to detect these experimentally.
  2. The reactions in which only small amounts of products are formed and most of the reactants remain unaffected at equilibrium stage.
  3. When the system is in equilibrium for a reaction in which the concentrations of the reactants and products are comparable.
- An equilibrium involving ions in aqueous solutions known as ionic equilibrium.

### Equilibrium in physical processes:

Equilibrium can be understood properly if we examine some physical processes like phase transformation reactions:





## 1. Solid-Liquid Equilibrium

- Water and ice kept in an insulated thermos flask at 273K and at room pressure are in equilibrium state.
- It is observed that mass of ice and water do not change with time, as the rates of transfer of molecules from ice into water and of reverse transfer from water into ice are equal at atmospheric pressure and 273 K.
- Here the system is in dynamic equilibrium and we can conclude the following:
  - (i) Both the opposing processes occur simultaneously.
  - (ii) Both the processes happen with same rate so the amount of ice and water remains constant.
- ❖ For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are in equilibrium is called the normal melting point or normal freezing point of that substance.

## 2. Liquid-Vapour Equilibrium

- To understand the Liquid-vapour equilibrium we consider an example of a transparent box which containing a U-tube with manometer.
- Drying agent for e.g. Anhydrous  $\text{CaCl}_2$  or  $\text{P}_2\text{O}_5$  is placed for a few hours in the box. After removing the drying agent by slanting the box on one side, a petri dish filled with water is quickly placed inside the box.

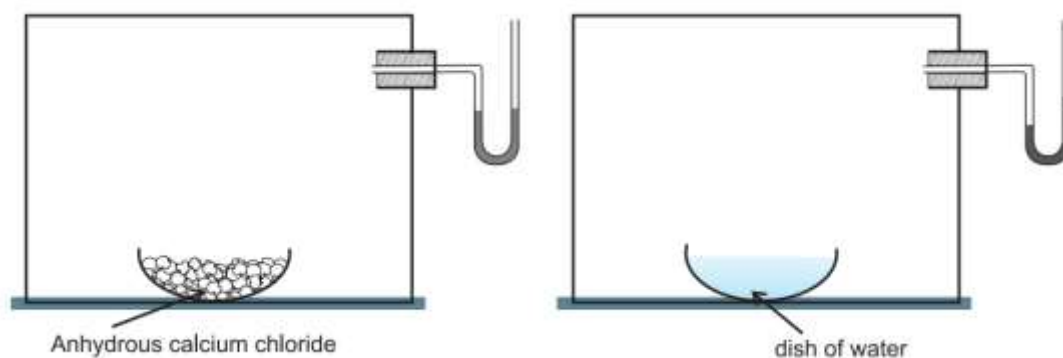
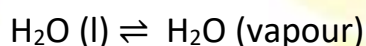


Figure: Measuring equilibrium vapour pressure of water at a constant temperature

- It is observed that the mercury level slowly increases in the right limb of the manometer and finally reaches a constant value, this indicates that pressure inside the box increases and attains a constant value.
- The volume of water in petri dish decreases. There was no water vapour inside the box in the beginning. As water gets evaporated the pressure in the box increases because of addition of water molecules into the gaseous phase inside the box.
- The rate of evaporation is constant. On the other hand the rate of increase with decreasing time due to condensation of vapour into water. At the equilibrium condition there is no net evaporation. We can conclude that the number of water molecules from the gaseous state into the liquid state also increases till the equilibrium is achieved.

Rate of evaporation = rate of condensation



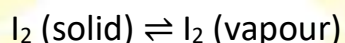
- At equilibrium the pressure applied by the H<sub>2</sub>O molecules at a given temperature remains constant and it is called the equilibrium vapour pressure of water. Vapour pressure of water increases with temperature.
- In the above experiment if water is replaced by methyl alcohol, acetone or ether, it is observed that different liquids have different equilibrium vapour pressures at the same temperature. The liquid having highest vapour pressure is more volatile and has a lower b.p.
- If we expose all three watch glasses containing separately 1mL each of CH<sub>3</sub>COCH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH, and H<sub>2</sub>O to atmosphere and repeat the experiment with different volumes of the liquids in a warmer room, it is observed that in all such cases the liquid eventually disappears and the time taken for complete evaporation depends on:
  1. The nature of the liquid,
  2. The amount of the liquid and
  3. The temperature.
- When the watch glass is placed in open to the atmosphere, then the rate of evaporation remains constant but the molecules are dispersed into large volume of atmosphere. Due to this the rate of

condensation from vapour to liquid state is much less than the rate of evaporation. It is not possible to attain equilibrium in an open system.

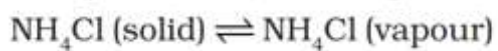
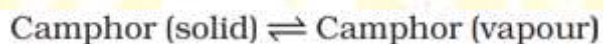
### 3. Solid – Vapour Equilibrium

- Let's consider a system in which solids sublime to vapour phase. If solid iodine is placed in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of color increases with time.

- After some time the intensity of color becomes constant and at this stage equilibrium is achieved. From this time solid iodine sublimes to give iodine vapour and the iodine vapour condenses to give solid iodine. The equilibrium can be expressed as:



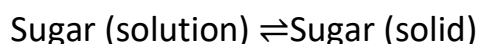
Some examples:



### Equilibrium involving dissolution of solid or gases in liquids

#### Solids in liquids

- There is a limited amount of salt or sugar can be dissolved into a given amount of water at room temperature. A thick sugar syrup solution is made by dissolving sugar at high temperature, if we cool the syrup to the room temperature sugar crystals will separate out.
- If there is not possible to dissolve any more solute in a solution at a given temperature then the solution is known as saturated solution.
- The solute's concentration in a saturated solution depends upon the temperature. There is a dynamic equilibrium in a saturated solution between the solute molecules in the solid state and in the solution:



- The rate of dissolution of sugar is equals to the rate of crystallization of sugar.

- Equality of the two rates and dynamic nature of equilibrium is confirmed by radioactive sugar.
- If we drop some radioactive sugar into saturated solution of non-radioactive sugar, then after some time radioactivity is observed both in the solution and in the solid sugar.
- In the beginning there was no any radioactive sugar molecules in the solution but due to dynamic equilibrium, there is an exchange of the radioactive and non-radioactive sugar molecules between the two phases.
- The ratio of the radioactive to non-radioactive molecules in the solution increases till reaches to a constant value.

### Gases in liquids

- When a soda water bottle is opened, some of the CO<sub>2</sub> gas dissolved in it fizzes out swiftly. The phenomenon arises due to difference in solubility of CO<sub>2</sub> at different pressures. There is equilibrium between the molecules of the gaseous state and the molecules dissolved of the liquid under pressure i.e.,
 
$$\text{CO}_2 (\text{gas}) \rightleftharpoons \text{CO}_2 (\text{in solution})$$
- This equilibrium is ruled by Henry's law, According to it the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas.
- This amount decreases with increase of temperature. When the bottle is opened, some of the dissolved CO<sub>2</sub> gas escapes to reach a new equilibrium condition required for the lower pressure, i.e. its partial pressure in the atmosphere. Thus the soda water bottle should not be left open to the air, otherwise it turns flat. It can be generalized that:
  1. For solid  $\rightleftharpoons$  liquid equilibrium, there is only one temperature (melting point) at 1 atm (1.013 bar) at which the two phases can coexist.
  2. The solubility is constant at a given temperature for dissolution of solids in liquids.
  3. For liquid vapour equilibrium, the vapour pressure is constant at a given temperature.

4. The concentration of a gas in liquid is proportional to the pressure of the gas over the liquid for dissolution of gases in liquids.

Table: Some Features of Physical Equilibrium

Process	Conclusion
Liquid $\rightleftharpoons$ Vapour $\text{H}_2\text{O (l)} \rightleftharpoons \text{H}_2\text{O (g)}$	$p_{\text{H}_2\text{O}}$ constant at given temperature
Solid $\rightleftharpoons$ Liquid $\text{H}_2\text{O (s)} \rightleftharpoons \text{H}_2\text{O (l)}$	Melting point is fixed at constant pressure
Solute(s) $\rightleftharpoons$ Solute(solution) Sugar(s) $\rightleftharpoons$ Sugar (solution)	Concentration of solute ) in solution is constant at a given temperature
Gas(g) $\rightleftharpoons$ Gas (aq) $\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{aq})$	$[\text{gas}(\text{aq})]/[\text{gas}(\text{g})]$ is constant at a given temperature $[\text{CO}_2(\text{aq})]/[\text{CO}_2(\text{g})]$ is constant at a given temperature

### General Characteristics of Equilibrium Involving Physical Processes

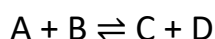
1. Equilibrium is possible only in a closed system at a given temperature.
2. There is a dynamic but stable condition and opposing reactions occur at the same rate.
3. When equilibrium is attained for a physical process, it is characterized by constant value of one of its parameters at a given temperature.
4. All properties of the system which are measurable remain constant.
5. The magnitude of measurable properties at any stage indicates the degree to which the physical process has proceeded before attaining equilibrium.

### Equilibrium in chemical processes – Dynamic equilibrium

- Analogous to the physical systems chemical reactions also attain a state of equilibrium. These reactions can take place in both forward and backward directions. When the rates of the forward and reverse

reactions turn out to be equal, the concentrations of the reactants and the products remain constant.

- This is the stage of chemical equilibrium. It consists of a forward reaction in which the reactants give products and reverse reaction in which products gives the original reactants so this equilibrium is dynamic in nature.
- Let's consider a reversible reaction



- As the reaction proceed, products C and D accumulate and depletion of the reactants A and B. This results a decrease in the rate of forward reaction and an increase in the rate of the reverse reaction.

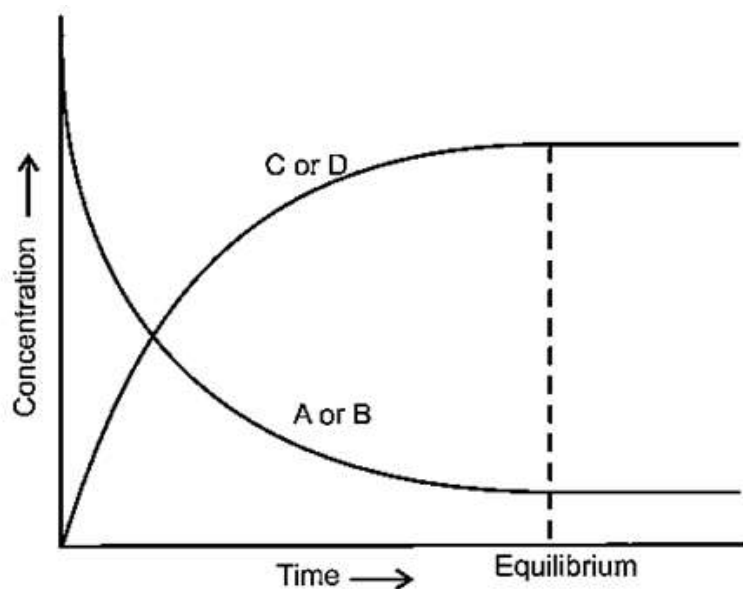
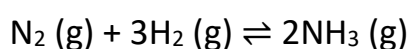


Figure: Attainment of chemical equilibrium.

- Finally, the two reactions occur at the same rate and the system attains a state of equilibrium.
- The reaction can meet the state of equilibrium even if we start with only C and D; there is no A and B being present initially.
- The dynamic nature of chemical equilibrium could be explained by the synthesis of ammonia by Haber's process. He takes known amounts of  $N_2$  and  $H_2$  maintained at high temperature and pressure and at regular intervals determined the amount of ammonia present in the reaction.

- He was successful in determining also the concentration of unreacted  $H_2$  and  $N_2$ . After some time composition of the mixture remains the same even though some of the reactants are still present, as the equilibrium attained.
- Synthesis of ammonia can explain well the dynamic equilibrium.  $D_2$  is taken in place of  $H_2$ .
- The reaction mixtures starting with either  $H_2$  or  $D_2$  attain equilibrium at the same composition, except that  $D_2$  and  $ND_3$  are present in place of  $H_2$  and  $NH_3$ . After equilibrium is attained, these two mixtures ( $H_2, N_2, NH_3$  and  $D_2, N_2, ND_3$ ) are mixed together.



- After some time this mixture is analysed, it is found that the concentration of ammonia is just the same as before.
- On the other hand, when this mixture is analysed by a mass spectrometer, it is found that ammonia and all deuterium containing forms of ammonia ( $NH_3, NH_2D, NHD_2$  and  $ND_3$ ) and  $H_2$  and its deuterated forms ( $H_2, HD$  and  $D_2$ ) are present.
- Thus it can be concluded that scrambling of H and D atoms in the molecules result from a continuation of the forward and reverse reactions in the mixture.

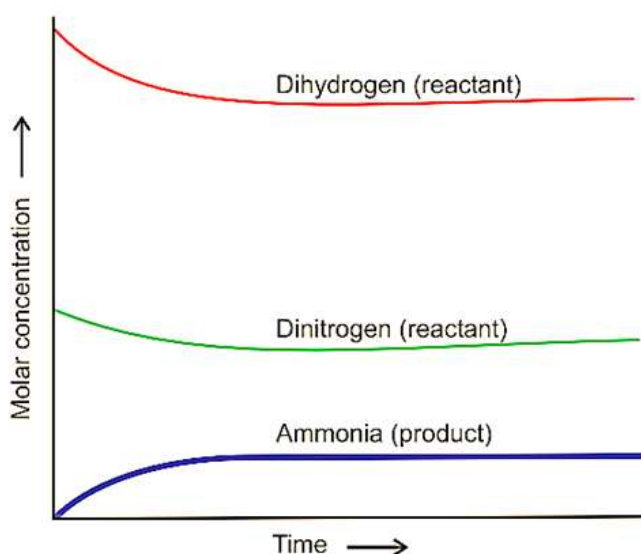
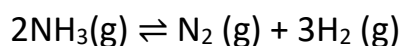
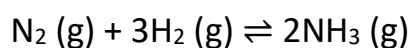


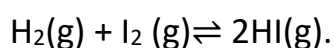
Figure: Depiction of equilibrium for the reaction



- If the reaction had stopped at equilibrium, then there would be no mixing of isotopes. Use of isotope like  ${}^2_1\text{H}$  in the formation of ammonia clearly indicates that reaction reach a state of dynamic equilibrium. Equilibrium can be attained by both sides.



### In case of HI



- If we start with equal initial concentration of  $\text{H}_2$  and  $\text{I}_2$ , the reaction proceeds in the forward direction and the concentration of  $\text{H}_2$ ,  $\text{I}_2$  decreases and HI increases, until equilibrium attained.

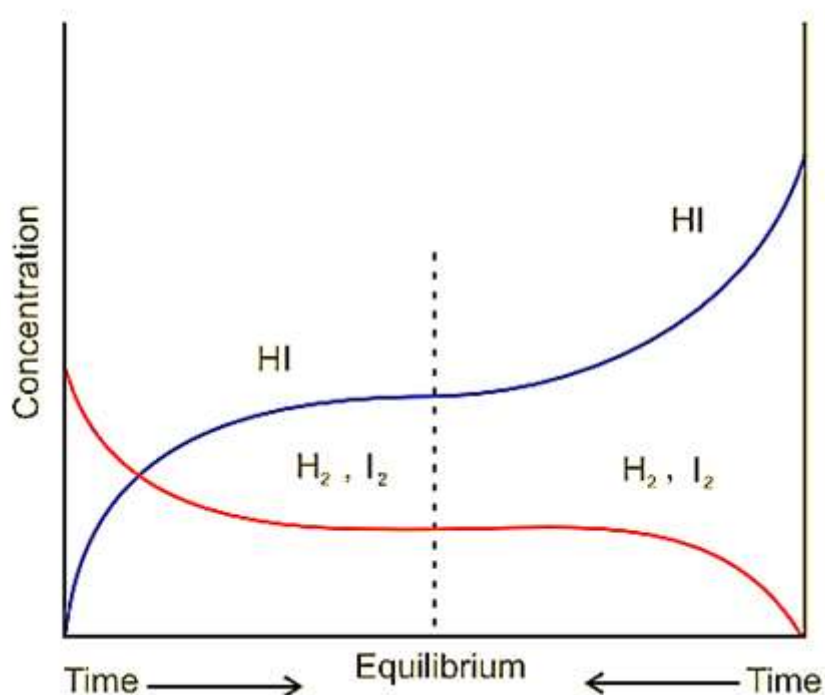


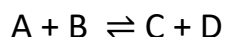
Figure: Chemical equilibrium in the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  can be attained from either direction

- If we start the reaction with only HI and make the reaction to proceed in the reverse direction.

- The concentration of HI is decreases and concentration of H<sub>2</sub> and I<sub>2</sub> is increases until the equilibrium is attained.

### Law of chemical equilibrium and equilibrium constant

- To understand the factors affecting equilibrium mixture; which is a mixture of products and reactants, let's consider a reversible reaction:



Here A and B = reactants

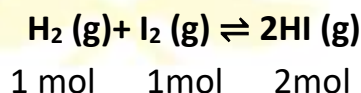
C and D = products in the balanced chemical equation.

- Cato Maximillian Guldberg and Peter Waage propounded in 1864 that the concentrations in an equilibrium mixture are related by the following equilibrium equation:

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

Here K<sub>c</sub> = equilibrium constant.

- The equilibrium equation is known as the law of mass action because in the early days of chemistry, concentration was called "active mass".
- Let's consider reaction between gaseous H<sub>2</sub> and I<sub>2</sub> carried out in a sealed vessel at temperature 731K.



- Six sets of experiments with varying initial conditions were performed in a sealed reaction vessel starting with gaseous H<sub>2</sub> and I<sub>2</sub> in 1, 2, 3 and 4 experiment and only HI in experiment 5 and 6. Experiment 1, 2, 3 and 4 were performed with different concentrations of H<sub>2</sub> or I<sub>2</sub>, and intensity of the purple color remained constant and equilibrium was attained.
- In experiments 5 and 6, the equilibrium was attained from the opposite direction.  
Data obtained from all six sets of experiments are given in Table below.

Experiment number	Initial concentration (mol L <sup>-1</sup> )			Equilibrium concentration (mol L <sup>-1</sup> )		
	[H <sub>2</sub> (g)]	[I <sub>2</sub> (g)]	[HI (g)]	[H <sub>2</sub> (g)]	[I <sub>2</sub> (g)]	[HI (g)]
1.	2.4 × 10 <sup>-2</sup>	1.38 × 10 <sup>-2</sup>	0	1.14 × 10 <sup>-2</sup>	0.12 × 10 <sup>-2</sup>	2.52 × 10 <sup>-2</sup>
2.	2.4 × 10 <sup>-2</sup>	1.68 × 10 <sup>-2</sup>	0	0.92 × 10 <sup>-2</sup>	0.20 × 10 <sup>-2</sup>	2.96 × 10 <sup>-2</sup>
3.	2.44 × 10 <sup>-2</sup>	1.98 × 10 <sup>-2</sup>	0	0.77 × 10 <sup>-2</sup>	0.31 × 10 <sup>-2</sup>	3.34 × 10 <sup>-2</sup>
4.	2.46 × 10 <sup>-2</sup>	1.76 × 10 <sup>-2</sup>	0	0.92 × 10 <sup>-2</sup>	0.22 × 10 <sup>-2</sup>	3.08 × 10 <sup>-2</sup>
5.	0	0	3.04 × 10 <sup>-2</sup>	0.345 × 10 <sup>-2</sup>	0.345 × 10 <sup>-2</sup>	2.35 × 10 <sup>-2</sup>
6.	0	0	7.58 × 10 <sup>-2</sup>	0.86 × 10 <sup>-2</sup>	0.86 × 10 <sup>-2</sup>	5.86 × 10 <sup>-2</sup>

- It is evident from the experiments 1, 2, 3 and 4 :  
No. of moles of H<sub>2</sub> reacted = no. of moles of I<sub>2</sub> reacted =  
½ (no. of moles of HI formed).

- Experiments 5 and 6 indicate that-

$$[\text{H}_2(\text{g})]_{\text{eq}} = [\text{I}_2(\text{g})]_{\text{eq}}$$

- The relationship between concentrations of the reactants and products is as follows:

$$[\text{HI}(\text{g})]_{\text{eq}} / [\text{H}_2(\text{g})]_{\text{eq}} [\text{I}_2(\text{g})]_{\text{eq}}$$

Table: Expression Involving the Equilibrium Concentration of Reactants H<sub>2</sub> (g) + I<sub>2</sub> (g) ⇌ 2HI(g)

Experiments Number	$\frac{[\text{HI}(\text{g})]_{\text{eq}}}{[\text{H}_2(\text{g})]_{\text{eq}} [\text{I}_2(\text{g})]_{\text{eq}}}$	$\frac{[\text{HI}(\text{g})]_{\text{eq}}^2}{[\text{H}_2(\text{g})]_{\text{eq}} [\text{I}_2(\text{g})]_{\text{eq}}}$
	1	1840
2	1610	47.6
3	1400	46.7
4	1520	46.9
5	1970	46.4
6	790	46.4

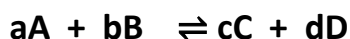
- The equilibrium constant :

$$K_c = \frac{[\text{HI}(\text{g})]_{\text{eq}}^2}{[\text{H}_2(\text{g})]_{\text{eq}} [\text{I}_2(\text{g})]_{\text{eq}}}$$

- Here K<sub>c</sub> is expressed in concentrations of mol L<sup>-1</sup>.
- At a given temperature, the product of concentrations of the products raised to their stoichiometric coefficient in the balanced

chemical equation divided by the product of concentrations of the reactants raised to their stoichiometric coefficients has a constant value. This is called the Law of Chemical Equilibrium.

- The equilibrium constant ( $K_c$ ) for a reaction :



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

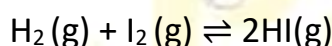
Here [A], [B], [C] and [D] are the equilibrium concentrations of the reactants and products.

- Example: Equilibrium constant for the reaction,



$$K_c = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$$

- Example: Equilibrium constant for the reaction,



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

- Example: Equilibrium constant for the reverse reaction,  $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$  :

$$K'_c = \frac{[H_2][I_2]}{[HI]^2}$$

$$= 1/x = 1/K_c$$

Table: Relations between equilibrium constants for a general reaction and its multiples

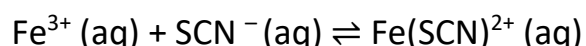
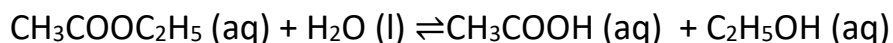
Chemical equation	Equilibrium constant
$aA + bB \rightleftharpoons cC + dD$	$K_c$
$cC + dD \rightleftharpoons aA + bB$	$K'_c = (1/K_c)$
$naA + nbB \rightleftharpoons ncC + ndD$	$K''_c = (K_c^n)$

## Homogeneous Equilibrium

- The reactants and products are in the same phase in this system.
- Example:  $\text{N}_2 (\text{g}) + 3\text{H}_2 (\text{g}) \rightleftharpoons 2\text{NH}_3 (\text{g})$

Here reactants and products are in the homogeneous phase.

Similarly, for the reactions,



- All the reactants and products are in homogeneous solution phase.

## Equilibrium Constant in Gaseous Systems

- For reactions involving gases, on the other hand, it is convenient to express the equilibrium constant in terms of partial pressure. The ideal gas equation is as follows:

$$pV = nRT$$

$$p = \frac{n}{V} RT$$

Here  $p$  = pressure in Pa,

$n$  = no. of moles of the gas,

$V$  = volume in  $\text{m}^3$

$T$  = temperature in Kelvin

- $n/V$  is concentration expressed in  $\text{mol}/\text{m}^3$ . If concentration  $c$  is in  $\text{mol}/\text{L}$ , and  $p$  is in bar then:

$$p = cRT$$

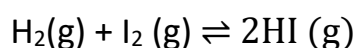
$$p = [\text{gas}]RT$$

Here  $R = 0.0831 \text{ bar litre mol}^{-1}\text{K}^{-1}$

- At constant  $T$ , the  $P$  of the gas is proportional to its concentration.

$$p \propto [\text{gas}]$$

- For reaction in equilibrium



We can write:

$$K_c = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}$$

$$\text{or } K_c = \frac{(p_{\text{HI}})^2}{(p_{\text{H}_2})(p_{\text{I}_2})}$$

$$p_{\text{HI}} = [\text{HI}(\text{g})]RT$$

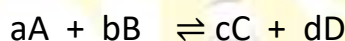
$$p_{\text{I}_2} = [\text{I}_2(\text{g})]RT$$

$$p_{\text{H}_2} = [\text{H}_2(\text{g})]RT$$

So

$$\begin{aligned} K_p &= \frac{(p_{\text{HI}})^2}{(p_{\text{H}_2})(p_{\text{I}_2})} = \frac{[\text{HI}(\text{g})]^2 [RT]^2}{[\text{H}_2(\text{g})]RT \cdot [\text{I}_2(\text{g})]RT} \\ &= \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]} = K_c \end{aligned}$$

- Here  $K_p = K_c$
- For a general reaction:

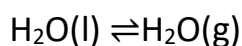


$$\begin{aligned} K_p &= \frac{(p_C^c)(p_D^d)}{(p_A^a)(p_B^b)} = \frac{[\text{C}]^c [\text{D}]^d (RT)^{(c+d)}}{[\text{A}]^a [\text{B}]^b (RT)^{(a+b)}} \\ &= \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} (RT)^{(c+d)-(a+b)} \\ &= \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} (RT)^{\Delta n} = K_c (RT)^{\Delta n} \end{aligned}$$

- Here  $\Delta n = (\text{no. of moles of products (g)}) - (\text{no. of moles of reactants(g)})$  in a balanced chemical equation.
- Pressure should be in Bar.  
1 pascal, Pa =  $1\text{Nm}^{-2}$ , and 1 bar =  $10^5$  Pa

## Heterogeneous Equilibrium

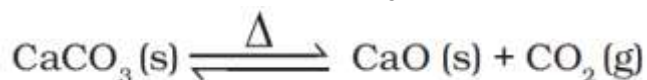
- In a system, if equilibrium have more than one phase then it is termed as heterogeneous equilibrium.
- Example: The equilibrium between water vapour and liquid water in a closed container.



- The equilibrium between a solid and its saturated solution:



- It is a heterogeneous equilibrium. It is often comprises pure solids or liquids.
- We can simplify equilibrium expressions for the heterogeneous equilibrium involving a pure liquid or a pure solid, as the molar concentration of a pure solid or liquid is constant.
- In case of thermal dissociation of  $\text{CaCO}_3$ :



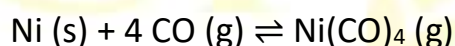
$$K_c = \frac{[\text{CaO} (\text{s})] [\text{CO}_2(\text{g})]}{[\text{CaCO}_3 (\text{s})]}$$

- As  $[\text{CaO} (\text{s})]$  and  $[\text{CaCO}_3 (\text{s})]$  are constant so

$$K'_c = [\text{CO}_2(\text{g})]$$

$$K_p = p_{\text{CO}_2}$$

- Example: in the equilibrium between Ni, CO and  $[\text{Ni}(\text{CO})_4]$



- The equilibrium constant is as follows:

$$K_c = \frac{[\text{Ni}(\text{CO})_4]}{[\text{CO}]^4}$$

- Example:  $\text{Ag}_2\text{O}(\text{s}) + 2\text{HNO}_3 (\text{aq}) \rightleftharpoons 2\text{AgNO}_3 (\text{aq}) + \text{H}_2\text{O}(\text{l})$

$$K_c = \frac{[\text{AgNO}_3]}{[\text{HNO}_3]^2}$$

Important features of equilibrium constants are as follows:

1. The equilibrium constant is valid only when concentrations of reactants as well as of products have attained constant value at equilibrium state.
2. The value of equilibrium constant is not depending upon initial concentrations of the reactants and products.

3. Equilibrium constant depends upon temperature.
4. The inverse of the equilibrium constant for the forward reaction is equal to the equilibrium constant for the reverse reaction.

## Applications of equilibrium constants

### Predicting the Extent of a Reaction

- The value of the equilibrium constant for a reaction indicates the degree of the reaction. But it does not give any information about rate at which the equilibrium is attained.
- The magnitude of  $K_c$  or  $K_p$  is inversely proportional to the concentrations of the reactants and directly proportional to the concentrations of products.
- This indicates that a high value of  $K$  is indication of a high concentration of products and vice-versa.
- If  $K_c > 10^3$ , then the products dominates over reactants, that mean if  $K_c$  is very large, then reaction proceeds approximately to completion.

Examples:

1. The reaction of  $H_2$  with  $O_2$  at 500 K has a large equilibrium constant,  $K_c = 2.4 \times 10^{47}$ .
  2.  $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$  at 300K has  $K_c = 4.0 \times 10^{31}$ .
  3.  $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$  at 300 K,  $K_c = 5.4 \times 10^{18}$
- If  $K_c < 10^{-3}$ , then the reactants dominate over the products, that mean if  $K_c$  is too small, then reaction proceeds hardly. Examples:
1. The decomposition of  $H_2O$  into  $H_2$  and  $O_2$  at 500 K temperature has a small equilibrium constant,  $K_c = 4.1 \times 10^{-48}$
  2.  $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ , at 298 K temperature has  $K_c = 4.8 \times 10^{-31}$ .

- If  $K_c$  is in the range of  $10^{-3}$  to 1000, then considerable concentrations of both reactants and products are present.

Examples:

1. For reaction of  $H_2$  with  $I_2$  to give  $HI$ ,  $K_c = 57.0$  at 700K temperature.
2. Gas phase decomposition of  $N_2O_4$  to  $NO_2$  has value of  $K_c = 4.64 \times 10^{-3}$  at 25°C temperature. The equilibrium mixtures have significant concentrations of  $N_2O_4$  and  $NO_2$ .



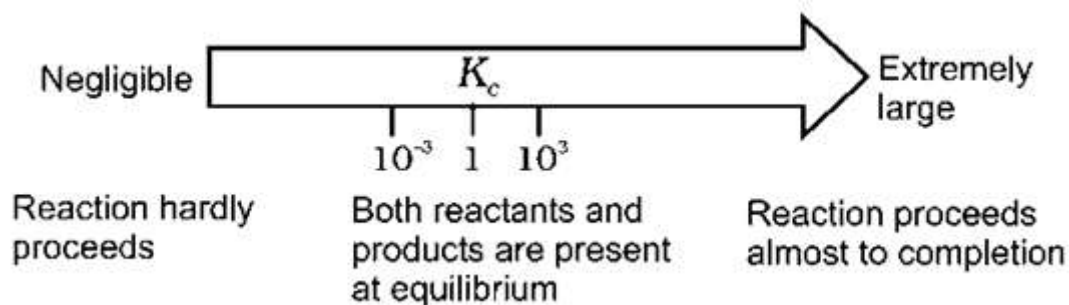
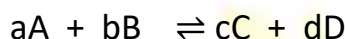


Figure: Dependence of extent of reaction on  $K_c$

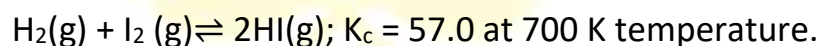
### Predicting the direction of the reaction

- The equilibrium constant helps to predict the direction of reaction.
- For this purpose, we need the reaction quotient ( $Q$ ).  $Q_c$  is used for molar concentrations and  $Q_p$  used for partial pressures.
- For a general reaction:



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

- If  $Q_c > K_c$ , then reaction will proceed in the direction of reactants means towards reverse reaction.
- If  $Q_c < K_c$ , then reaction will proceed in the direction of the products means towards forward reaction.
- If  $Q_c = K_c$ , then reaction mixture is already at equilibrium.
- Example:



Consider  $[H_2]_t = 1M$ ,

$[I_2]_t = 2 M$

$[HI]_t = 4 M$ .

$$Q_c = \frac{[HI]_t^2}{[H_2]_t [I_2]_t} = \frac{(4)^2}{(1)(2)} = 8.0$$

Here  $Q_c$  is not equal to  $K_c$  so there is no equilibrium, thus hydrogen react with more iodine to form hydrogen iodide till the  $Q_c = K_c$ .

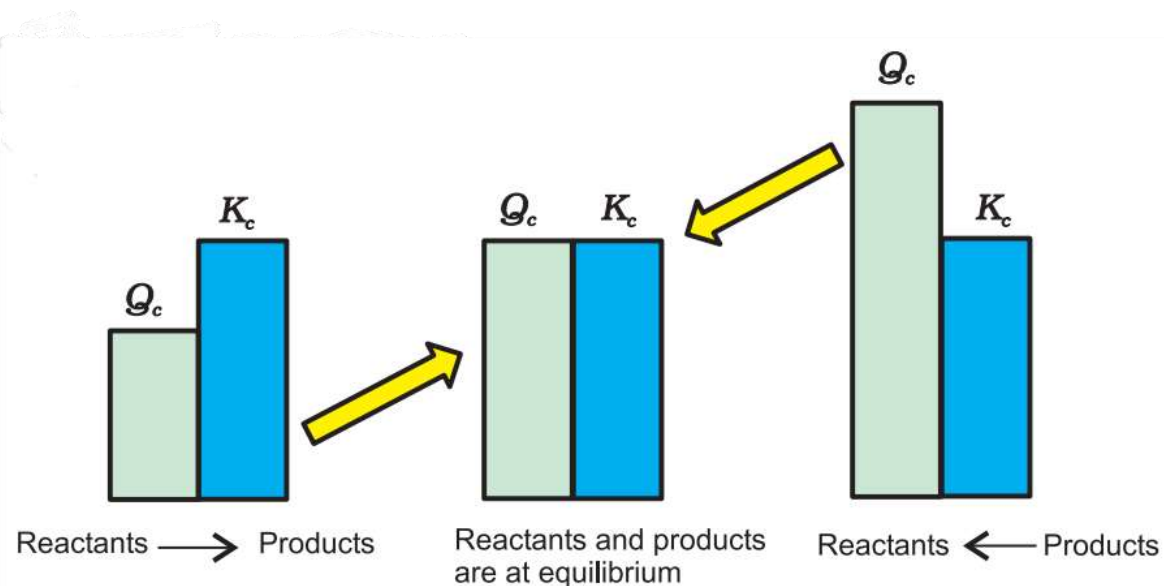


Figure: Predicting the direction of the reaction

- Thus we can make following assumptions:
  1. If  $Q_c < K_c$ , then net reaction goes from left to right
  2. If  $Q_c > K_c$ , then net reaction goes from right to left.
  3. If  $Q_c = K_c$ , then no reaction occurs.

### Relationship between equilibrium constant $K$ , reaction quotient $Q$ and Gibbs energy $G$

- The value of  $K_c$  for a reaction independent on the rate of the reaction. It is directly related to the thermodynamics and to the  $\Delta G$ . If,
  1.  $\Delta G$  is -ve, and then the reaction is spontaneous and proceeds in the forward direction.
  2.  $\Delta G$  is +ve, then reaction is considered non-spontaneous. As an alternative, as reverse reaction would have a -ve  $\Delta G$ , the products of the forward reaction will be converted to the reactants.
  3.  $\Delta G$  is 0, reaction has achieved equilibrium; at this point, there is no longer any free energy left to drive the reaction.

A mathematical expression is as follows:

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

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

$$\ln K = -\Delta G^\circ / RT$$

After taking antilog

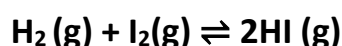
$$K = e^{-\Delta G^\circ / RT}$$

- The reaction spontaneity can be interpreted in terms of the value of  $\Delta G^\ominus$ 
  1. If  $\Delta G^\ominus < 0$ , then  $-\Delta G^\ominus / RT$  is +ve, and  $e^{-\Delta G^\ominus / RT} > 1$ , making  $K > 1$ , which implies a spontaneous reaction or the reaction which proceeds in the forward direction to such an extent that the products are present predominantly.
  2. If  $\Delta G^\ominus > 0$ , then  $-\Delta G^\ominus / RT$  is -ve, and  $e^{-\Delta G^\ominus / RT} < 1$ , that is,  $K < 1$ , which implies a non-spontaneous reaction which proceeds in the forward direction to very small extent that only a very negligible quantity of product is formed.

## Factors affecting Equilibrium

### 1. Effect of concentration change-

- When equilibrium is disturbed by the addition or removal of any reactant or products, Le Chatelier's principle predicts that:
  - a. The concentration stress of an added reactant or product is released by reaction in the direction that consumes the added substance.
  - b. The concentration stress of a removed reactant or product is relieved by net reaction in the direction that replaces the removed substance.
- When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes to minimize the effect of concentration changes.
- **Le Chatelier's principle**- According to it 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 thwart the effect of the change.
- Example:



The equilibrium of reaction will be disturbed if  $\text{H}_2$  is added to the reaction mixture. To restore it the reaction proceeds in a direction where in  $\text{H}_2$  is consumed, that means more of  $\text{H}_2$  and  $\text{I}_2$  react to form  $\text{HI}$  and finally the equilibrium will shift in forward direction.

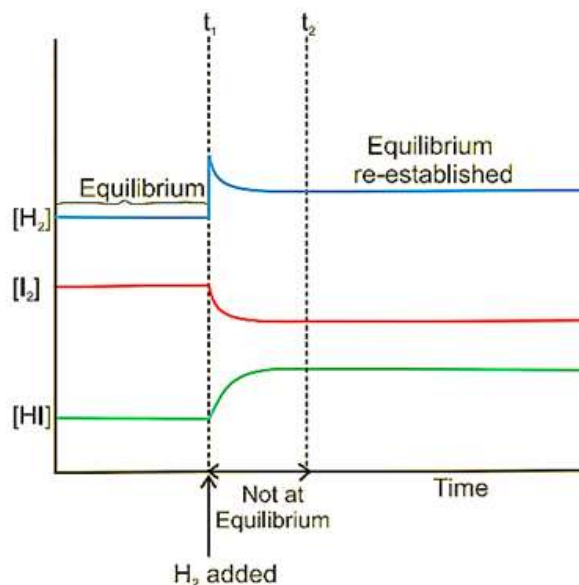


Figure: Effect of addition of  $H_2$  on change of concentration for the reactants and products in the reaction,  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

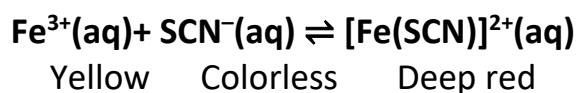
- In terms of the reaction quotient ( $Q_c$ )

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

- It can be concluded that removal of a product boosts the forward reaction and increases the concentration of the products.
- In case of large scale production of ammonia, being liquefied it is removed from the reaction mixture so that reaction keeps moving in forward direction.
- The industrial production of  $CaO$  from  $CaCO_3$ , constant removal of  $CO_2$  from the kiln pushes the reaction towards completion.
- Continuous removal of a product maintains  $Q_c < K_c$  and reaction move towards forward direction.

### Experiment –

- Effect of concentration can be explained by this experiment:

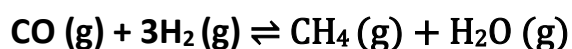


$$K_c = \frac{[Fe(SCN)^{2+}(aq)]}{[Fe^{3+}(aq)][SCN^-(aq)]}$$

- A red color appears on adding two drops of 0.002 M KSCN solution to 1 mL of 0.2 M iron(III) nitrate solution due to the formation of  $[\text{Fe}(\text{SCN})]^{2+}$ .
- The intensity of the red color becomes constant on achieving equilibrium.
- The equilibrium can be shifted in the opposite direction by adding reagents that remove  $\text{Fe}^{3+}$  or  $\text{SCN}^-$  ions. For example, if oxalic acid  $(\text{COOH})_2$  is added, then it reacts with  $\text{Fe}^{3+}$  ions to form the stable complex ion which is  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ , as a result concentration of free  $\text{Fe}^{3+}(\text{aq})$  will be decreased.
- The concentration stress of removed  $\text{Fe}^{3+}$  is released by dissociation of  $[\text{Fe}(\text{SCN})]^{2+}$ . As the concentration of  $[\text{Fe}(\text{SCN})]^{2+}$  decreases, the intensity of red color also decreases.
- The addition of aq.  $\text{HgCl}_2$  decreases intensity of red color as  $\text{Hg}^{2+}$  reacts with  $\text{SCN}^-$  ions to form a stable complex ion which is  $[\text{Hg}(\text{SCN})_4]^{2-}$ .
- Removal of free  $\text{SCN}^-$  (aq) shifts the equilibrium from right to left side.
- Addition of KSCN increases the color intensity of the solution as it shifts the equilibrium to right side.

## 2. Effect of pressure change –

- A pressure change achieved by changing the volume can affect the yield of products in case of a gaseous reaction where the total number of moles of gaseous reactants and products are different.
- Example:



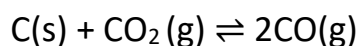
Here 4 mol of gaseous reactants ( $\text{CO} + 3\text{H}_2$ ) to give 2 mol of gaseous products ( $\text{CH}_4 + \text{H}_2\text{O}$ ). Assume the equilibrium mixture placed in a cylinder fitted with a piston at constant temperature is compressed to one half of its original volume. The total pressure will be doubled as  $pV = \text{constant}$ .

- The partial pressure and concentration of reactants and products have changed and the mixture is no longer at equilibrium. The direction in which the reaction goes to re-establish the equilibrium can be predicted by applying the Le Chatelier's principle.

- Meanwhile pressure has doubled so the equilibrium now shifts in the forward direction. This can also be understood by using reaction quotient ( $Q_c$ ). Let  $[CO]$ ,  $[H_2]$ ,  $[CH_4]$  and  $[H_2O]$  be the molar concentrations at equilibrium for methanation reaction.
- When the reaction mixture's volume is halved, the concentration and the partial pressure are doubled.
- The reaction quotient ( $Q_c$ ) is as follows:

$$Q_c = \frac{[CH_4(g)] [H_2O(g)]}{[CO(g)] [H_2(g)]^3}$$

- $Q_c < K_c$  so the reaction proceeds in the forward direction.
- In reaction:



By increasing the pressure, above reaction moves in the reverse direction because the number of moles of gas increases in the forward direction.

### 3. Effect of inert gas addition

- If the volume is kept constant and an inert gas like Ar is added which does not take part in the reaction, the equilibrium remains undisturbed. As the addition of an inert gas at constant volume does not change the partial pressures or the molar concentrations of the substance involved in the reaction.
- The reaction quotient changes only if the added gas is a reactant or product involved in the reaction.

### 4. Effect of temperature change

- If a change occurs in temperature, then value of equilibrium constant,  $K_c$  will be changed.
- The temperature dependence of the equilibrium constant depends on the sign of  $\Delta H$  for the reaction which is described below:
  1. The equilibrium constant for an exothermic ( $\Delta H = -ve$ ) reaction will decrease with temperature rise.
  2. The equilibrium constant for an endothermic ( $\Delta H = +ve$ ) reaction will increase with temperature rise.





- At room temperature, due to  $[\text{CoCl}_4]^{2-}$  the equilibrium mixture is blue. When cooled in a freezing mixture, the color of the mixture turns pink due to  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ .

## 5. Effect of catalyst

- The rate of the chemical reaction increase with the help of catalyst. As it provides a new low activation energy pathway for the formation of products from reactants.
- It increases the rate of forward as well as of reverse reactions that pass through the same transition state. It drops the activation energy for the forward and reverse reactions with same amount.
- The equilibrium composition of a reaction mixture is not affected by the presence of catalyst.
- Example: Formation of  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2$  which is exothermic reaction and proceeds with decrease in total number of moles formed as compared to the reactants. With increase in temperature the equilibrium constant decreases.
- German chemist, Fritz Haber discovered that a catalyst consisting of iron catalyze the reaction to occur at a satisfactory rate at temperatures, where the equilibrium concentration of  $\text{NH}_3$  is reasonably favorable.
- The number of moles formed in the reaction is less than those of reactants, so the yield of  $\text{NH}_3$  can be improved by increasing the pressure.
- Optimum conditions of temperature and pressure for the synthesis of  $\text{NH}_3$  using catalyst are around  $500^\circ\text{C}$  and 200 atm.
- Similarly, in manufacture of sulphuric acid by contact process,

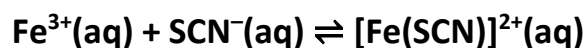


- The value of K suggests the reaction's completion, but practically the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  is very slow. To increase the rate of the reaction Pt or  $\text{V}_2\text{O}_5$  is used as the catalyst.

## Ionic Equilibrium in solution

- Under the effect of change of concentration on the direction of equilibrium, you have incidentally come across with the following equilibrium which involves ions:





- There are numerous equilibrium in which only ions are involved.
- The aqueous solution of sugar is not able to conduct electricity. If common salt i.e. sodium chloride is added to water it conducts electricity. And the conductance of electricity increases with an increase in concentration of common salt.
- Michael Faraday classified the substances into two classes based on their ability to conduct electricity. One class of substances conduct electricity in their aqueous solutions and are called electrolytes while the other do not and are termed as non-electrolytes. Electrolytes further classified into strong and weak electrolytes.
- On dissolving the strong electrolytes in water, they ionized completely, while the weak electrolytes are partially dissociated. Example: an aqueous solution of NaCl is containing sodium ions and chloride ions, while the aqueous solution of CH<sub>3</sub>COOH mainly contain unionized acetic acid molecules and only some CH<sub>3</sub>COO<sup>-</sup> ions and H<sub>3</sub>O<sup>+</sup> ions. This is because there is almost 100% ionization in case of NaCl as compared to less than 5% ionization of CH<sub>3</sub>COOH which is a weak electrolyte.
- In case of weak electrolytes, equilibrium is established between ions and the unionized molecules. The equilibrium which involves ions in aqueous solution is called ionic equilibrium.

## Acids, Bases and Salts

- Acids, bases and salts are ubiquitous in nature. Hydrochloric acid present in the gastric juice is secreted by the lining of our stomach in a significant amount of 1.2-1.5 L/day and is essential for digestive processes.
- CH<sub>3</sub>COOH is the main constituent of vinegar. Lemon and orange juices contain citric and ascorbic acids and tartaric acid is found in tamarind.
- As most of the acids taste sour, the word **acid** has been derived from a Latin word **acidus** meaning sour.
- Acids turn blue litmus paper into red and liberate H<sub>2</sub> gas on reacting with some metals.
- Bases turn red litmus paper blue, taste bitter and feel soapy. Example: washing soda.
- When acids and bases are mixed in the right proportion they react with each other and give salts. Some commonly known examples of salts are sodium chloride, barium sulphate, and sodium nitrate.

- NaCl is an important component of our diet and is formed by reaction between HCl and NaOH. It is found in solid state as a cluster of sodium cations and chloride anions which are held together due to electrostatic interactions.
- The dielectric constant of the medium is inversely proportional to electrostatic forces between two charges.
- Water is a universal solvent. It has a very high dielectric constant. When NaCl is dissolved in water, the electrostatic interactions are reduced by a factor of 80 and this facilitates the ions to move freely in the solution. Also, they are well separated due to hydration with water molecules.

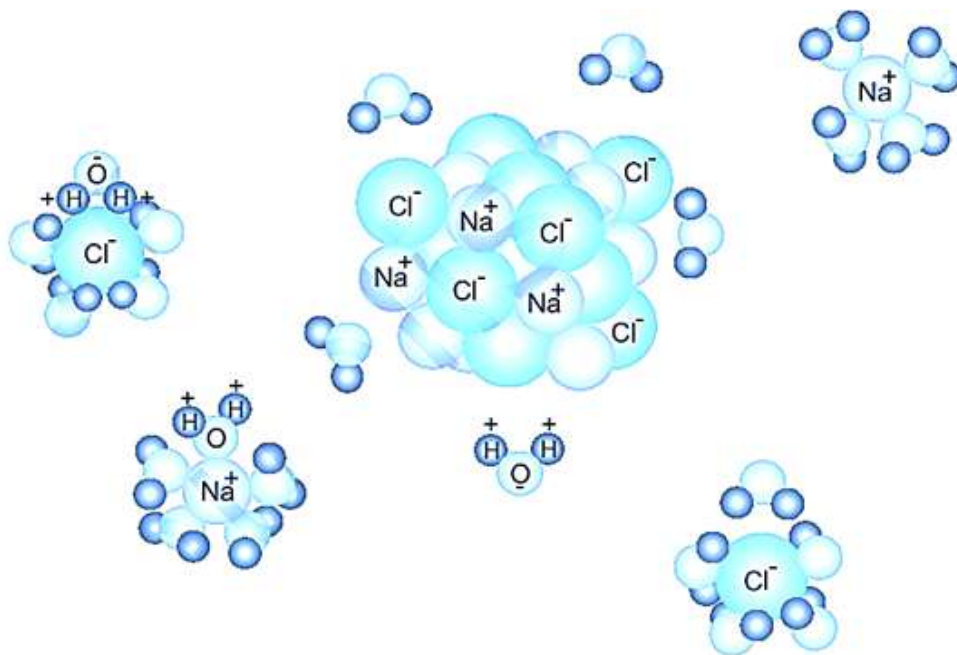
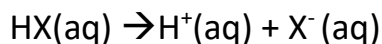


Figure: Dissolution of sodium chloride in water.  $\text{Na}^+$  and  $\text{Cl}^-$  ions are stabilized by their hydration with polar water molecules

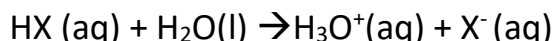
- On comparing the ionization of HCl with  $\text{CH}_3\text{COOH}$  in  $\text{H}_2\text{O}$  it is found that both are polar covalent molecules, former is more ionized into its constituent ions, whereas the later one is partially ionized.
- The degree of ionization depends upon the strength of the bond and the extent of solvation of ions produced.
- Dissociation is the process of separation of ions in water already existing as such in the solid state of the solute, as in NaCl.

### Arrhenius concept of acids and bases

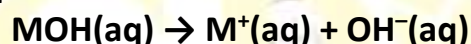
- According to Arrhenius theory, acids are substances that dissociates in water to give hydrogen ions  $H^+(aq)$  and bases are substances that produce hydroxyl ions  $OH^-(aq)$ .
- The ionization of an acid  $HX(aq)$  can be represented by the following equations:



Or



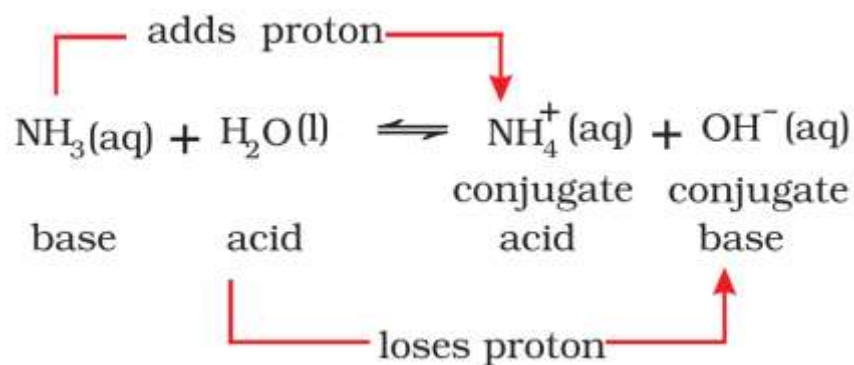
- A bare proton,  $H^+$  is very reactive and cannot exist freely in aqueous solutions. Thus, it bonds to the oxygen atom of a solvent water molecule to give trigonal pyramidal hydronium ion,  $H_3O^+ \{ [H(H_2O)]^+ \}$ .
- In this chapter we shall use  $H^+(aq)$  and  $H_3O^+(aq)$  interchangeably to mean the same i.e., a hydrated proton.
- Likewise, a base molecule like  $MOH$  ionizes in aqueous solution according to the equation:



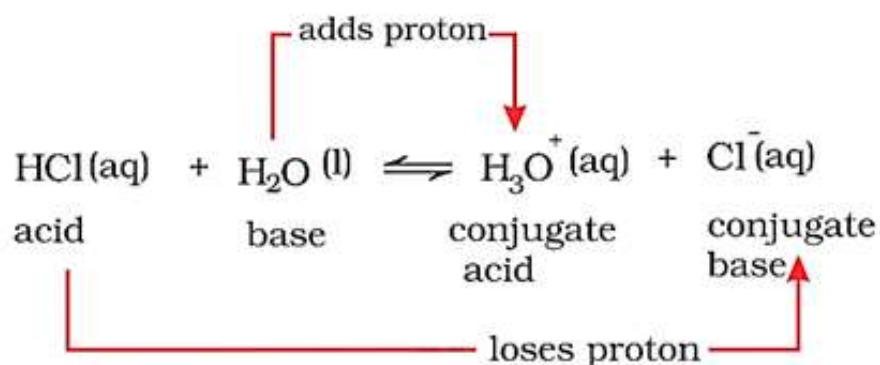
- The  $OH^-$  ion also exists in the hydrated form in the aqueous solution. Arrhenius concept of acid and base suffers from the limitation of being applicable only to aqueous solutions and cannot explain the basicity of substances like, ammonia which do not possess a hydroxyl group.

### The Bronsted-Lowry acids and bases

- The Danish chemist, Johannes Bronsted and the English chemist, Thomas M. Lowry defined the acids and bases very well.
- According to Bronsted-Lowry theory, acid is a substance that is capable of donating a hydrogen ion  $H^+$  and bases are substances capable of accepting a hydrogen ion,  $H^+$ . Example: dissolution of  $NH_3$  in  $H_2O$



- The basic solution is formed due to the presence of hydroxyl ions.
  - In this reaction, water molecule acts as proton donor and ammonia molecule acts as proton acceptor and are thus, called Lowry-Brönsted acid and base, respectively.
  - In the reverse reaction,  $\text{H}^+$  is transferred from  $\text{NH}_4^+$  to  $\text{OH}^-$ . In this case,  $\text{NH}_4^+$  acts as a Bronsted acid while  $\text{OH}^-$  acted as a Bronsted base.
  - The acid-base pair is differing by only one proton is termed as conjugate acid-base pair. So  $\text{OH}^-$  is called the conjugate base of an acid  $\text{H}_2\text{O}$  and  $\text{NH}_4^+$  is called conjugate acid of the base  $\text{NH}_3$ .
  - If Bronsted base is a strong base then its conjugate acid is a weak acid and viceversa.
  - Each conjugate base has one less proton and conjugate acid has one extra proton.
  - Example: Ionization of HCl in water.  $\text{HCl}(\text{aq})$  acts as acid by donating a proton to water molecule which acts as a base.

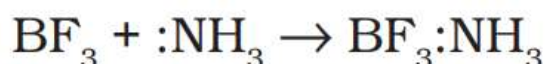


- In equation water acts as a base because it accepts the proton. The species  $\text{H}_3\text{O}^+$  is produced when water accepts a proton from HCl. So  $\text{Cl}^-$  is a conjugate base of HCl and HCl is the conjugate acid of base  $\text{Cl}^-$ . Also,  $\text{H}_2\text{O}$  is a conjugate base of an acid  $\text{H}_3\text{O}^+$  and  $\text{H}_3\text{O}^+$  is a conjugate acid of base  $\text{H}_2\text{O}$ .

- The water plays dual role as an acid and a base. Water acts as a base in reaction with HCl but in case of ammonia it acts as an acid by donating a proton.

### Lewis acids and bases

- G.N. Lewis in 1923 propounded that an acid is a species which accepts electron pair and base which donates an electron pair.
- The base provides a lone pair according to Bronsted-Lowry as well as Lewis concepts.
- In Lewis concept many acids do not have proton. Example: reaction between  $\text{BF}_3$  with  $\text{NH}_3$ .
- $\text{BF}_3$  does not have a proton but acts as an acid and reacts with  $\text{NH}_3$  by accepting the lone pair of electrons. The reaction can be represented by following reaction:

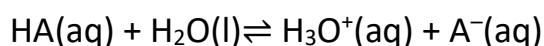


- Electron deficient species like  $\text{AlCl}_3$ ,  $\text{Co}^{3+}$ ,  $\text{Mg}^{2+}$ , etc. act as Lewis acids while species which can donate a pair of electrons like  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{OH}^-$  etc. act as Lewis bases.

### Ionization of acids and bases

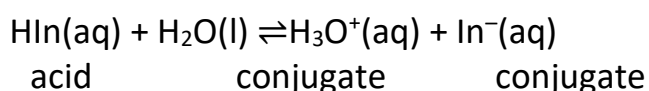
- Arrhenius concept of acids and bases is useful in case of ionization of acids and bases in aqueous medium.
- Strong acids like perchloric acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, nitric acid and sulphuric acid are termed strong because they are almost completely dissociated into their constituent ions in an aqueous medium, thereby acting as proton ( $\text{H}^+$ ) donors.
- In the same way, strong bases like lithium hydroxide, sodium hydroxide, potassium hydroxide, caesium hydroxide and barium hydroxide are almost completely dissociated into ions in an aqueous medium giving hydroxyl ions ( $\text{OH}^-$ ).

- According to Arrhenius concept they are strong acids and bases as they are able to completely dissociate and produce  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions respectively in the medium.
- The strength of an acid or base may also be determined in terms of Bronsted Lowry concept of acids and bases, wherein a strong acid means a good proton donor and a strong base means a good proton acceptor. Example: The acid-base dissociation equilibrium of a weak acid HA,



Acid                  base      conjugate acid      conjugate base

- Acid dissociation equilibrium is dynamic involving a transfer of proton in forward and reverse directions.
- Let's consider the two acids HA and  $\text{H}_3\text{O}^+$  present in the above mentioned acid-dissociation equilibrium. One of them is a stronger proton donor.
- Say, if HA is a stronger acid than  $\text{H}_3\text{O}^+$ , and then HA will donate protons and not  $\text{H}_3\text{O}^+$ , and the solution will mainly contain  $\text{A}^-$  and  $\text{H}_3\text{O}^+$  ions.
- The equilibrium moves towards the formation of weaker acid.
- A strong acid dissociates completely in water and the resulting base formed would be very weak means strong acids possess weak conjugate bases. Strong acids like perchloric acid, hydrochloric acid, hydro bromic acid, hydro iodic acid, nitric acid and sulphuric acid will give conjugate base ions  $\text{ClO}_4^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$  and  $\text{HSO}_4^-$ .
- A strong base gives a weak conjugate acid. A weak acid HA is partially dissociated in aqueous medium and the solution contains some undissociated HA molecules.
- Typical weak acids are nitrous acid, hydrofluoric acid and acetic acid.
- Certain water soluble organic compounds like phenolphthalein and bromothymol blue behave as weak acids and exhibit different colors in their acid (HIn) and conjugate base ( $\text{In}^-$ ) forms.

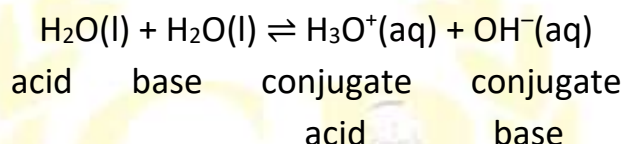


Indicator	acid	base
colour A		colour B

- Such compounds are useful as indicators in acid-base titrations, and finding out H<sup>+</sup> ion concentration.

### The ionization constant of water and its ionic product

- Water is unique in its ability of acting both as an acid and a base.
- In presence of an acid, H<sub>2</sub>O accepts a proton and acts as the base while in the presence of a base, H<sub>2</sub>O acts as an acid by donating a proton.
- The following equilibrium exists in pure water:



- The dissociation constant is represented by :
 
$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$
- The concentration of water is removed from the denominator as its concentration remains constant.
- [H<sub>2</sub>O] is incorporated within the equilibrium constant to give a new constant (K<sub>w</sub>), which is termed as ionic product of water.

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

- K<sub>w</sub> is an equilibrium constant which is temperature dependent.
- Acidic, neutral and basic aqueous solutions can be distinguished by the relative values of the OH<sup>-</sup> and H<sub>3</sub>O<sup>+</sup> concentrations:

Acidic: [H<sub>3</sub>O<sup>+</sup>] > [OH<sup>-</sup>]

Basic: [H<sub>3</sub>O<sup>+</sup>] < [OH<sup>-</sup>]

Neutral: [H<sub>3</sub>O<sup>+</sup>] = [OH<sup>-</sup>]



## The pH Scale:

- $[H_3O^+]$  ion concentration in molarity expressed on a logarithmic scale is termed as the pH scale.
- The pH of a solution is defined as the -ve logarithm to base 10 of the activity ( $a_{H^+}$ ) of hydrogen ion.
- In dilute solutions ( $< 0.01$  M), activity of hydrogen ion ( $H^+$ ) is equal in magnitude to molarity represented by  $[H^+]$ . It should be noted that activity has no units and it is defined as:

$$(a_{H^+}) = [H^+] / \text{mol L}^{-1}$$

- According to the definition of pH:

$$\text{pH} = -\log a_{H^+} = -\log \{[H^+] / \text{mol L}^{-1}\}$$

- An acidic solution of HCl ( $10^{-2}$  M) have a pH = 2. Similarly, a basic solution of NaOH have  $[OH^-] = 10^{-4}$  M and  $[H_3O^+] = 10^{-10}$  M will have a pH = 10. At 25 °C.
- Pure water has a concentration of hydrogen ions,  $[H^+] = 10^{-7}$  M. The pH of pure water is as follows:

$$\text{pH} = -\log(10^{-7}) = 7$$

- Acidic solutions possess a concentration of hydrogen ions,  $[H^+] > 10^{-7}$  M, while basic solutions possess a concentration of hydrogen ions,  $[H^+] < 10^{-7}$  M. thus, we can summarize that

**Acidic solution has pH < 7**

**Basic solution has pH > 7**

**Neutral solution has pH = 7**

- $K_w = [H_3O^+] [OH^-] = 10^{-14}$

Taking negative logarithm on both sides of above equation:

$$-\log K_w = -\log \{ [H_3O^+] [OH^-] \}$$

$$= -\log [H_3O^+] - \log [OH^-]$$

$$= -\log 10^{-14}$$

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



- $pK_w$  is a very important quantity for aqueous solutions and it controls the relative concentrations of  $H^+$  and  $OH^-$  ions as their product is a constant.
- If  $[H^+]$  ion concentration changes by a factor of 100, the value of pH changes by 2 units.
- The pH of a solution can be measured by pH paper; it shows different color in solutions of different pH.

Table: The pH of some common substances

Name of the fluid	pH
Saturated solution of NaOH	~15
0.1 M NaOH solution	13
Lime water	10.5
Milk of magnesia	10
Egg white, sea water	7.8
Human blood	7.4
Milk	6.8
Human saliva	6.4
Black coffee	5.0
Tomato juice	~4.2
Soft drink and vinegar	~3.0
Lemon juice	~2.2
Gastric juice	~1.2
1M HCl solution	~0
Concentrated HCl	~1.0

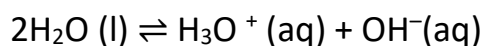
**Example:** The concentration of hydrogen ion in a sample of soft drink is  $3.8 \times 10^{-3}M$ . What is its pH ?

**Solution:**

$$\begin{aligned}
 \text{pH} &= -\log[3.8 \times 10^{-3}] \\
 &= -\{\log[3.8] + \log[10^{-3}]\} \\
 &= -\{(0.58) + (-3.0)\} \\
 &= -\{-2.42\} = 2.42
 \end{aligned}$$

So the pH of the soft drink is 2.42 and it can be concluded that it is acidic in nature.

**Example:** Calculate pH of a  $1.0 \times 10^{-8} M$  solution of HCl.

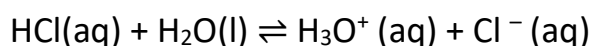
**Solution:**

$$K_w = [\text{OH}^-][\text{H}_3\text{O}^+] \\ = 10^{-14}$$

Let,  $x = [\text{OH}^-] = [\text{H}_3\text{O}^+]$  from  $\text{H}_2\text{O}$ .

The  $\text{H}_3\text{O}^+$  concentration is generated:

(i) From the ionization of HCl dissolved gives following ions:



(ii) From ionization of  $\text{H}_2\text{O}$ . In these very dilute solutions, both sources of  $\text{H}_3\text{O}^+$  must be considered:

$$[\text{H}_3\text{O}^+] = 10^{-8} + x$$

$$K_w = (10^{-8} + x)(x) = 10^{-14}, \text{ or}$$

$$x^2 + 10^{-8}x - 10^{-14} = 0$$

$$[\text{OH}^-] = x = 9.5 \times 10^{-8}$$

$$\text{So, pOH} = 7.02 \text{ and pH} = 6.98$$

**Ionization Constants of Weak Acids**

➤ Consider a weak acid HX that is partially ionized in the aqueous solution. The equilibrium can be expressed by:



Initial concentration (M)

$$c \qquad 0 \qquad 0$$

Let  $\alpha$  is the extent of ionization  
change(M)

$$-c\alpha \qquad +c\alpha \qquad +c\alpha$$

Equilibrium concentration (M)

$$c - c\alpha \qquad c\alpha \qquad c\alpha$$

Here,  $c$  = initial concentration of the undissociated acid,

HX at time,  $t = 0$ .

$\alpha$  = degree up to which HX is ionized into ions.

- The equilibrium constant for acid- dissociation equilibrium:

$$K_a = \frac{c^2\alpha^2}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

Here  $K_a$  = Dissociation or ionization constant of acid HX.

- In terms of molar concentrations:

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

- $K_a$  is a measure of the strength of the acid HX at a given temperature T. this means larger the value of  $K_a$ , the stronger is the acid.
- $K_a$  is a dimensionless quantity.

Table: The Ionization constants of some selected weak acids (at 298K)

Acid	Ionization constant ( $K_a$ )
Hydrofluoric acid (HF)	$3.5 \times 10^{-4}$
Acetic acid ( $CH_3COOH$ )	$1.74 \times 10^{-5}$
Nitrous acid	$4.5 \times 10^{-4}$
Formic acid ( $HCOOH$ )	$1.8 \times 10^{-4}$
Niacin ( $C_5H_4NCOOH$ )	$1.5 \times 10^{-5}$
Benzoic acid ( $C_6H_5COOH$ )	$6.5 \times 10^{-5}$
Hydrocyanic acid (HCN)	$4.9 \times 10^{-10}$
Hypochlorous acid (HClO)	$3.0 \times 10^{-8}$
Phenol ( $C_6H_5OH$ )	$1.3 \times 10^{-10}$

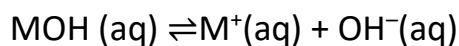
- Thus, we have:

$$pK_a = -\log (K_a)$$

- With the help of ionization constant ( $K_a$ ) of an acid and its initial concentration,  $c$ , we can calculate the equilibrium concentration of all species and also the pH of solution and the degree of ionization of the acid.

## Ionization of weak bases

- The ionization of base MOH can be represented by equation:



- In a weak base there is partial ionization of MOH into  $\text{M}^+$  and  $\text{OH}^-$  ion.
- The equilibrium constant for base ionization is termed as base ionization constant ( $K_b$ ).
- It can be expressed in terms of concentration in molarity of various species in equilibrium as follows:

$$K_b = \frac{[\text{M}^+][\text{OH}^-]}{[\text{MOH}]}$$

- if  $c$  = initial concentration of base  
 $\alpha$  = degree of ionization of base i.e. the extent to which the base ionizes.  
When equilibrium is reached, the equilibrium constant is as follows:

$$K_b = \frac{(c\alpha)^2}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)}$$

Table: The Values of the Ionization Constant of Some Weak Bases at 298K

Base	$K_b$
Dimethylamine, $(\text{CH}_3)_2\text{NH}$	$5.4 \times 10^{-4}$
Triethylamine, $(\text{C}_2\text{H}_5)_3\text{N}$	$6.45 \times 10^{-5}$
Quinine, (A plant product)	$1.10 \times 10^{-6}$
Ammonia, $\text{NH}_3$ or $\text{NH}_4\text{OH}$	$1.77 \times 10^{-5}$
Pyridine, $\text{C}_5\text{H}_5\text{N}$	$1.77 \times 10^{-9}$
Aniline, $\text{C}_6\text{H}_5\text{NH}_2$	$4.27 \times 10^{-10}$
Urea, $\text{CO}(\text{NH}_2)_2$	$1.3 \times 10^{-14}$

- Methylamine, nicotine, codeine, and quinine all behave as very weak bases due to their very small value of  $K_b$ . Ammonia produces  $\text{OH}^-$  in aqueous solution:

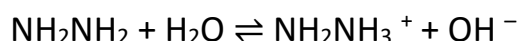


- The pH scale for the  $\text{H}^+$  concentration has been extended to get:

$$\text{p}K_b = -\log(K_b)$$

**Example:** The pH of 0.004M  $\text{NH}_2\text{NH}_2$  solution is 9.7. Calculate its ionization constant and  $\text{p}K_b$ .

**Solution:**



The hydrogen ion concentration:

$$[\text{H}^+] = \text{antilog}(-\text{pH})$$

$$= \text{antilog}(-9.7) = 1.67 \times 10^{-10}$$

$$[\text{OH}^-] = K_w / [\text{H}^+] = 1 \times 10^{-14} / 1.67 \times 10^{-10} = 5.98 \times 10^{-5}$$

The concentration of hydrazinium ion and hydroxyl ion is very small so the concentration of the undissociated base can be taken equal to 0.004M. Thus:

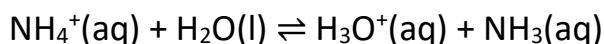
$$K_b = \frac{[\text{NH}_2\text{NH}_3^+][\text{OH}^-]}{[\text{NH}_2\text{NH}_2]}$$

$$= \frac{(5.98 \times 10^{-5})^2}{0.004} = 8.96 \times 10^{-7}$$

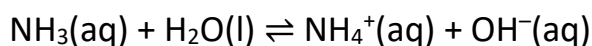
$$\text{p}K_b = -\log K_b = -\log(8.96 \times 10^{-7}) = 6.04.$$

### Relationship between $K_a$ and $K_b$

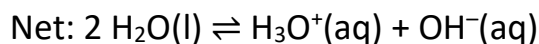
- In case of a conjugate acid-base pair,  $K_a$  and  $K_b$  are related in a simple manner. We can calculate one of them with the help of other one.
- Example:  $\text{NH}_4^+$  and  $\text{NH}_3$ :



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = 5.6 \times 10^{-10}$$



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ M}$$

Here  $K_a$  = Strength of  $\text{NH}_4^+$  as an acid

$K_b$  = Strength of  $\text{NH}_3$  as a base.

➤ We can conclude:

$$K_a \times K_b = \left\{ \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} \right\} \times \left\{ \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \right\}$$

$$= [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

$$= (5.6 \times 10^{-10}) \times (1.8 \times 10^{-5}) = 1.0 \times 10^{-14} \text{ M}$$

➤ The equilibrium constant for a net reaction is equals the product of the individual reaction's equilibrium constants:

$$K_{\text{NET}} = K_1 \times K_2 \times \dots$$

In case of a conjugate acid-base pair:

$$K_a \times K_b = K_w$$

❖ A strong base have a weak conjugate acid and vice-versa.

➤ The base-dissociation equilibrium reaction:



$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

➤ The concentration of  $\text{H}_2\text{O}$  remains constant. Then multiplying and dividing the above equation by  $[\text{H}^+]$ :

$$K_b = \frac{[\text{BH}^+][\text{OH}^-][\text{H}^+]}{[\text{B}][\text{H}^+]}$$

$$= \frac{[\text{OH}^-][\text{H}^+]}{[\text{B}][\text{H}^+]} \left\{ \frac{[\text{BH}^+]}{[\text{B}][\text{H}^+]} \right\}$$

$$= K_w / K_a$$

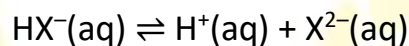
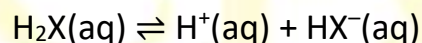
$$K_a \times K_b = K_w$$

- On taking the -ve logarithm of both sides of the equation, then pK values of the conjugate acid and base are as follows:

$$pK_a + pK_b = pK_w = 14 \text{ (At 298K temperature)}$$

### Di and polybasic acids and di-and poly acidic bases

- The ionization reactions for a dibasic acid  $\text{H}_2\text{X}$  are represented by the equations:



- The corresponding equilibrium constants  $K_{a1}$  and  $K_{a2}$  are as follows:

$$K_{a1} = \frac{[\text{H}^+][\text{HX}^-]}{[\text{H}_2\text{X}]}$$

$$K_{a2} = \frac{[\text{H}^+][\text{X}^{2-}]}{[\text{HX}^-]}$$

- Here,  $K_{a1}$  and  $K_{a2}$  = the first and second ionization constants respectively of the acid  $\text{H}_2\text{X}$ .
- For tribasic acids like  $\text{H}_3\text{PO}_4$  ; have three ionization constants.

Table: The Ionization constants of some common poly-protic acids (298K)

Acid	$K_{a1}$	$K_{a2}$	$K_{a3}$
Oxalic Acid	$5.9 \times 10^{-2}$	$6.4 \times 10^{-5}$	

Ascorbic Acid	$7.4 \times 10^{-4}$	$1.6 \times 10^{-12}$	
Sulphurous Acid	$1.7 \times 10^{-2}$	$6.4 \times 10^{-8}$	
Carbonic Acid	Very large	$1.2 \times 10^{-2}$	
Sulphuric Acid	$4.3 \times 10^{-7}$	$5.6 \times 10^{-11}$	
Citric Acid	$7.4 \times 10^{-4}$	$1.7 \times 10^{-5}$	$4.0 \times 10^{-7}$
Phosphoric Acid	$7.5 \times 10^{-3}$	$6.2 \times 10^{-8}$	$4.2 \times 10^{-13}$

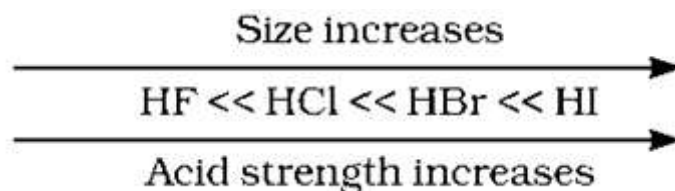
- For a poly-protic acid; the higher order ionization constants ( $K_{a2}$ ,  $K_{a3}$ ) are smaller than the lower order ionization constant ( $K_{a1}$ ).
- The reason for this is that it is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces. This can be seen in the case of removing a proton from the uncharged  $H_2CO_3$ . As compared from a negatively charged  $HCO_3^-$ .
- Other similar example: It is difficult to remove a proton from a doubly charged  $HPO_4^{2-}$  anion as compared to  $H_2PO_4^-$ .
- Polyprotic acid solutions contain a mixture of acids like  $H_2A$ ,  $HA^-$  and  $A^{2-}$  in case of a diprotic acid.
- $H_2A$  is a strong acid, the primary reaction involves the dissociation of  $H_2A$ , and  $H_3O^+$  in the solution comes mainly from the first dissociation step.

### Factors affecting acid strength

- The degree of dissociation of an acid depends on the strength and polarity of the H-A bond.
- When strength of H-A bond decreases, means the energy required to break the bond decreases; HA becomes a strong acid.
- When the H-A bond becomes more polar means the electronegativity difference between the atoms H and A increases and there is marked charge separation, cleavage of the bond becomes easier thereby increasing the acidity.
- Comparing elements in the same group of the periodic table bond strength of HA is a more important factor to determining acidity. As the

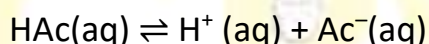
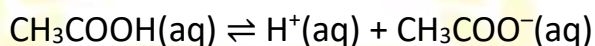


size of A increases down the group, H-A bond strength decreases and consequently the acid strength increases. Example:



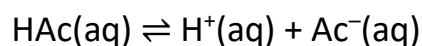
### Common ion effect in the ionization of acids and bases

- Common ion effect is a shift in equilibrium on adding a substance that offers more of an ionic species already present in the dissociation equilibrium.
- Example: Acetic acid dissociation equilibrium:



$$K_a = [\text{H}^+][\text{Ac}^-] / [\text{HAc}]$$

- Addition of acetate ions to an acetic acid solution results in decreasing the concentration of hydrogen ions,  $[\text{H}^+]$ .
- If  $\text{H}^+$  ions are added from an external source then the equilibrium moves in the direction of undissociated acetic acid means in a direction of reducing the concentration of  $[\text{H}^+]$  ions.
- To evaluate the pH of the solution resulting on addition of 0.05M acetate ion to 0.05M  $\text{CH}_3\text{COOH}$  solution, we shall consider the acetic acid dissociation equilibrium once again:



Initial concentration (M)

**0.05                    0                    0.05**

Let x be the degree of ionization of acetic acid.

Change in concentration (M)

**-x                    +x                    +x**

Equilibrium concentration (M)

**0.05-x**                      **x**                      **0.05+x**

So,

$$K_a = \frac{[H^+][Ac^-]}{[HAc]}$$
$$= \frac{\{(0.05+x)(x)\}}{(0.05-x)}$$

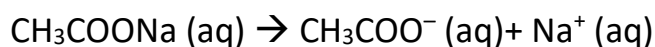
As the value of  $K_a$  is small for a weak acid,  $x \ll 0.05$ .

$$\text{So, } (0.05 + x) \approx (0.05 - x) \approx 0.05$$

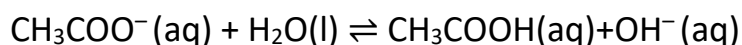
$$1.8 \times 10^{-5} = \frac{(x)(0.05 + x)}{(0.05 - x)}$$
$$= \frac{x(0.05)}{(0.05)} = x = [H^+] = 1.8 \times 10^{-5} \text{ M}$$
$$\text{pH} = -\log(1.8 \times 10^{-5}) = 4.74$$

### Hydrolysis of salts and the pH of their solutions

- Salts formed by the reactions between acids and bases in definite proportions, undergo ionization in water.
- The cations/anions formed ions in aqueous solutions or interact with water to reform corresponding acids/bases depending upon the nature of salts. The process of interaction between water and cations/anions or both of salts is known as hydrolysis.
- The pH of the solution gets affected by this interaction. The cations (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ , etc.) of strong bases and anions (e.g.,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  etc.) of strong acids get hydrated but do not hydrolyse, and so the solutions of salts formed from strong acids and bases are neutral which means their pH is 7. Yet, the other category of salts do undergo hydrolysis.
- Let's consider the hydrolysis of the salts of the following types :
  1. Salts of weak acid and strong base e.g.,  $\text{CH}_3\text{COONa}$ :
    - $\text{CH}_3\text{COONa}$  is a salt of weak acid, acetic acid and sodium hydroxide gets completely ionised in aqueous solution.



- Acetate ion thus formed undergoes hydrolysis in water to give acetic acid and hydroxyl ions.



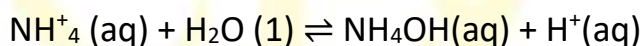
- Acetic acid being a weak acid ( $K_a = 1.8 \times 10^{-5}$ ) remains mainly unionised in solution. This results in increase of hydroxyl ion concentration in solution making it alkaline. The pH of solution is greater than 7.

## 2. Salts of strong acid and weak base e.g., $\text{NH}_4\text{Cl}$ .

- $\text{NH}_4\text{Cl}$  made from weak base which is  $\text{NH}_4\text{OH}$  and strong acid  $\text{HCl}$ ,  $\text{NH}_4\text{Cl}$  in water completely dissociates as follows:



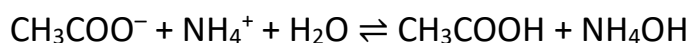
- Ammonium ions undergo hydrolysis with water to form  $\text{NH}_4\text{OH}$  and  $\text{H}^+$  ions.



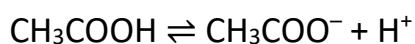
- Ammonium hydroxide is a weak base ( $K_b = 1.77 \times 10^{-5}$ ) and therefore remains almost unionised in solution. This results in increased of  $\text{H}^+$  ion concentration in solution making the solution acidic. The pH of  $\text{NH}_4\text{Cl}$  solution in water is  $< 7$ .

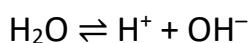
## 3. Salts of weak acid and weak base, e.g., $\text{CH}_3\text{COONH}_4$

- Consider the hydrolysis of  $\text{CH}_3\text{COONH}_4$  salt formed from weak acid and weak base. The ions formed undergo hydrolysis as follow:



- $\text{CH}_3\text{COOH}$  and  $\text{NH}_4\text{OH}$ , also remain into partially dissociated form:





- The extent of hydrolysis is not depend upon concentration of solution, and pH of solution can be determined by pK values.

$$\text{pH} = 7 + \frac{1}{2} (\text{pK}_a - \text{pK}_b)$$

**Example:** The  $\text{pK}_a$  of  $\text{CH}_3\text{COOH}$  and  $\text{pK}_b$  of  $\text{NH}_4\text{OH}$  are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution.

**Solution:**

$$\begin{aligned}\text{pH} &= 7 + \frac{1}{2} [\text{pK}_a - \text{pK}_b] \\ &= 7 + \frac{1}{2} [4.76 - 4.75] \\ &= 7 + \frac{1}{2} [0.01] \\ &= 7 + 0.005 = 7.005\end{aligned}$$

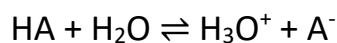
## Buffer Solutions

- The solutions which on dilution resist the change in pH or with the addition of small amounts of acid or alkali are called Buffer Solutions.
- A mixture of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$  acts as buffer solution around pH 4.75 and a mixture of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  act as a buffer around pH 9.25.

## Designing buffer solution

### Preparation of acidic buffer:

- To prepare a buffer of acidic pH a weak acid and its salt formed with strong base is used.
- An equation developed which relate the pH, the equilibrium constant ( $K_a$ ) of weak acid and ratio of concentration of weak acid and its conjugate base.
- For the general case where the weak acid HA ionises in water,



The expression for above reaction is as follows:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

After rearrangement:

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

After taking log on both sides and rearranging them:

$$\text{p}K_a = \text{pH} - \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Or

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Conjugate base, A}^-]}{[\text{Acid, HA}]}$$

- This expression is termed as Henderson–Hasselbalch equation. The quantity  $[\text{A}^-]/[\text{HA}]$  is the ratio of concentration of conjugate base of the acid and acid present in mixture.
- Since acid is a weak acid, it ionises very little and concentration of  $[\text{HA}]$  is negligibly different from concentration of acid taken to form buffer.
- Most of the conjugate base  $[\text{A}^-]$  comes from the ionisation of salt of the acid. Consequently the concentration of conjugate base will be negligibly different from the concentration of salt.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{Acid}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

- In above equation if  $[A^-] = [HA]$ , then  $pH = pK_a$  because value of  $\log 1$  is zero. Thus it can be concluded that if molar concentration of acid and salt are same, then  $pH$  of the buffer solution will be equal to the  $pK_a$  of the acid.
- Analysis of a buffer made with a weak base and its conjugate acid:

$$pOH = pK_b + \log \frac{[\text{Conjugate acid, } BH^+]}{[\text{Base, B}]}$$

- $pH$  of the buffer solution can be calculated by using the formula =  $pH + pOH = 14$ .
- As we know  $pH + pOH = pK_w$  and  $pK_a + pK_b = pK_w$ . On putting these values in above equation:

$$pK_w - pH = pK_w - pK_a + \log \frac{[\text{Conjugate acid, } BH^+]}{[\text{Base, B}]}$$

Or

$$pH = pK_a + \log \frac{[\text{Conjugate acid, } BH^+]}{[\text{Base, B}]}$$

- If molar concentration of base and its conjugate acid (cation) is same then  $pH$  of the buffer solution will be same as  $pK_a$  for the base.
- $pK_a$  value for ammonia is 9.25; so a buffer of  $pH$  close to 9.25 can be obtained by taking ammonia solution and ammonium chloride solution of same molar concentration.
- For a buffer solution formed by  $NH_4Cl$  and  $NH_4OH$

$$pH = 9.25 + \log \frac{[\text{Conjugate acid, } BH^+]}{[\text{Base, B}]}$$

### Solubility equilibrium of sparingly soluble salts

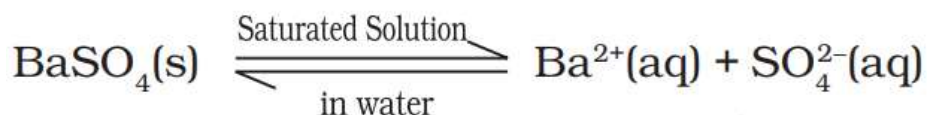
- The solubility of ionic solid depends on a number of factors. Such as lattice enthalpy of the salt and the solvation enthalpy of the ions in a solution.
- The solvation enthalpy of ions is energy is released in the process of solvation, it is always –ve.
- The solvation enthalpy dependent of the nature of the solvent.
- For a salt to be able to dissolve in a particular solvent, solvation enthalpy > lattice enthalpy.
- Each salt's solubility depends on temperature.

Table: classification of salts on the basis of their solubility

<b>Category I</b>	Soluble	Solubility > 0.1M
<b>Category II</b>	Slightly soluble	0.01M < solubility < 0.1M
<b>Category III</b>	Sparingly soluble	Solubility < 0.01M

### Solubility Product Constant

- If a solid like BaSO<sub>4</sub> comes in contact with its saturated aqueous solution. The equilibrium is as follows:



- The equilibrium constant (K) is given by the equation:

$$K = \{[\text{Ba}^{2+}][\text{SO}_4^{2-}]\} / [\text{BaSO}_4]$$

The concentration remains constant for a pure solid substance and we can write:

$$K_{\text{sp}} = K[\text{BaSO}_4] = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

- K<sub>sp</sub> the solubility product constant or simply solubility product. The experimental value of K<sub>sp</sub> in above equation at 298K is 1.1 × 10<sup>-10</sup>.
- This means that for solid BaSO<sub>4</sub> in equilibrium with its saturated solution, the product of the concentrations of barium and sulphate ions is equal to its solubility product constant.

$$1.1 \times 10^{-10} = S^2$$

Or

$$S = 1.05 \times 10^{-5}$$

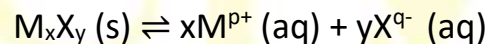
- Molar solubility of  $\text{BaSO}_4$  will be equal to  $1.05 \times 10^{-5} \text{ mol L}^{-1}$ .
- A salt on dissociation gives two or more than two anions and cations carrying different charges.
- Example: zirconium phosphate  $(\text{Zr}^{4+})_3 (\text{PO}_4^{3-})_4$  dissociates into three zirconium cations of charge +4 and four phosphate anions of charge -3.
- If the molar solubility of zirconium phosphate is  $S$ , according to the stoichiometry of the compound:

$$[\text{Zr}^{4+}] = 3S \text{ and } [\text{PO}_4^{3-}] = 4S$$

$$\text{and } K_{\text{sp}} = (3S)^3 (4S)^4 = 6912 (S)^7$$

$$\text{or } S = \{K_{\text{sp}} / (3^3 \times 4^4)\}^{1/7} = (K_{\text{sp}} / 6912)^{1/7}$$

- A solid salt of the general formula  $\text{M}_x^{\text{p}+} \text{X}_y^{\text{q}-}$  with molar solubility  $S$  in equilibrium with its saturated solution can be represented as follows:



Here  $x \times \text{p}^+ = y \times \text{q}^-$

Solubility product constant is as follows:

$$K_{\text{sp}} = [\text{M}^{\text{p}+}]^x [\text{X}^{\text{q}-}]^y = (xS)^x (yS)^y$$
$$= x^x \cdot y^y \cdot S^{(x+y)}$$

$$S^{(x+y)} = K_{\text{sp}} / x^x \cdot y^y$$

$$S = (K_{\text{sp}} / x^x \cdot y^y)^{1 / x+y}$$

- The term  $K_{\text{sp}}$  is given by  $Q_{\text{sp}}$  when the concentration of one or more species is not the concentration under equilibrium.
- Under equilibrium conditions

$$K_{\text{sp}} = Q_{\text{sp}}$$

**Example:** Calculate the solubility of  $\text{A}_2\text{X}_3$  in pure water, assuming that any kind of ion does not react with water. The solubility product of  $\text{A}_2\text{X}_3$ ,  $K_s = 1.1 \times 10^{-23}$ .



### Solution:



$$K_{sp} = [A^{3+}]^2 [X^{2-}]^3 = 1.1 \times 10^{-23}$$

If S = solubility of  $A_2X_3$  then

$$[A^{3+}] = 2S; [X^{2-}] = 3S$$

$$\text{So, } K_{sp} = (2S)^2 (3S)^3 = 108S^5$$

$$= 1.1 \times 10^{-23}$$

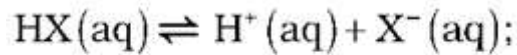
$$\text{Thus, } S^5 = 1 \times 10^{-25} \quad S = 1.0 \times 10^{-5} \text{ mol/L.}$$

### Common ion effect on solubility of ionic salts

- According to Le Chatelier's principle that if the concentration of any one of the ions is increased, it must combine with the ion of its opposite charge and some of the salt will precipitate till  $K_{sp} = Q_{sp}$ .
- If the concentration of one of the ions is decreased, more salt will dissolve to increase the concentration of both the ions till once again  $K_{sp} = Q_{sp}$ .
- This is applicable even to soluble salts like NaCl except that due to higher concentrations of the ions. Thus if we take a saturated solution of NaCl and pass HCl gas through it, then NaCl is precipitated due to increased concentration of chloride ion available from the dissociation of HCl. NaCl thus obtained is of very high purity and we can get rid of impurities like sodium and magnesium sulphates.
- The common ion effect is used for complete precipitation of a particular ion such as sparingly soluble salt, with low solubility product for gravimetric estimation. Through this silver ion can be precipitate as silver chloride, ferric ion as hydrated ferric oxide and barium ion as barium sulphate for quantitative estimations.

- At lower pH solubility of salts of weak acids like phosphates increases. Due to protonation at lower pH the concentration of the anion decreases. This in turn increase the solubility of the salt to make  $K_{sp} = Q_{sp}$ .

$$K_{sp} = [M^+][X^-]$$



$$K_a = \frac{[H^+(aq)][X^-(aq)]}{[HX(aq)]}$$

$$[X^-] / [HX] = K_a / [H^+]$$

- inverting both side and adding 1 to it:

$$\frac{[HX]}{[X^-]} + 1 = \frac{[H^+]}{K_a} + 1$$

$$\frac{[HX] + [X^-]}{[X^-]} = \frac{[H^+] + K_a}{K_a}$$

- After taking inverse again :

$$[X^-] / \{[X^-] + [HX]\} = f = K_a / (K_a + [H^+])$$

- If S is the solubility of the salt at a given pH then:

$$K_{sp} = [S] [f S] = S^2 \{K_a / (K_a + [H^+])\}$$

$$S = \{K_{sp}([H^+] + K_a) / K_a\}^{1/2}$$

Thus solubility S increases with increase in  $[H^+]$  or decrease in pH