

# 13

## IONIC EQUILIBRIA

### 13.1. INTRODUCTION

We have studied law of chemical equilibrium and various types of chemical and physical equilibria in our previous lessons. In the present lesson, we will study the equilibria which involve ionic species and occur in aqueous solutions. All of the general characteristics of equilibrium that you have studied earlier are exhibited in these systems, too. Le Chatelier's principle, for example, is of great value in predicting equilibrium changes in aqueous solutions. As is the case of gaseous or other molecular systems / reactions, all the ionic system in aqueous solutions tend to approach equilibrium. Thus, law of chemical equilibrium can be applied to all such ionic systems which we are going to study.

In this lesson, we shall consider those aqueous solution equilibria that are classed as acid base equilibria, solubility equilibria and some other interrelated aspects concerning these equilibria such as pH, buffer solutions and common ion effects. These equilibria come under category of homogeneous and heterogeneous equilibria. The life process of plants and animals occur in aqueous solution or in contact with water. In most of these cases ionic equilibria are involved.

### 13.2. OBJECTIVES

After reading this lesson you will be able to

- explain hydrogen and hydronium ions, and concept of proton transfer in solution.
  - define an acid and a base in terms of the Bronsted Lowry theory.
-

- define conjugate acid base pairs and identify them in different solutions.
- explain an amphiprotic substance.
- derive the expression for ionization constant for weak acids and bases.
- solve numerical problems based on ionization constant.
- write an equation for the self ionization of water and derive an expression for ionic product of water  $K_w$ .
- define acidic, basic and neutral solutions in terms of their hydrogen ion concentration.
- use the ionic product of water to calculate the concentration of hydroxide ion in a solution of known hydrogen ion concentration.
- define pH and calculate it from hydrogen ion concentration.
- use the expression of  $K_w$  to calculate pH from hydroxide ion concentration.
- calculate hydrogen ion concentration from pH.
- explain a buffer solution in terms of its properties and its composition and apply Le Chatelier's principle and equilibrium law to explain the buffer action.
- explain solubility equilibrium and write an expression for the solubility product of slightly soluble salts.
- calculate the solubility products from solubility data and vice versa through a few solved numerical problems.
- illustrate common ion effect.
- calculate solubility product and ionic product.

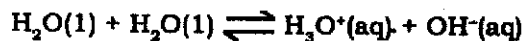
### 13.3. CONCEPT OF ACIDS AND BASES

We are familiar with acids, like HCl,  $H_2SO_4$ ,  $HNO_3$  etc. and bases like NaOH, KOH etc. In the nineteenth century, the concept of acids and bases were not very clear. In 1884, Svante Arrhenius constructed a simple picture of acids and bases. He defined an acid as a compound that produces hydrogen ions ( $H^+$ ) and a base as a compound that produces hydroxide ions ( $OH^-$ ) in aqueous solutions.

Here in acids, hydrogen ion,  $H^+$  does not remain as base proton but it is bonded with water and forms  $H_3O^+(aq)$ . This species, called the hydronium ions, is itself associated through hydrogen bonding with a variable number of water molecules.

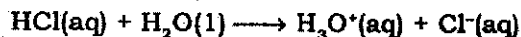
The special role of the hydronium ion (or hydrogen ion) and the hydroxide ion in aqueous solution arises from the following reaction.

---

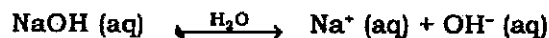


Thus addition of acids and bases alters the concentrations of these ions in water,

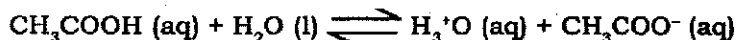
According to Arrhenius theory, a strong acid is a substance that completely ionizes in aqueous solution to give  $\text{H}_3\text{O}^+$  (aq) and an anion. An example is hydrochloric acid, HCl.



Other examples of strong acids are  $\text{H}_2\text{SO}_4$ , HBr, HI,  $\text{HNO}_3$  and  $\text{HClO}_4$ . A strong base completely ionises in aqueous solution to give  $\text{OH}^-$  and a cation. Sodium hydroxide is an example of a strong base.



The principal strong bases are hydroxides of Groups 1 and 2 elements (except Be). Most of the other acids and bases we come across are weak. They are not completely ionised in solution and exist in equilibrium, with the corresponding ions. Let us consider acetic acid,  $\text{CH}_3\text{COOH}$ .



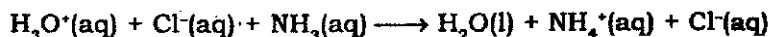
In such case we denote dissociation by  $\rightleftharpoons$  since ionisation is not complete and an equilibrium exists between dissociated and undissociated molecules of the acid. In case of strong electrolytes we normally write dissociation by putting only single  $\rightarrow$ . Experimental evidence of weak and strong electrolytes comes from heat of neutralisation.

### 13.3.1 - The Bronsted-Lowry Concept of Acids and Bases

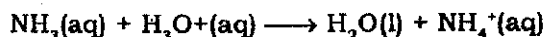
In 1923, the Danish Chemist Johannes M. Bronsted and the British chemist Thomas M. Lowry pointed out independently that acid-base reactions can be interpreted as proton-transfer reactions. *An acid is defined as a proton,  $\text{H}^+$  donor, and a base is Defined as a proton acceptor.* The definitions are sufficiently broad, that any hydrogen-containing molecule or ion capable of releasing a proton,  $\text{H}^+$ , is an acid, while any molecule or ion that can accept a proton is a base.

**According to Bronsted-Lowry theory an acid base reaction is the transfer of a proton from an acid to a base**

Let us consider the reaction of hydrochloric acid with ammonia. If we write ionic equation, we have



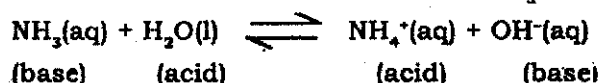
After cancelling  $\text{Cl}^-$ , we get ionic equation



Here, in aqueous solution, a proton  $\text{H}^+$  is transferred from the  $\text{H}_3\text{O}^+$  ion to the  $\text{NH}_3$  molecule, giving  $\text{H}_2\text{O}$  and  $\text{NH}_4^+$ . Here  $\text{H}_3\text{O}^+$  is proton donor or acidic and

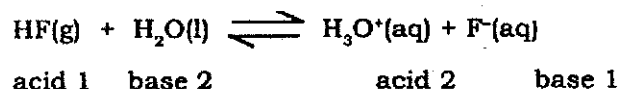
$\text{NH}_3$  is proton acceptor, or base. It should be noted that in the Bronsted Lowry Concept, acids, (and bases) can be ion as well as molecular substances.

In any acid-base equilibrium both forward and reverse reactions involve proton transfers. Let us consider the reaction of  $\text{NH}_3$  with  $\text{H}_2\text{O}$ .



In this forward reaction,  $\text{NH}_3$  accepts a proton from  $\text{H}_2\text{O}$ . Thus,  $\text{NH}_3$  is a base and  $\text{H}_2\text{O}$  is an acid. In the reverse reaction,  $\text{NH}_4^+$  donates proton to  $\text{OH}^-$ . The  $\text{NH}_4^+$  ion is the acid and  $\text{OH}^-$  is the base. Here you find that  $\text{NH}_3$  and  $\text{NH}_4^+$  differ by a proton. That is,  $\text{NH}_3$  becomes the  $\text{NH}_4^+$  ion gaining a proton, whereas  $\text{NH}_4^+$  ion becomes the  $\text{NH}_3$  molecule by losing a proton. The species  $\text{NH}_4^+$  and  $\text{NH}_3$  are *conjugate acid-base pair*. A conjugate acid-base pair consists of two species in an acid-base reaction, one acid and one base, that differ by the gain or loss of a proton. The acid in such a pair is called conjugate acid of the base, whereas the base is the conjugate base of acid. Thus  $\text{NH}_4^+$  is the conjugate acid of  $\text{NH}_3$ , and  $\text{NH}_3$  is the conjugate base of  $\text{NH}_4^+$ . The member of each conjugate pair are designated by the same numerical subscript.

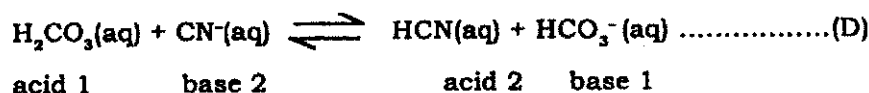
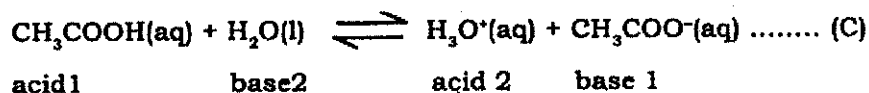
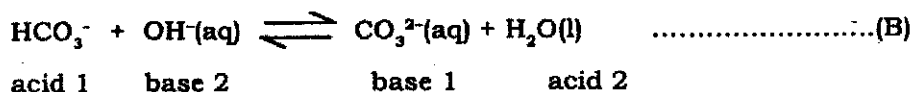
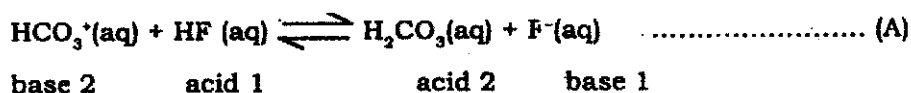
Let us take ionisation of hydrogen fluoride in water



Where HF is dissolved in water, the HF molecules give up some  $\text{H}^+$  ions that can be accepted by either of the two bases,  $\text{F}^-$  and  $\text{H}_2\text{O}$ . The fact that HF is only slightly ionised tells us that  $\text{F}^-$  is a stronger base than  $\text{H}_2\text{O}$ .

When HCl (a strong acid) is dissolved in water, the HCl molecules give up  $\text{H}^+$  ions that can be accepted by either of two bases,  $\text{Cl}^-$  and  $\text{H}_2\text{O}$ . The fact that HCl is completely ionised in dilute aqueous solution tells us that  $\text{Cl}^-$  is a weaker base than  $\text{H}_2\text{O}$ . Thus, the stronger acid, HCl has the weaker base,  $\text{Cl}^-$ . The weaker acid, HF, has the stronger conjugate base,  $\text{F}^-$ . We can generalize : *The weaker an acid is, the greater is the base strength of its conjugate acid.* Likewise, **the weaker a base is, the stronger is its conjugate acid.** Here you should understand that 'strong' and 'weak' like many other adjectives are used in a relative sense. We do not mean to imply that the fluoride ion,  $\text{F}^-$  is a strong base compared to species such as the hydroxide ion,  $\text{OH}^-$ . We mean that relative to an ions of strong acids, which are very weak bases,  $\text{F}^-$  is a much stronger base.

Let us write a few reactions involving conjugate acid-base pairs.



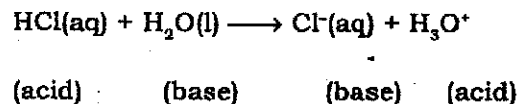
If we examine closely, we find that *some species can act both as an acid and as a base. Such species are called amphoteric species.* In example A and D,  $\text{HCO}_3^-$  (aq) acts as a base in presence of HF but an acid in presence of  $\text{CN}^-$ . Similarly in (B) and (C)  $\text{H}_2\text{O}$  behaves as an acid and a base respectively

Thus, we have now seen several ways in which the Bronsted Lowry concept of acids and bases has greater scope than the Arrhenius concept. In the Bronsted Lowry concept.

- A base is a species that accepts protons;  $\text{OH}^-$  is an example of a base.
- Acids and bases can be ion as well as molecular substance.
- Acid base reaction are not restricted to aqueous solutions.
- Some species can act as either acids or bases, depending on what the other reactant is.

### 13.3.2 Relative Strength of Acids and Bases

Strong acid are those which lose their protons more easily than others. Similarly, stronger bases are those which hold on to protons more strongly than others. In reaction



the reverse reaction occurs only to an extremely small extent. As stated earlier, in this equation acid HCl is stronger acid than  $\text{H}_3\text{O}^+$  or that, of the two,  $\text{H}_3\text{O}^+$  is the weaker acid. *An acid base reaction goes in the direction of weaker acids.* We can use this fact to compare the relative strength of any two acids

The relative order of acid strengths by comparing their relative ionisations in water, can not be determined in case of strong acids such as HCl, HI etc. When these acids are dissolved in water, they are essentially 100% ionized. However, if we look at solutions of equal concentrations of these acids in another solvent that is less basic than water say pure acetic acid we do see a greater difference. Neither acid is completely ionised but a greater fraction of HI molecules is found to be ionised. Thus, HI is stronger acid than HCl. In water, the acid strengths of the strong acids appear to be the same, that is, they are 'levelled out'. We say that water exhibits a levelling effect on the strengths of the strong acids. Table 13.1 provides relative strengths of acids and bases.

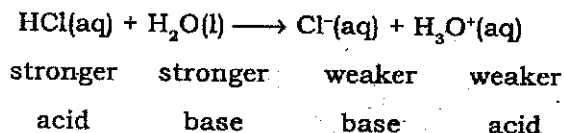
TABLE 13.1

Strongest acid	Acid	Base	Weakest base
	HClO <sub>4</sub>	ClO <sub>4</sub> <sup>-</sup>	
	H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	
	HI	I <sup>-</sup>	
	HBr	Br <sup>-</sup>	
	HCl	Cl <sup>-</sup>	
	HNO <sub>3</sub>	NO <sub>3</sub> <sup>-</sup>	
	H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O	
	HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	
	H <sub>2</sub> SO <sub>3</sub>	HSO <sub>3</sub> <sup>-</sup>	
	H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	
	HNO <sub>2</sub>	NO <sub>2</sub> <sup>-</sup>	
	HF	F <sup>-</sup>	
	CH <sub>3</sub> COOH	CH <sub>3</sub> COO <sup>-</sup>	
	Al (H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>	Al (H <sub>2</sub> O) <sub>5</sub> OH <sup>2+</sup>	
	H <sub>2</sub> CO <sub>3</sub>	HCO <sub>3</sub> <sup>-</sup>	
	H <sub>2</sub> S	HS <sup>-</sup>	
	HClO	ClO <sup>-</sup>	
	HBrO	BrO <sup>-</sup>	
	NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub>	
	HCN	CN <sup>-</sup>	
	HCO <sub>3</sub>	CO <sub>3</sub> <sup>2-</sup>	
	H <sub>2</sub> O <sub>2</sub>	HO <sub>2</sub> <sup>-</sup>	
	HS <sup>-</sup>	S <sup>2-</sup>	
Weakest acid	H <sub>2</sub> O	OH <sup>-</sup>	Strongest base

In case of the reaction,  $\text{HCl(aq)} + \text{H}_2\text{O(l)} \longrightarrow \text{Cl}^{\text{-}}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$  the arrow points from HCl (acid) towards H<sub>3</sub>O<sup>+</sup>, the direction in which the reaction occurs. This reaction can also be viewed in terms of the bases, H<sub>2</sub>O and Cl<sup>-</sup>. A stronger base picks up a proton more readily than does a weaker one. Water has greater base strength than the Cl<sup>-</sup> ion, that is, H<sub>2</sub>O picks up proton more readily than Cl<sup>-</sup> does. The reaction goes in the direction of weaker base.

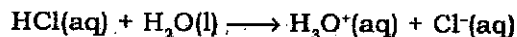
**Remember, the strongest acids have the weakest conjugate bases, and the strongest bases have the weakest conjugate acids.**

You can use Table 13.1 to predict the direction of an acid-base reaction. The direction for an acid-base reaction always favours the weaker acid and weaker base. That is, the normal direction is from the stronger acid and base to the weaker acid and base. For the reaction we have been discussing, we have



### 11.3.3 Equilibria in Aqueous Solutions of Acids and Bases

Some of the most important applications of equilibria are concerned with reactions in aqueous solutions. We have just seen that dissociation of strong acids and bases in aqueous solutions is nearly complete and equilibrium lies far to the right. Let us reconsider the dissociation of HCl. We write



If you apply law of chemical equilibrium you can write

$$k = \frac{[\text{H}_3\text{O}^+]_{\text{aq}} [\text{Cl}^-]_{\text{aq}}}{[\text{H}_2\text{O}]_{\text{aq}} [\text{HCl}]_{\text{aq}}}$$

The value of  $k$  is very large. Contrary to this, weak acids and bases do not dissociate completely. Then dissociation is to a small extent and equilibrium constant in such case is small. In case of weak acids and bases we can compare their strength based on the values of dissociation constants.

#### Weak Acids

As stated weak acids do not react with water completely or we say they do not dissociate completely. For example in case of acetic acid following equilibrium is established.



Applying law of chemical equilibrium as in other cases, we can write equilibrium constant  $K$  as

$$k = \frac{[\text{CH}_3\text{COO}^-] [\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}] [\text{H}_2\text{O}]} \dots \dots \dots (1)$$

As you might be aware, in solutions all concentrations are measured in moles per litre. It would be desirable to mention here that we will consider here only dilute solutions of acids and bases in which there is excess of water compared with the solute species. Therefore, in the expression (1) we can take  $[\text{H}_2\text{O}]$  to be constant\*. Therefore (1) can be written as

\*  $[\text{H}_2\text{O}]$  here is  $\frac{1000}{18}$  mol/litre i.e. 55.5 mol/litre. As compared to the concentration of acids,

concentration term for water is very high and as such can be taken as constant.

$$K [\text{H}_2\text{O}] = \frac{[\text{CH}_3\text{COO}^-] [\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

Since  $[\text{H}_2\text{O}]$  is constant,  $k [\text{H}_2\text{O}]$  in the above expression also comes as constant. We can write

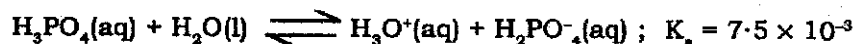
$$K [\text{H}_2\text{O}] = K_a = \frac{[\text{H}_3\text{O}^+] [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Here  $K_a$  is called dissociation constant of the weak acid.

Dissociation constant of other weak acids also can be written. For example, HF is a weak acid in water. We can write  $K_a$  for this ( $\text{HF}(\text{aq}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{F}^-$ ) as

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

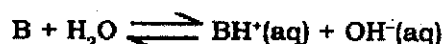
Like other dissociation constants,  $K_a$  value depends on the temperature. The values of  $K_a$  show the extent to which the acids are dissociated in water. As mentioned earlier strong acids have very large dissociation constants that can not be measured. Relative strength of acids is judged on the basis of dissociation constant. For example



On the basis of  $K_a$  values we can say that phosphoric acid is much more ionized than hydrocyanic acid. In other words phosphoric acid is stronger acid than hydrocyanic acid although both are weak; neither is completely ionized.

### Weak Bases

A weak base is not completely protonated by water



The solution contains the base, B, the protonated base,  $\text{BH}^+$ , hydroxide ion  $\text{OH}^-$ , and water in equilibrium. The equilibrium constant for the reaction is

$$K = \frac{[\text{BH}^+] [\text{OH}^-]}{[\text{B}] [\text{H}_2\text{O}]}$$

here  $[\text{H}_2\text{O}]$  is constant, hence

$$K [\text{H}_2\text{O}] = \frac{[\text{BH}^+] [\text{OH}^-]}{[\text{B}]} = K_b$$

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



The constant  $K_b$  is called the *base dissociation constant* similar to  $K_a$ . Similar to values of  $K_a$ ,  $K_b$  values also give the idea about the relative strength of weak bases.

### Polyprotic Acids

Many acids have more than one available proton. These acids are called diprotic if there are two available protons per molecule. (e.g.  $H_2SO_3$ ,  $H_2CO_3$ ), triprotic if there are three available protons (e.g.  $H_3PO_4$ , etc). Such acids dissociate in more than one steps or stages, each with its own dissociation constant. In case of sulphurous acid  $H_2SO_3$ , these steps can be



$$K_1 = \frac{[H_3O^+][HSO_3^-]}{[H_2SO_3]} = 1.3 \times 10^{-2}$$



$$K_2 = \frac{[H_3O^+][SO_3^{2-}]}{[HSO_3^-]} \text{ or } K_2 = 6.3 \times 10^{-8}$$

### 13.3.4 Calculating the Extent of Dissociation of Weak Acids and Bases

In order to understand how to calculate the extent of dissociation, let us take an example

**Example 13.1 :** Calculate the concentration of  $H_3O^+$  in 0.50M solution of acetic acid. Dissociation constant of acetic acid is given  $K_a = 1.8 \times 10^{-5} \text{ mol L}^{-1}$

**Solution :** **First step** in solving any equilibrium problem is to write the equation reaction. In this case the reaction is

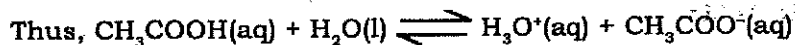


The **second step** is to write for expression equilibrium constant which is for  $1.8 \times 10^{-5} \text{ mol L}^{-1}$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5} \text{ mol L}^{-1}$$

The **third step** is to write the expression for the concentration of each of the species present at equilibrium.

Now suppose  $x$  mol per litre of acetic acid dissociates and we get  $x$  mol  $L^{-1}$  of  $H_3O^+$  and  $x$  mol  $L^{-1}$  of  $CH_3COO^-$  ions. Therefore, the concentration of acetic acid which remains at equilibrium i.e. concentration of undissociated acetic acid will be  $(0.50 - x)$  mol  $L^{-1}$



Initial concentration	0.50	0	0 mol $L^{-1}$
Equilibrium concentration	$(0.50 - x)$	$x$	$x$ mol $L^{-1}$

The fourth step is to substitute these concentrations in the expression for  $K_a$  and solve for  $x$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x \text{ mol } L^{-1})(x \text{ mol } L^{-1})}{(0.5 - x) \text{ mol } L^{-1}}$$

$$= 1.8 \times 10^{-5} \text{ mol } L^{-1}$$

$$\text{or, } \frac{x^2}{0.5 - x} \text{ mol } L^{-1} = 1.8 \times 10^{-5} \text{ mol } L^{-1}$$

Here in case of weak acids  $x$  is much less than 0.50 ( $x \ll 0.50$ ), and can be neglected, then

$$0.50 - x = 0.50$$

and, therefore

$$\frac{x^2}{0.5} \text{ mol } L^{-1} = 1.8 \times 10^{-5} \text{ mol } L^{-1}$$

$$x^2 = 0.50 \times 1.8 \times 10^{-5}$$

$$x = 3.0 \times 10^{-3}$$

Thus  $[H_3O^+] = 3.0 \times 10^{-3} \text{ mol } L^{-1}$ ,  $[CH_3COO^-] = 3.0 \times 10^{-3} \text{ mol } L^{-1}$

Suppose some one asks what is the percent dissociation of 0.5M acetic acid molecules? Then it would be easy.

**The percent dissociation of acid is the number of moles dissociated per litre divided by initial (predissociated) number of moles per litre into 100.**

$$\text{i.e. percent dissociation} = \frac{3.0 \times 10^{-3} \text{ mol } L^{-1} \text{ dissociated}}{0.50 \text{ mol } L^{-1} \text{, initial or undissociated}} \times 100$$

$$= 0.60 \%$$

**Example 13.2.** What is the concentration of  $OH^-$  ions in a 0.10 M aqueous solution of ammonia if dissociation constant of ammonia,  $K_b$  is  $1.8 \times 10^{-5} \text{ mol } L^{-1}$

**Solution:** First step,  $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$

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

Third step,  $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$

Initial concentration                      0.10                      0                      0 mol L<sup>-1</sup>

Equilibrium concentration              (0.10-x)                      x                      x mol L<sup>-1</sup>

The fourth step

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{(0.10-x)} \text{ mol L}^{-1} = 1.8 \times 10^{-5} \text{ mol L}^{-1}$$

For ammonia, extent of ionization will be small and therefore x is much less than 0.10. Hence (0.10-x) = 0.10.

The equation becomes

$$\frac{x^2}{0.10} = 1.8 \times 10^{-5}$$

$$x^2 = 1.8 \times 10^{-6}$$

$$x = 1.3 \times 10^{-3}$$

Hence  $[\text{OH}^-] = 1.3 \times 10^{-3} \text{ mol L}^{-1}$

(Thus  $[\text{OH}^-]$  is approximately 1% of the initial concentration of  $\text{NH}_3$ , 0.10 mol L<sup>-1</sup>, hence the assumption that we made in solving the equation was justified).

### INTEXT QUESTIONS 13.1

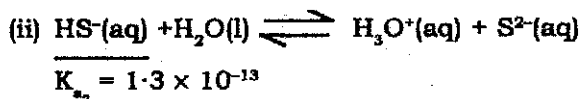
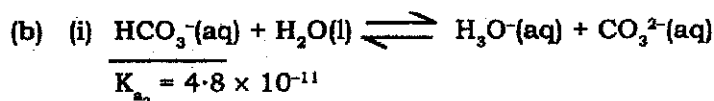
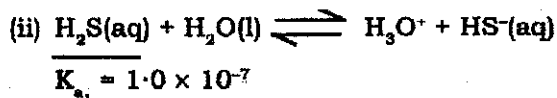
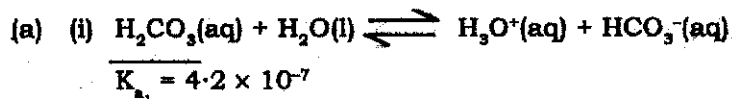
1. (a) In the following reaction, identify the acid on the left and its conjugate base on the right. Similarly, identify the base on the left and its conjugate acid on the right.



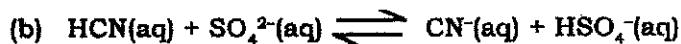
- (b) What is the conjugate base of  $\text{H}_2\text{S}$ ?

- (c) What is the conjugate acid of  $\text{NO}_3^-$ ?

2. Examine each underlined acids and find out which of the acids in the following pairs are stronger?



3. For each of the following reactions predict whether the equilibrium lies predominantly to the left or to the right. Explain your prediction briefly.



4. What is the  $\text{H}_3\text{O}^+$  concentration in a 0.20 M solution of hydrocyanic acid, HCN? What is the correct dissociation of the acid?

### 13.4. THE DISSOCIATION OF WATER

We have seen that water can act as a very weak acid and also as a very weak base. Very small concentration of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are therefore formed in water due to its self-ionisation.

The reaction is



The equilibrium constant condition is expressed as

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

since the concentration of  $\text{H}_2\text{O}$  molecule is constant,

$[\text{H}_3\text{O}^+][\text{OH}^-] = K' [\text{H}_2\text{O}]^2 = K_w$  (a new constant) The constant,  $K_w$ , is called the dissociation constant or **ionic product constant of water**.

Measurement of electrical conductivity of carefully purified water has shown that at  $25^\circ\text{C}$ ,  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7} \text{ mol L}^{-1}$

$$\begin{aligned} K_w &= [\text{H}_3\text{O}^+][\text{OH}^-] = (1.0 \times 10^{-7} \text{ mol L}^{-1})(1.0 \times 10^{-7} \text{ mol L}^{-1}) \\ &= 1.00 \times 10^{-14} \text{ mol}^2\text{L}^{-2} \text{ at } 25^\circ\text{C} \end{aligned}$$

### Acidic, basic and neutral solutions:

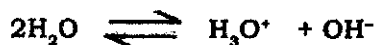
An acidic solution is defined as one in which the hydrogen ion concentration (hydronium ion concentration) is greater than the hydroxide ion concentration. A basic solution is one in which the reverse is true, that is, one in which  $[\text{OH}^-]$  exceeds  $[\text{H}^+]$ . Finally a neutral solution is one in which  $[\text{OH}^-]$  equals  $[\text{H}^+]$ . Because the  $[\text{H}^+][\text{OH}^-]$  product is constant, then two concentrations can be conserved to be balanced 'against each other', when either increases the other decreases. They are not independent but are linked by the relationship  $[\text{H}^+][\text{OH}^-] = K_w$  which gives us easy way to calculate one concentration from the other.

We can see that equilibrium constant applies not only to pure water but also to the self-ionization of water in any aqueous solution. Hydronium ions and hydroxide ions are present in any aqueous solution, and they are always in equilibrium with water molecules.

**Example 13.3 :** Calculate  $\text{OH}^-$  ion concentration in 0.01 solution of HCl.

**Solution:** Here, concentration of  $\text{OH}^-$  will be less than it is in a pure water because  $\text{H}_3\text{O}^+$  from the ionization of HCl will shift the position of the equilibrium of the self-ionization reaction to the left. Suppose concentration of  $\text{OH}^-$  is  $x \text{ mol L}^{-1}$ , then concentration of  $\text{H}_3\text{O}^+$  from the self-ionization of water must also be  $x \text{ mol L}^{-1}$ . The concentration of  $\text{H}_3\text{O}^+$  from ionization of HCl is  $0.010 \text{ mol L}^{-1}$ . Therefore, total concentration of  $\text{H}_3\text{O}^+(\text{aq}) = (0.010 + x) \text{ mol L}^{-1}$

Thus



Equilibrium concentration       $(0.01 + x)$        $x$        $\text{mol L}^{-1}$

Substituting these values into the equilibrium constant for the self-ionization of water, we have

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (0.01 + x)(x) \text{ mol}^2\text{L}^{-2} = 1.0 \times 10^{-14} \text{ mol}^2\text{L}^{-2}$$

Since  $x$  must be very small, we can assume that  $x \ll 0.01$  and therefore

$$(0.01 + x) \cong 0.01, \text{ so}$$

$$0.01x = 1.0 \times 10^{-14}$$

$$\text{or } x = 1.0 \times 10^{-12}$$

$$x = 1.0 \times 10^{-12}$$

$$[\text{OH}^-] = 1.0 \times 10^{-12} \text{ mol L}^{-1}$$

Thus, we see that in acidic solution  $\text{OH}^-$  exist but their concentration is very small. Similarly in basic solutions the concentration of  $\text{H}_3\text{O}^+$  will be very small. Presence of acids and bases repress the self ionization of water.

### 13.5. pH SCALE:

Solutions of acids and bases in water may have  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  concentration that vary over a very wide range, that is, from greater than  $1 \text{ mol L}^{-1}$  down to  $10^{-14} \text{ mol L}^{-1}$  and  $[\text{OH}^-]$  less than  $10^{-7} \text{ mol L}^{-1}$  at  $25^\circ\text{C}$ . Similarly basic (alkaline) solutions have  $[\text{OH}^-]$  greater than  $10^{-7} \text{ mol L}^{-1}$  and  $[\text{H}_3\text{O}^+]$  less than  $10^{-7} \text{ mol L}^{-1}$  at  $25^\circ\text{C}$ . A neutral solution such as water will have  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7}$ .

You might be aware generally people telling acid and alkaline soil. In fact, this concentration is based on the  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  concentration. Plants tolerate only limited range of  $\text{H}_3\text{O}^+$  concentration in the soil. Many reactions in living systems occur only in very narrow ranges of  $\text{H}_3\text{O}^+$  concentration. Blood has a constant  $\text{H}_3\text{O}^+$  concentration very close to  $2.5 \times 10^{-7} \text{ mol L}^{-1}$  ( $\text{pH} = 7.4$ ).

While expressing the concentration of  $\text{H}_3\text{O}^+$  in a solution, we avoid the use of negative powers of 10 by using pH scale. The pH\* of a solution is the negative logarithm to the base 10 of the hydrogen ion concentration,  $[\text{H}_3\text{O}^+]$ .

$$\text{Thus } \text{pH} = -\log_{10} [\text{H}_3\text{O}^+]$$

Here it would be relevant to mention that units of  $[\text{H}_3\text{O}^+]$  are moles per litre, but when the logarithm is taken, the units are dropped because it is impossible to take the logarithm of a quantity with units. Therefore, pH has no units.

For pure water, the  $\text{H}_3\text{O}^+$  concentration is  $10^{-7} \text{ mol L}^{-1}$  then

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] = -\log_{10} [10^{-7}]$$

$$= -(-7.0) = +7.0$$

Hydrogen ion concentration in aqueous solution range from about  $10^{-15}$  to  $10$   $\text{mol L}^{-1}$ , so it is convenient to have a scale that is both negative and logarithmic. The negative sign produces positive pH values for almost all solutions we find in practice. The logarithmic scale reduces the extremely wide variation in  $[\text{H}_3\text{O}^+_{\text{aq}}]$  to a narrow range of pH from 15 to -1.

\*The 'p' in pH comes from the german word 'potenz' meaning power and 'H' from  $[\text{H}^+]$ .

**Example 13.4 :** What is the pH of 0.1 mol L<sup>-1</sup> HCl ?

**Solution :** Since HCl is fully dissociated and monobasic,

$$[\text{H}_3\text{O}^+(\text{aq})] \text{ in } 0.1 \text{ mol L}^{-1} \text{ HCl} = 1 \times 10^{-1} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(10^{-1}) = -(-1) = +1$$

**Example 13.5 :** What is the pH of 1 × 10<sup>-3</sup> mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> ?

**Solution :** Since H<sub>2</sub>SO<sub>4</sub> is fully dissociated and dibasic,

$$[\text{H}_3\text{O}^+(\text{aq})] \text{ in } 10^{-3} \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 = 2 \times 10^{-3} \text{ mol L}^{-1}$$

$$\therefore \text{pH} = -\log[\text{H}_3\text{O}^+(\text{aq})] = -\log(2 \times 10^{-3})$$

$$= -(+0.30 - 3.00)$$

$$= -(-2.70) = +2.70.$$

**Example 13.6 :** Calculate the pH of the following aqueous solutions

(i) 0.010 M NaOH

(ii) 0.134 M NaOH

**Solution :** Since NaOH is a strong base, it is fully ionized to give Na<sup>+</sup> and OH<sup>-</sup>

$$(i) \quad [\text{OH}^-] = 1.0 \times 10^{-2} \text{ mol L}^{-1}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$$

$$\text{So, } [\text{H}_3\text{O}^+] = \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}}{1.00 \times 10^{-2} \text{ mol L}^{-1}}$$

$$= 1.00 \times 10^{-12} \text{ mol L}^{-1}$$

$$\text{pH} = -\log_{10}(1.0 \times 10^{-12}) = 12.$$

$$(ii) \quad [\text{OH}^-] = 0.134 \text{ mol L}^{-1}$$

$$[\text{H}_3\text{O}^+] = \frac{1.00 \times 10^{-14} \text{ mol L}^{-2}}{0.134 \text{ mol L}^{-1}}$$

$$= 7.46 \times 10^{-14} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[7.46 \times 10^{-14}] = 13.13$$

**Example 13.7 :** The pH of pure water at 25°C is 7. What is hydrogen ion concentration ?

**Solution :** pH = -log[H<sub>3</sub>O<sup>+</sup>]

$$\text{or } 7 = -\log[\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 10^{-7} \text{ mol L}^{-1}.$$

### 13.5.1 Buffer Solutions

In laboratory reactions, in industrial processes and in the bodies of plants and animals, it is often necessary to keep the pH nearly constant despite the addition of acids and bases. The oxygen carrying capacity of haemoglobin in our blood and activity of the enzymes in our cells depends very strongly on the pH of our body fluids. pH of the blood is very close to 7.4 and pH of saliva is close to 6.8. Fortunately, animals and plants are protected against sharp changes in pH by the presence of buffers.

**Buffers are solutions which resist changes in pH on addition of acid or alkali in reasonable concentrations.**

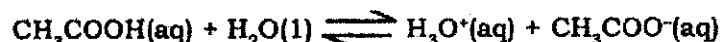
Two common kinds of buffer-solutions are known

- (i) a weak acid plus a soluble ionic salt of the weak acid e.g. ( $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ ) and,
- (ii) a weak base plus a soluble ionic salt of the weak base (e.g.  $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ )

A buffer solution contains a conjugate acid base pair with the acid and base in reasonable concentrations. The more acidic component reacts with added strong base, and more basic component reacts with added acids.

**A buffer solution is able to react with either  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions whichever is added.**

Let us consider a buffer solution containing acetic acid,  $\text{CH}_3\text{COOH}$ , and sodium acetate  $\text{CH}_3\text{COONa}$  (i.e. buffer made of weak acid and salt of weak acid). Here, more acidic component is  $\text{CH}_3\text{COOH}$ . The more basic component is  $\text{CH}_3\text{COONa}$  because the  $\text{CH}_3\text{COO}^-$  ions is conjugate base of  $\text{CH}_3\text{COOH}$ . The operation of this buffer depends on the equilibrium,



High concentration

High concentration from salt

If we add a strong acid such as HCl to this solution, it produces  $\text{H}_3\text{O}^+$ . As a result of the added  $\text{H}_3\text{O}^+$ , the reaction occurs to the left, to use up most of the added  $\text{H}_3\text{O}^+$  and re-establish equilibrium. Because of the  $[\text{CH}_3\text{COO}^-]$  in the buffer solution is high, this can occur to a great extent. The net reaction is,



or, as a formula unit equation



added acid base                      weak acid                      salt

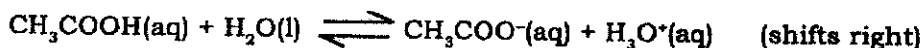
The reaction goes nearly to completion because  $\text{CH}_3\text{COOH}$  is a weak acid.



When a strong soluble base, such as NaOH, is added to the  $\text{CH}_3\text{COOH}$ - $\text{CH}_3\text{COONa}$  buffer solution, it is consumed by acetic component,  $\text{CH}_3\text{COOH}$ . This occurs in the following way. The additional  $\text{OH}^-$  causes the water auto ionization to proceed to left.



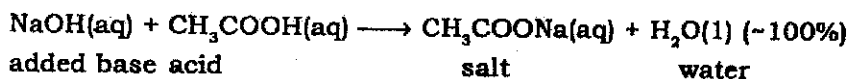
This uses up some  $\text{H}_3\text{O}^+$ , causing more  $\text{CH}_3\text{COOH}$  to ionize



Because the  $(\text{CH}_3\text{COOH})$  is high, this can occur to a great extent. The net result is the neutralisation of  $\text{OH}^-$  by  $\text{CH}_3\text{COOH}$ .

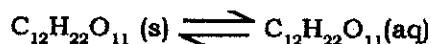


or as a formula unit equation,



### 13.6 THE SOLUBILITY OF IONIC SOLIDS AND SOLUBILITY PRODUCT.

When a solid non-electrolyte is dissolved in water, the resulting solution contains only one kind of solute species: neutral molecules. For example when sucrose (cane sugar) is dissolved we get equilibrium.

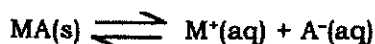


In which sucrose molecules in solution are in equilibrium with excess undissolved solute.

On the other hand, when solid electrolyte is dissolved, at least two kinds of particles (ions) are released in solution, and so at saturation the equilibrium is more complex. For example, in a saturated solution of NaCl, sodium and chloride ions are in equilibrium with excess solid NaCl.



NaCl is highly soluble in water. There are also compounds which are slightly soluble or sparingly soluble in water, such as  $\text{CaSO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{BaCO}_3$ ,  $\text{CaF}_2$ ,  $\text{AgCl}$  etc. Such salts are very important in natural phenomena. Our bone and teeth are mostly calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$  slightly soluble salt. In such cases, what amount of the salt is dissolved, fully dissociates in solution and an equilibrium is established between solid phase and aqueous ionic solution. Let us consider a slightly soluble ionic solid MA, composed of  $\text{M}^+$  and  $\text{A}^-$  ions located at crystal lattice. Suppose that enough MA is added to some water to produce a saturated solution with some solid MA left over. This establishes solubility equilibrium,



For which equilibrium constant is

$$\frac{[M^+][A^-]}{[MA]} = K'$$

As we have seen, the concentration of a substance in its solid phase is a constant. Therefore, the above equilibrium condition can be written as,

$$[M^+][A^-] = K' [MA]$$

$$\text{or } [M^+][A^-] = K_{sp}$$

where  $K_{sp}$  represents the product of the two constant terms  $K'$  and  $[MA]$ . The mass expression on the left, is called, ion product and the equilibrium constant  $K_{sp}$  is called **solubility product**, or **solubility product constant of substance MA**. At equilibrium, the ion product is equal to the solubility product. This is of course, just a statement of equilibrium condition. Equilibrium between  $MA(s)$  and  $M^+(aq)$  and  $A^-(aq)$  is an example of a heterogeneous equilibrium because it involves both a solid and a solution.

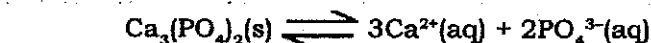
The form of the ion product depends on the stoichiometry of the reaction,

Thus for



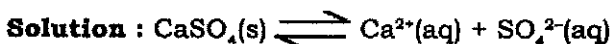
$$\text{solubility, } K_{sp} = [Ca^{2+}][F^-]^2$$

and for



$$\therefore K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2$$

**Example 13.8** : The solubility of calcium sulphate in water is  $4.9 \times 10^{-3}M$  at  $25^\circ C$ . Calculate the value of  $K_{sp}$  for  $CaSO_4$  at this temperature.



For this reaction

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

From the equation we see that when  $4.9 \times 10^{-3}$  mol of  $CaSO_4$  dissolves to make 1 L of a saturated solution, the reacting ionic concentration are

$$[Ca^{2+}] = 4.9 \times 10^{-3}M \text{ or } 4.9 \times 10^{-3} \text{ mol L}^{-1}$$

$$[SO_4^{2-}] = 4.9 \times 10^{-3}M \text{ or } 4.9 \times 10^{-3} \text{ mol L}^{-1}$$

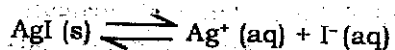
$$\begin{aligned} K_{sp} &= [Ca^{2+}][SO_4^{2-}] = (4.9 \times 10^{-3} \text{ mol L}^{-1})(4.9 \times 10^{-3} \text{ mol L}^{-1}) \\ &= 2.4 \times 10^{-5} \text{ mol}^2\text{L}^{-2} \end{aligned}$$

TABLE 13.2 Solubility product at 25°C

Component	$K_{sp}$	Component	$K_{sp}$
AgCl	$1.7 \times 10^{-10}$		
Ag <sub>2</sub> CrO <sub>4</sub>	$1.9 \times 10^{-12}$	CaSO <sub>4</sub>	$2.4 \times 10^{-5}$
Ag <sub>2</sub> S	$5.5 \times 10^{-51}$	CuS	$6 \times 10^{-37}$
Al(OH) <sub>3</sub>	$5 \times 10^{-33}$		
BaF <sub>2</sub>	$1.7 \times 10^{-6}$		
BaSO <sub>4</sub>	$1.5 \times 10^{-9}$	Fe(OH) <sub>2</sub>	$2 \times 10^{-15}$
		PbCl <sub>2</sub>	$1.6 \times 10^{-5}$
CaF <sub>2</sub>	$1.7 \times 10^{-10}$	ZnS	$1.2 \times 10^{-23}$

**Example 13.9 :** Solubility product of silver iodide, AgI is  $8.5 \times 10^{-17}$  at 25°C. What is the molar solubility of AgI in water at this temperature?

**Solution :** Silver iodide dissolves according to the equation



Here Ag<sup>+</sup> and I<sup>-</sup> ions are present in the ratio of 1:1. Therefore, if x be equal to the number of moles of AgI dissolved per litre of solution then

$$[\text{AgI}] = x$$

$$[\text{I}^-] = x$$

At equilibrium,  $[\text{Ag}^+][\text{I}^-] = K_{sp}$

Substituting the values, we have

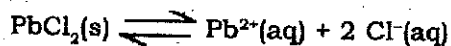
$$(x)(x) = 8.5 \times 10^{-17}$$

$$x = (8.5 \times 10^{-17})^{1/2} = 9.2 \times 10^{-9}$$

The solubility of AgI in water is therefore  $9.2 \times 10^{-9}\text{M}$  at 25°C.

### 13.7. COMMON ION EFFECT

Suppose we have saturated solution of PbCl<sub>2</sub> (molar solubility =  $9.2 \times 10^{-9}\text{M}$ ) in equilibrium with the solid salt.

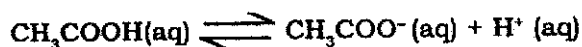


If we add NaCl or other soluble chloride salt to the solution and thus increase the concentration of Cl<sup>-</sup> ion, then according to Le Chatelier's principle the equilibrium will shift to left. In other words more lead chloride will precipitate and, concentration of lead ions in solution will decrease. Thus, solubility of lead chloride is less in a solution containing chloride ion than it is in pure water. The solubility of any salt is decreased in the presence of another salt that has common ion. This decrease in solubility is an example of the **Common Ion Effect**.

Common ion effect can be defined as

**The process in which the dissociation of a weak electrolyte is further suppressed by the addition of a strong electrolyte, containing common anions or cations is called common ion effect.**

We have studied dissociation of weak acids. In 0.1M solution of acetic acid, methyl orange\* assumes its colour, red. If sodium acetate is added to this solution, the colour changes to yellow, showing that the addition causes the acidity of the solution to decrease,



As stated above this also can be explained on the basis of Le Chatelier's principle and is another example of common ion effect.

**Example 13.10** : Calculate the solubility of AgI in 0.10M NaI at 25°C.  $K_{sp}$  for AgI is  $8.5 \times 10^{-7}$  at this temperature.

**Solution** : Here, you should remember that NaI is a strong electrolyte. When 0.1M NaI is dissolved, it will fully dissociate and will give 0.1M iodide ion. Thus, before any AgI has dissolved,  $[\text{I}^-] = 0.1\text{M}$ . Further, let  $x$  mole of AgI dissolves per litre of NaI solution at 25°C. Then at equilibrium  $[\text{Ag}^+] = x$ ,  $[\text{I}^-] = 0.10 + x$ .

We know that  $K_{sp} = [\text{Ag}^+][\text{I}^-]$

Substituting the value of  $[\text{Ag}^+]$  and  $[\text{I}^-]$ , we obtain

$$(x)(0.10+x) = 8.5 \times 10^{-17}$$

If we assume that  $x \ll 0.10$ , then  $0.10 + x \approx 0.10$ , and therefore

$$x(0.10) = 8.5 \times 10^{-17}$$

$$x = 8.5 \times 10^{-16}$$

(The number  $x$  is clearly negligible in comparison with 0.10 and thus justifies our assumption)

Therefore solubility of AgI in 0.10M, NaI solution is  $8.5 \times 10^{-16}\text{M}$ .

The common ion effect has wide application in *qualitative analysis* where we obtain precipitate of sparingly soluble salts /Compounds suitably by adjusting a common ion. We also suppress the dissociation of certain weak electrolytes (acids, bases and salts ) by adding common ions. For example in quantitative analysis of 2nd group radicals, copper, mercury, cadmium, bismuth) metal sulphides are precipitated when  $\text{H}_2\text{S}$  is added. Here HCl is added in solution of these radicals and then  $\text{H}_2\text{S}$  is passed. In presence of HCl,  $\text{H}_2\text{S}$  dissociates very feebly and sulphide ion concentration is so low that only sulphide of 2nd group elements precipitate not that of 4th group (which also give sulphide precipitate when  $\text{H}_2\text{S}$  is passed in alkaline medium).

\* Methyl orange is an indicator used in acid base titration.

---

**INTEXT QUESTIONS 13.2**


---

1. What is the hydrogen ion concentration in a neutral solution at 25°C ?  
-----
  2. What is the pH of a  $4.6 \times 10^{-3}$ M solution of HCl ?  
-----
  3. The pH of a certain solution is 11.8. What is the hydrogen ion concentration in this solution ?  
-----
  4. Which of the following combinations will provide buffering effect in a solution ?
    - (i)  $\text{CH}_3\text{COONa}$ ,  $\text{CH}_3\text{COOH}$
    - (ii)  $\text{HCOOH}$ ,  $\text{HCOONa}$
    - (iii)  $\text{Na}_3\text{PO}_4$ ,  $\text{Na}_2\text{SO}_4$
    - (iv)  $\text{H}_2\text{CO}_3$ ,  $\text{NaHCO}_3$
    - (v)  $\text{Na}_2\text{CO}_3$ ,  $\text{MgCO}_3$  
-----
  5. Silver chromate,  $\text{Ag}_2\text{Cr}_4$  (a red solution), dissolves in water to the extent of  $0.029 \text{ g L}^{-1}$  at 25°C. Estimate its solubility product  $K_{sp}$ .  
-----
- 

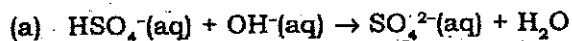
**13.8 WHAT YOU HAVE LEARNT**

- According to Arrhenius, a substance which gives out  $\text{H}^+$  is an acid and the one which gives out  $\text{OH}^-$  is a base.
  - An acid-base reaction is the transfer of a proton from an acid to a base. According to Bronsted Lowry, an acid is a proton donor and a base is a proton acceptor.
  - Conjugate acids and bases are related to one another by the gain or loss of proton. A weak acid has a strong conjugate base and a strong acid has a weak conjugate base and vice versa. In general, acid base reactions proceed in the direction favouring the weaker acid base pair.
  - Species which can act as an acid as well as a base are called amphiprotic species (such as  $\text{H}_2\text{O}$ ,  $\text{HCO}_3^-$  etc).
  - Strong acids and bases dissociate to nearly completion.
-

- Dissociation constant of acids,  $K_a$ , and dissociation constant of bases  $K_b$  give the idea of relative strengths of acids and bases respectively.
- There is self ionization of water into  $H^+$  and  $OH^-$  ions, and ionic product of water  $K_w = [H^+][OH^-]$  is equal to  $10^{-14}$
- pH is a measure of  $H^+$  ion concentration of a solution. It can be defined as negative logarithm to the base 10 of the hydrogen ion concentration i.e.  $pH = -\log [H_3O^+]$  For neutral solutions,  $pH = 7$ .
- Buffers are solutions which resist changes in pH on addition of an acid or an alkali. Buffer solutions are formed by (i) weak acids and their conjugate bases for example  $CH_3COOH$  and acetate ions  $CH_3COO^-$  (ii) weak bases and their conjugate acids for example  $NH_3$  and  $NH_4^+$
- The solubility product constant,  $K_{sp}$ , for a slightly soluble ionic substance is the equilibrium constant for the equilibrium between the solid and the dissolved ions in a saturated solution. It is the product of the concentration of the ions in the saturated solution raised to the powers indicated by coefficient in the balanced equation for the equilibrium.
- A slightly soluble salt will precipitate if ionic product of its constituent ions exceeds its solubility product.
- The common ion effect is the effect on a system at equilibrium caused by the addition of a substance with an ion common with one involved in the equilibrium.

### 13.9 TERMINAL EXERCISE

1. In the following reactions indicate conjugate and acid-base pairs.



2. Calculate the pH (at  $25^\circ C$ ) of a sample of water that has an  $OH^-(aq)$  concentration of  $1.2 \times 10^{-6} M$ .

-----

3. The degree of ionisation of acetic acid  $CH_3COOH$ , in  $0.10 M$  aqueous solution at  $25^\circ C$  is  $0.013$ .  $K_a$  at this temperature is  $1.7 \times 10^{-5}$ . Calculate the degree of ionisation of  $CH_3COOH$  in a  $0.010 M$   $HCl$ . How is degree of ionisation affected?

-----

4. Which of the following will act as a good buffer,
- (a)  $\text{CH}_3\text{COONa}$ ,  $\text{CH}_3\text{COONH}_4$   
-----
- (b)  $\text{CH}_3\text{COONa}$ ,  $\text{CH}_3\text{COOH}$   
-----
- (c)  $\text{CH}_3\text{COONa}$ ,  $\text{NaF}$   
-----
- (d)  $\text{NaF}$ ,  $\text{Na}_2\text{CO}_3$   
-----
5. Classify the following salts under acidic, basic and neutral category.  
 $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{KF}$ ,  $\text{BaCl}_2$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{KHSO}_4$ .  
-----
6. Calculate the following pH of 0.134M NaOH solution.  
-----
7. The concentration of calcium ion in blood is 0.0025M. If the concentration of oxalate ion is  $1.0 \times 10^{-7}\text{M}$  do you expect calcium oxalate to precipitate? ( $K_{sp}$  for calcium oxalate is  $2.3 \times 10^{-9}$ ).  
-----
8. A litre of a solution saturated at 25°C with calcium oxalate  $\text{CaC}_2\text{O}_4$  on evaporation upto dryness gave 0.0061g residue of  $\text{CaC}_2\text{O}_4$ . Calculate the solubility product for calcium oxalate at this temperature.  
-----

## CHECK YOUR ANSWERS

## INTEXT QUESTIONS 13.1

- Acid on the left is HBr and its conjugate base on the right is Br<sup>-</sup> and base on the left is NH<sub>3</sub> and its conjugate acid on the right is NH<sub>4</sub><sup>+</sup>.
  - Conjugate base of H<sub>2</sub>S is HS<sup>-</sup>.
  - Conjugate acid of NO<sub>3</sub><sup>-</sup> is HNO<sub>3</sub>.
- (a) and (ii) (a) are stronger acids
- Right, H<sub>2</sub>S is a stronger acid than HCO<sub>3</sub><sup>-</sup>.
  - Left, HCN is a weaker acid than HSO<sub>4</sub><sup>-</sup>.
  - Left, CN<sup>-</sup> is a much weaker base than NH<sub>2</sub><sup>-</sup>.
  - Left, CH<sub>3</sub>COOH is a weaker acid than HSO<sub>4</sub><sup>-</sup>.
- Equation for equilibrium is



$$\text{at equilibrium, } K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} = 4.9 \times 10^{-10} \text{ mol L}^{-1}$$

Let  $x$  be the concentration at equilibrium, then  $x = [\text{H}_3\text{O}^+]$

Then we have

	$\text{HCN}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CN}^-(\text{aq})$			
Initial	0.20	0	0	mol L <sup>-1</sup>
concentration				
Equilibrium	0.20 - $x$	$x$	$x$	mol L <sup>-1</sup>
concentration				

Let us substitute these values in the expression of  $K_a$ , we have

$$K_a = \frac{x^2}{(0.20 - x)} \text{ mol L}^{-1} = 4.9 \times 10^{-10} \text{ mol L}^{-1}$$

Since  $x$  is very small in comparison with 0.20, we can write

$$0.20 - x = 0.20$$

$$\text{Then, } \frac{x^2}{0.20} = 4.9 \times 10^{-10}$$

$$x^2 = 0.98 \times 10^{-10} = 98 \times 10^{-12}$$

$$\text{or } x = 9.9 \times 10^{-6}$$



Therefore  $[\text{H}_3\text{O}^+] = 9.9 \times 10^{-6} \text{ mol L}^{-1}$

Since the concentration of HCN that is dissociated is equal to the concentration of  $[\text{H}_3\text{O}^+]$  that is formed,  $9.9 \times 10^{-6} \text{ mol L}^{-1}$ , the percent dissociation of the acid is

$$\frac{9.9 \times 10^{-6} \text{ mol L}^{-1}}{0.20 \text{ mol L}^{-1}} \times 100 = 0.005\%$$

Thus we find that HCN is extremely weak acid. Only 5 molecules in 100,000 are ionised.

## INTEXT QUESTIONS 13.2

1. We have seen in a neutral solution

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

Therefore,

$$[\text{H}^+][\text{OH}^-] = [\text{H}^+]^2 = K_w = 1.0 \times 10^{-14}$$

$$[\text{H}^+] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \text{ mol L}^{-1}$$

2. Because HCl is a strong acid (and because contribution of  $\text{H}_2\text{O}$  for  $\text{H}^+$  is so small),  $[\text{H}^+] = 4.6 \times 10^{-3} \text{ M}$ . Therefore,

$$\text{pH} = -\log [4.6 \times 10^{-3}] = 2.34$$

3. We know,

$$\text{pH} = -\log[\text{H}^+]$$

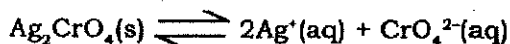
$$[\text{H}^+] = \text{antilog}(-\text{pH})$$

$$= \text{antilog}(-11.68) = 10^{-11.68}$$

$$= 2.1 \times 10^{-12} \text{ mol L}^{-1}$$

4. Only (i), (ii), (iv) will provide buffering effect
5. Molar solubility is calculated from the gram solubility and molar mass of silver chromate, which is  $331.73 \text{ g mol}^{-1}$ ,

$$\begin{aligned} \text{Molar solubility of } \text{Ag}_2\text{CrO}_4 &= \frac{0.029 \text{ g L}^{-1} \text{ Ag}_2\text{CrO}_4}{331.73 \text{ g mol}^{-1}} \\ &= 8.74 \times 10^{-5} \text{ mol L}^{-1} \text{ Ag}_2\text{CrO}_4 \end{aligned}$$



Since 1 mol of  $\text{Ag}_2\text{CrO}_4$  dissolved gives 2 mol of  $\text{Ag}^+$ , and 1 mol of  $\text{CrO}_4^{2-}$  ions.

$$\begin{aligned}\therefore \text{Concentration of Ag}^+ \text{ i.e. } [\text{Ag}^+] &= 2 \times 8.74 \times 10^{-5} \text{ mol L}^{-1} \\ &= 1.75 \times 10^{-4} \text{ mol L}^{-1}\end{aligned}$$

$$\therefore \text{Concentration of CrO}_4^{2-} \text{ i.e. } [\text{CrO}_4^{2-}] = 8.74 \times 10^{-5} \text{ mol L}^{-1}$$

$$\begin{aligned}K_{sp} &= [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] \\ &= (1.75 \times 10^{-4})^2 \times (8.74 \times 10^{-5}) \\ &= 2.7 \times 10^{-12} \text{ mol}^3 \text{L}^{-3}\end{aligned}$$

### TERMINAL EXERCISE

- Conjugate acid-base pairs (i)  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$  (ii)  $\text{H}_2\text{O}$ ,  $\text{OH}^-$
  - Conjugate acid-base pairs (i)  $\text{H}_3\text{O}^+$ ,  $\text{H}_2\text{O}$  (ii)  $\text{H}_2\text{S}$ ,  $\text{S}^{2-}$
- The concentration of  $\text{H}_3\text{O}^+(\text{aq})$  in this sample is

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.2 \times 10^{-6}} = 8.3 \times 10^{-9} \text{ M}$$

$$\text{pH} = -\log (8.3 \times 10^{-9}) = 8.08$$

- Starting concentrations are

$$[\text{CH}_3\text{COOH}] = 0.10 \text{ M}$$

$$[\text{H}^+] = 0.01 \text{ M (from HCl), and } [\text{CH}_3\text{COO}^-] = 0$$

The acetic acid ionizes to give an additional  $x \text{ mol L}^{-1}$  of  $\text{H}^+$  and  $x \text{ mol L}^{-1}$  of  $\text{CH}_3\text{COO}^-$ .

The Table is ,

Concentration (M)	$\text{CH}_3\text{COOH}(\text{aq})$	$\rightleftharpoons$	$\text{H}^+(\text{aq})$	$+$	$\text{CH}_3\text{COO}^-(\text{aq})$
Starting	0.10		0.010		0
Change	-x		+x		+x
Equilibrium	0.10-x		0.010+x		x

Now substituting these value in equation

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$\text{we get, } = \frac{(0.010 + x)(x)}{(0.10 - x)} = 1.7 \times 10^{-5}$$

In order to solve the equation, let us assume that  $x$  is small as compared to 0.010, then

$$0.010 + x = 0.010 \text{ and } 0.10 - x = 0.10$$

The equation becomes,

$$\frac{0.010x}{0.10} = 1.7 \times 10^{-5}$$

Solving for x, we get,  $x = 1.7 \times 10^{-5} \times \frac{0.10}{0.010} = 1.7 \times 10^{-4}$

The degree of ionisation for  $\text{CH}_3\text{COOH}$  is

$$\frac{x}{0.10} = \frac{1.7 \times 10^{-4}}{0.10} = 0.0017$$

This value of degree of ionisation is much smaller than the value of degree of ionisation (0.013) for 0.10M acetic acid, because the addition of HCl suppresses the ionisation of  $\text{CH}_3\text{COOH}$ .

4. (b)  
 5. Basic :  $\text{NaCN}$ ,  $\text{KF}$ ,  $\text{Na}_2\text{CO}_3$   
 Neutral :  $\text{KCl}$ ,  $\text{BaCl}_2$ ,  $\text{Ca}(\text{NO}_3)_2$   
 Acidic :  $\text{NH}_4\text{Cl}$ ,  $\text{KHSO}_4$

6.  $[\text{OH}^-] = 0.134 \text{ mol L}^{-1}$

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}}{0.134 \text{ mol L}^{-1}} = 7.46 \times 10^{-14} \text{ mol L}^{-1}$$

$$\text{pH} = -\log(7.46 \times 10^{-14}) = 13.13$$

7. The ion product for calcium oxalate is given by

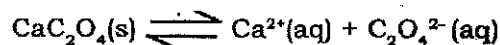
$$\begin{aligned} \text{ion product} &= [\text{Ca}^{2+}] [\text{C}_2\text{O}_4^{2-}] \\ &= (0.0025) (1.0 \times 10^{-7}) \\ &= 2.5 \times 10^{-10} \end{aligned}$$

The value of ion product is smaller than the solubility product. Therefore we should not expect precipitation to occur.

8. Since 1 litre of saturated solution on evaporation gave 0.0061g. Therefore solubility of calcium oxalate = 0.0061g/L. Now in order to have solubility in mol/L we should divide 0.0061g/L by 128(formula mass of calcium oxalate).

$$\text{Molar solubility of calcium oxalate} = 0.0061 \text{ g CaC}_2\text{O}_4 \text{ L}^{-1} \times \frac{1 \text{ mol CaC}_2\text{O}_4}{128 \text{ g CaC}_2\text{O}_4}$$

$$= 4.8 \times 10^{-5} \text{ mol/L}$$



$$K_{sp} = [\text{Ca}^{2+}] [\text{C}_2\text{O}_4^{2-}]$$

$$= (4.8 \times 10^{-5}) (4.8 \times 10^{-5}) = 2.3 \times 10^{-9} \text{ mol}^2 \text{ L}^{-2}$$