

## MODULE - 5

### Chemical Dynamics



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# IONIC EQUILIBRIUM

In the first lesson of this module you learnt about chemical equilibrium, its types and the factors affecting the state of equilibrium. In this the lesson you will learn about the equilibria involving ionic species. The equilibria involving acids and bases are critically important for a wide variety of reactions. The use of buffer solutions for pH control is of significance in living systems, agriculture and industrial processes. Similarly, the solubility equilibrium established in the solutions of sparingly soluble salts is also very important. For example, our bones and teeth are mostly calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , a slightly soluble salt. We would focus our attention primarily on the acid-base and the solubility equilibria and some interrelated aspects concerning these equilibria such as pH, buffer solutions and common ion effect. In this process you would apply the concepts learnt in the first lesson.



## OBJECTIVES

After reading this lesson, you will be able to:

- Differentiate between strong and weak electrolyte ;
- Correlate the degree of dissociation and dissociation constant of a weak electrolyte
- define and explain various concepts of acids and bases;
- define conjugate acid-base pairs and identify them in an acid-base equilibrium;
- derive the expressions for the ionisation constants of weak acids and bases;
- correlate the ionisation constants and the strength of acids and bases;
- explain self ionisation of water and derive an expression for its ionic product;
- define pH and correlate it with the nature of aqueous solutions- neutral, acidic or basic;

- define and explain common ion effect in ionisation of weak acids and bases;
- define buffer solutions;
- apply Henderson equation to calculate the pH of acidic and basic buffers;
- explain hydrolysis of salts with the help of chemical equations;
- express solubility equilibrium with the help of an equation;
- identify the relationship between solubility and solubility product for salts of AB, AB<sub>2</sub>, A<sub>2</sub>B and A<sub>2</sub>B<sub>3</sub> types;
- illustrate and explain the common ion effect on solubility equilibrium and
- recall some applications of common ion effect .

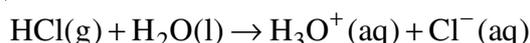
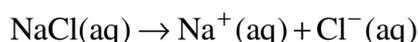


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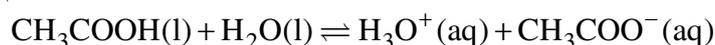
## 12.1 STRONG AND WEAK ELECTROLYTES

**Electrolytes** are the compounds which when dissolved in water produce ions in their solutions. These ions are free to move about and can carry electric charge through the solution when an electric field is applied. Such solutions are therefore good conductors of electricity. Thus, electrolytes are the compounds whose solutions can conduct electricity.

Many electrolytes, when dissolved in water, are almost completely converted into ions. Such electrolytes are called **strong electrolytes**. All ionic compounds like NaCl, KCl, KNO<sub>3</sub>, NH<sub>4</sub>Cl and some covalent compounds like HCl, etc are strong electrolytes. In their case, the process of formation of ions (ionization or dissociation) is represented with the help of a single arrow.



On the other hand, many electrolytes ionize only partially. Such electrolytes are called **weak electrolytes**. Many covalent compounds like CH<sub>3</sub>COOH, NH<sub>4</sub>OH, C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> are weak electrolytes. In its solution, such a compound is present partly in the unionized molecular form and partly in the form of ions. A dynamic equilibrium is established between the two forms when the rate of ionization of molecules to form ions and the rate of combination of ions to form molecules become equal. An equilibrium involving ions is called **ionic equilibrium**. This equilibrium between unionized molecules and the ions is represented by 'reversible arrows'. For example:



The extent to which a weak electrolyte ionizes is expressed with the help of its **degree of ionization**,  $\alpha$ . It is defined as the fraction or percentage of the total amount (or concentration) of the electrolyte that is present in the form of ions.



This expression for  $\alpha$  is known as *Ostwald's Dilution Law*. According to it  $\alpha$ , the degree of ionization of a weak electrolyte depends upon:

- (i) temperature (since  $K$  depends upon  $T$ )
- (ii) concentration of the electrolyte,  $c$ .

At a constant temperature,  $\alpha$  is inversely proportion to the square root of the concentration. Qualitatively,  $\alpha$  increases with the dilution of the solution.

**Example:** Calculate the degree of ionization of  $\text{NH}_4\text{OH}$  in 0.001 M solution at  $25^\circ\text{C}$ . The ionisation constant of  $\text{NH}_4\text{OH}$  is  $1.8 \times 10^{-5} \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$ .

**Solution:**

According to the Ostwald's dilution law

$$\begin{aligned}\alpha &= \sqrt{\frac{K}{c}} \\ &= \sqrt{\frac{1.8 \times 10^{-5}}{0.001}} \\ &= 0.134\end{aligned}$$

## 12.2 GENERAL CONCEPTS OF ACIDS AND BASES

You are quite familiar with the terms acid, base, acidic and acidity etc. But how do we define an acid or a base? There is no general definition of acids and bases. There are three different concepts of acids and bases (proposed by Arrhenius, Brønsted and Lowry and Lewis respectively) which are well known. Each of these emphasize a different aspect of acid - base chemistry. Let us try to understand these concepts.

### 12.2.1 Arrhenius Concept

The most commonly used concept of acids and bases was developed by Svante Arrhenius (1884). According to this concept an acid is a substance that is capable of producing hydrogen ion ( $\text{H}^+$ ) by dissociating in aqueous solution. The reaction can be represented as



Where HA represents the acid and  $\text{A}^-$  refers to the acid molecule (ion) without the hydrogen ion. Hydrochloric acid, HCl is an example of an Arrhenius acid whose ionisation can be represented as



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The proton or hydrogen ion binds itself to a water molecule and form  $\text{H}_3\text{O}^+$  ion which is called **hydronium ion**.



The **hydronium ion** is also known as **oxonium ion** or the **hydroxonium ion**.

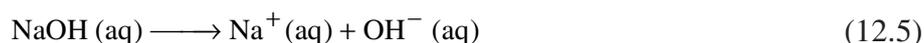
In the light of this fact the equation 12.1 can be rewritten as



A base on the other hand is defined as a substance capable of providing a hydroxyl ion  $\text{OH}^-$  on dissociation in aqueous solutions.



Where  $\text{M}^+$  refers to the base molecule (ion) without the hydroxyl ion. Sodium hydroxide is an example of a Arrhenius base, dissociating as,



Arrhenius concept is quite useful and explains the acid- base behaviour to a good extent. However it has certain drawbacks like,

- It is limited to only aqueous solutions and require dissociation of the substance.
- It does not explain the acidic behaviour of some substances which do not contain hydrogen. for example,  $\text{AlCl}_3$ . Similarly it does not explain the basic character of substances like  $\text{NH}_3$  and  $\text{Na}_2\text{CO}_3$  which do not have a hydroxide groups.

### 12.2.2 Brønsted and Lowry Concept

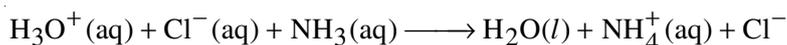
In 1923, Brønsted and Lowry pointed out independently that acid-base reactions can be interpreted as proton-transfer reactions. According to them, *an acid is defined as a proton ( $\text{H}^+$ ) donor, and a base is defined as a proton acceptor*. The definition is sufficiently broad and removes the first limitation of Arrhenius concept. Any hydrogen-containing molecule or ion capable of donating or transferring a proton is an acid, while any molecule or ion that can accept a proton is a base.

For example, in a reaction between ammonia ( $\text{NH}_3$ ) and hydrogen fluoride ( $\text{HF}$ ); ammonia acts as a base (accepts a proton) while  $\text{HF}$  behaves as an acid (donates a proton).

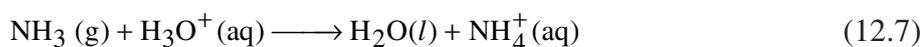


**According to Bronsted-theory an acid is a substance that can donate a proton whereas a base is a substance that can accept a proton.**

You may note in this example that there is no role of a solvent. Let us consider the reaction of hydrochloric acid with ammonia in a solvent like water. We can write ionic equation as

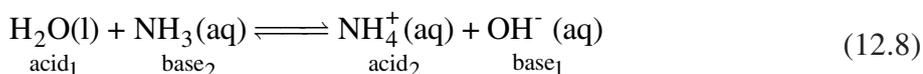


The hydronium and chloride ions are obtained from the ionisation of HCl. After cancelling  $\text{Cl}^-$  on both sides, we get the following ionic equation as



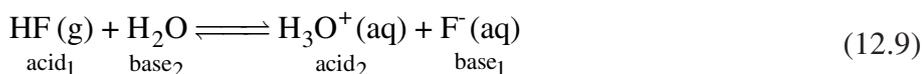
Here, in aqueous solution, a proton is transferred from the hydronium ion,  $\text{H}_3\text{O}^+$ , to the  $\text{NH}_3$  molecule, giving  $\text{H}_2\text{O}$  and  $\text{NH}_4^+$ . In this case  $\text{H}_3\text{O}^+$  acts as proton donor or an acid and  $\text{NH}_3$  as proton acceptor or a base. We may visualise water (the solvent) playing the role of mediator in the transfer of proton from hydrochloric acid to ammonia. It should be noted that in the **Bronsted-Lowry concept, acids and bases can be either ions or 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 the 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 a proton to  $\text{OH}^-$ . Thus  $\text{NH}_4^+$  ion acts as an acid and  $\text{OH}^-$  as a base. Here you find that  $\text{NH}_3$  and  $\text{NH}_4^+$  differ by a proton. That is,  $\text{NH}_3$  becomes  $\text{NH}_4^+$  ion by gaining a proton, whereas  $\text{NH}_4^+$  ion becomes  $\text{NH}_3$  molecule by losing a proton. The species  $\text{NH}_4^+$  and  $\text{NH}_3$  are called **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. It can be represented as  $\text{NH}_4^+ / \text{NH}_3$ . The acid in such a pair is called conjugate acid of the base, where as 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 members of each conjugate pair are designated by the same numerical subscript e.g.,  $\text{NH}_4^+ / \text{NH}_3$  pair is marked as 2 while the  $\text{H}_2\text{O} / \text{OH}^-$  pair is marked as 1.

Let us take another example say of ionization of hydrogen fluoride in water. It can be represented as



The equilibrium sign indicates that the reaction does not go to completion. The  $\text{H}^+$  ions obtained from the ionisation of HF molecule can be accepted by either of



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the two bases,  $F^-$  and  $H_2O$ . The fact that the equilibrium is only slightly towards right tells us that it is the  $F^-$  that accepts the proton and make the reaction go to the left i.e.,  **$F^-$  is a stronger** base than  $H_2O$ .

Similarly when HCl is dissolved in water, the HCl molecules give up  $H^+$  ions that can be accepted by either of two bases,  $Cl^-$  and  $H_2O$ .



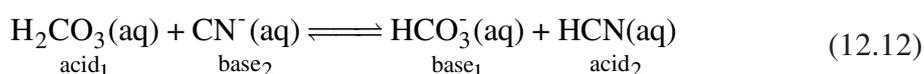
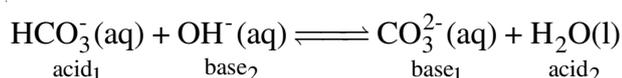
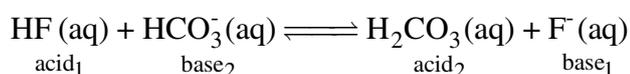
The fact that HCl is completely ionized in dilute aqueous solution ( indicated by a single arrow) tells us that  $Cl^-$  is a weaker base than  $H_2O$ . We can conclude from these two examples that, a stronger acid (HCl) has a weaker conjugate base,  $Cl^-$  and the weaker acid, (HF) has a stronger conjugate base,  $F^-$ . We can generalize that in a conjugate acid-base pair the **weaker an acid is, stronger is its conjugate base. Likewise, the weaker a base is, the stronger is its conjugate acid.**

Here you should understand that the terms ‘strong’ and ‘weak’ like many other adjectives are used in a relative sense. Consider the following reaction



In this case  **$F^-$  is a weaker base** as compared to  $OH^-$ .

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



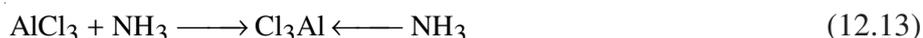
If you examine the above reactions closely, you would find that some species can act both as an acid and as a base. Such species are called **amphiprotic** species. In the above reactions  $HCO_3^-(aq)$  acts as a base in presence of HF but an acid in presence of  $CN^-$ . Similarly  $H_2O$  behaves as an acid and a base.

- Thus, we have seen that the Brønsted- Lowry concept of acids and bases has greater scope than the Arrhenius concept.

### 12.2.3 Lewis Concept

As discussed above the Brønsted- Lowry concept does not depend on the nature of the solvent ( a short coming of the Arrhenius concept removed ). However, like Arrhenius concept it does not explain the acidity of the substances which do not have a hydrogen atom (e.g.,  $AlCl_3$ ) and the basicity of the substances devoid

of a OH group (e.g.,  $\text{Na}_2\text{CO}_3$ ). G.N.Lewis proposed (1923) a yet another concept of acids and bases that includes such substances also. According to him, an acid may be defined as, 'any atom, molecule or ion that can accept an electron pair from any other atom, molecule or ion, A lewis base on the other hand can be defined as, 'any atom, molecule or ion that can donate a pair of electrons, Let us take an example



In the above example  $\text{AlCl}_3$  is an electron deficient species. It accepts an electron pair from a molecule of  $\text{NH}_3$  which has a lone pair of electrons on N atom. Thus,  $\text{AlCl}_3$  is a Lewis acid and  $\text{NH}_3$  is a Lewis base.



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### INTEXT QUESTIONS 12.1

1. Define Arrhenius acid and give two examples.
2. What are the limitations of Arrhenius definition?
3. How does a Brønsted- Lowry base differ from an Arrhenius base?
4. Classify the following into Brønsted- Lowry acid or Brønsted- Lowry base.



5. The degree of dissociation of two electrolytes X and Y are  $1.0 \times 10^{-4}$  and 0.96. Comment on the nature of these electrolytes.

## 12.3 RELATIVE STRENGTH OF ACIDS AND BASES

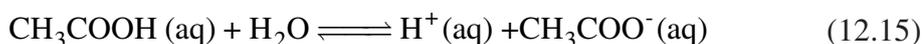
Different acids and bases have different strength depending on their nature. Since there are different ways of defining acids and bases, there are different ways of comparing their relative strengths also.

### 12.3.1 Relative strength according to Arrhenius concept

According to Arrhenius concept strong electrolytes (like HCl) which dissociate completely in aqueous solutions and produce  $\text{H}^+$  ( or  $\text{H}_3\text{O}^+$ ) ions are called strong acids.



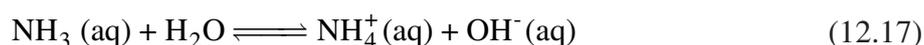
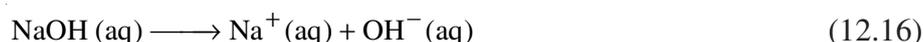
Other examples of strong acids are  $\text{H}_2\text{SO}_4$ , HBr, HI,  $\text{HNO}_3$  and  $\text{HClO}_4$ . On the other hand weak electrolytes like  $\text{CH}_3\text{COOH}$  whose ionisation is not complete, ( because the process is reversible) and produce  $\text{H}^+$  ( or  $\text{H}_3\text{O}^+$ ) ions are called weak acids.





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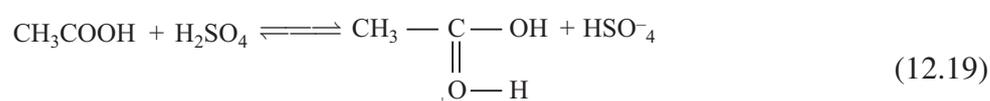
Similarly strong bases may be defined as the electrolytes with complete ionisation and weak bases as the electrolytes with incomplete ionisation. NaOH and  $\text{NH}_3$  are typical examples of strong and weak bases respectively. Their ionisation can be represented as



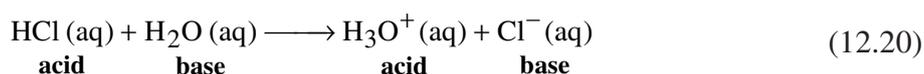
The principal strong bases are hydroxides of Groups 1 and 2 elements (except Be). Most of the other acids and bases we come across are weak bases.

### 12.3.2 Relative strength according to Brønsted- Lowry concept

You have learnt that according to **Brønsted- Lowry concept** an acid is a species that donates a protons while a base is a species that accepts a protons. The tendency of a substance to donate a proton also depends on the species accepting the proton. A given acid may have different strengths in different solvents ( of varying basic strength or proton accepting tendencies) e.g.,



Acetic acid loses a proton to a basic solvent aniline but in sulphuric acid it infact accepts a proton and acts as a base. Therefore the relative strengths of different acids and bases are compared in the same solvent which normally is water. Therefore, in Brønsted- Lowry concept, we may define the relative strength of an acid as its relative tendency to lose (or donate) a proton to water. According to the Brønsted- Lowry concept strong acid are those which lose their protons almost entirely to water. The reaction,



goes completely to the right indicating that HCl is a strong acid. Acetic acid donates its proton to water to the extent of only about 3% and the following equilibrium exists.



Acetic acid is, therefore, termed as a weak acid.

## 12.4 QUANTITATIVE ASPECTS OF STRENGTHS OF ACIDS AND BASES

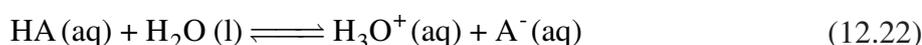
We have so far discussed the relative strengths of acids and bases only qualitatively i.e., which is strong and which one is weak. Many a times we need to know the quantitative aspects also i.e., how much?. That is if a acid is stronger than the other we would like to know how many times stronger. Let us learn how do we quantify it ?



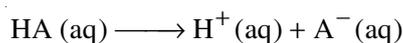
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### 12.4.1 Ionisation of weak acids

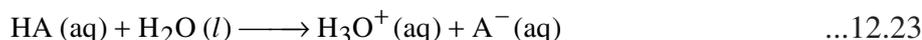
The dissociation or ionisation of a weak acid, HA, can be represented as



As you know that in case of strong acids the ionisation is almost complete or close to 100% or we may say that the equilibrium lies far to the right. In such cases the sign of equilibrium may be replaced by a single arrow ( $\rightarrow$ )



or



The reaction given above (eq 12.22) is referred to as ionisation equilibrium and is characterized by an equilibrium constant

$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{H}_2\text{O}][\text{HA}]} \quad \dots 12.24$$

Since the concentration of a pure liquid or a solid is taken as 1, we can rewrite the above expression can as

$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = K_a \quad \dots 12.25$$

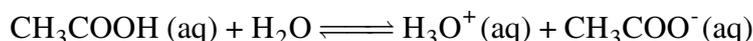
where  $K_a$  is a new constant called acid dissociation constant or ionisation constant of the acid.

The magnitude of the equilibrium constant is a measure of the strength of the acid. Higher the value of the equilibrium constant the stronger is the acid. For all strong acids the values of the equilibrium constants is quite high and does not help much in suggesting their relative strengths. However, for a weak acid, this constant is quite useful.



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**Example 12.1 :** Write down the expression for the dissociation constant for acetic acid- a weak acid that ionizes as



**Solution :** Applying the law of chemical equilibrium, we can write equilibrium constant K as

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

Rearranging, we can write .

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

Dissociation constant of other weak acids also can be written in the same way.

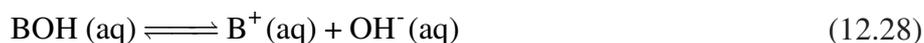
The values of  $K_a$  show the extent to which the acids are dissociated in water. Relative strength of acids is judged on the basis of dissociation constant. Like other equilibrium constants the dissociated constant,  $K_a$  also depends on the temperature. Therefore, the ionisation constants or dissociation constants are compared at the same temperature. For example



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

### 12.4.2 Ionisation of weak bases

The ionisation of weak bases (BOH) can be expressed as :

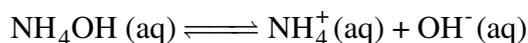


(The equilibrium sign may be replaced by  $\rightarrow$  in case of a strong base.)

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

$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} \quad (12.29)$$

For example, the dissociation of  $\text{NH}_4\text{OH}$  is represented as



and is characterized by

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad (12.30)$$

The constant  $K_b$  is called dissociation constant of the base. Similar to values of  $K_a$ ,  $K_b$  values also give us the idea about the relative strengths of weak bases. Higher the value of  $K_b$  the stronger is the base.

### 12.4.3 Polyprotic Acids

Many acids have more than one ionizable protons. These are called polyprotic acids. The acids are called diprotic if there are two ionizable protons per molecule. (e.g.  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{CO}_3$ ), and triprotic if there are three ionizable protons (e.g.  $\text{H}_3\text{PO}_4$ , etc). Such acids dissociate in more than one steps or stages, each with its own ionization constant. In the case of sulphurous acid,  $\text{H}_2\text{SO}_3$ , these steps are



$$K_1 = \frac{[\text{H}_3\text{O}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]} = 1.3 \times 10^{-2}$$



$$K_2 = \frac{[\text{H}_3\text{O}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} = 6.3 \times 10^{-8}$$

The values of the two ionisation constants ( $K_1$  and  $K_2$ ) are quite different ;  $K_1$  being twenty million times  $K_2$ . It suggests that the first ionisation of sulphurous acid is much more than the second one. In other words the sulphurous acid behaves as a much stronger acid than the bisulphite ion.

### 12.4.4 Degree of Ionisation or Degree of Dissociation

As you know that the weak acids / bases do not ionize completely and an equilibrium exists between the ionized and unionized species. The degree of ionisation may be defined as the fraction of total amount of a weak acid or a base that exists in the ionized form. It is denoted by a Greek letter ' $\alpha$ '. The equilibrium constant can be used to calculate the degree of ionisation of a weak acid or a base. An expression relating  $\alpha$  and  $K_a$  or  $K_b$  can be derived as follows.

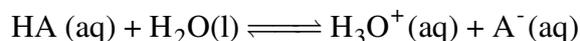


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Consider a weak acid HA which partially dissociates in its aqueous solutions and the following equilibrium is established



Initial concentrations (in moles)	$c$	$\sim 55$	$0$	$0$
Equilibrium concentrations	$c(1-\alpha)$	$\sim 55$	$c\alpha$	$c\alpha$

The equilibrium constant expression can be written as

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{H}_2\text{O}][\text{HA}]} = \frac{[c\alpha][c\alpha]}{c(1-\alpha)55}$$

rearranging we get,

$$\Rightarrow 55K = K_a = \frac{[c\alpha][c\alpha]}{c[1-\alpha]} = \frac{c^2\alpha^2}{c[1-\alpha]} = \frac{c\alpha^2}{(1-\alpha)} \quad (12.33)$$

Since the acid HA is very weak,  $\alpha \ll 1$ ; we can neglect  $\alpha$  in comparison to 1 in the denominator to get

$$K_a = c\alpha^2 \quad \text{or} \quad \alpha^2 = \frac{K_a}{c} \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{c}} \quad (12.34)$$

So if we know the value of the dissociation constant of the acid and the concentration of the weak acids we can find its degree of dissociation or ionisation. Let us take up an example to see the application of this relationship.

**Example 12.2:** Compute the degree of dissociation and percent dissociation of acetic acid in its 0.1 M solution. Given  $K_a = 1.8 \times 10^{-5}$ .

**Solution:** Using the formula  $\alpha = \sqrt{\frac{K_a}{c}}$  and substituting the values of  $K_a$  and  $c$ , we get,

$$\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}} = \sqrt{1.8 \times 10^{-4}} = 1.34 \times 10^{-2} = 0.0134$$

The percent dissociation of a weak acid is defined as

$$\begin{aligned} \text{Percent dissociation} &= \frac{\text{The number of moles of acid in the dissociation}}{\text{Total number of moles of the acid}} \\ &= \text{Degree of dissociation} \times 100\% \\ \Rightarrow &= \alpha \times 100\% = 0.0134 \times 100 = 1.34\% \end{aligned} \quad (12.35)$$

Thus acetic acid is dissociated to the extent of only 1.34 % in a 0.1 M aqueous solution.

A similar expression can be obtained for the degree of dissociation of a weak base. The desired expression is

$$\alpha = \sqrt{\frac{K_b}{c}} \quad (12.36)$$



Notes

## 12.5 THE AUTO-IONISATION OR SELF-IONISATION OF WATER

We have seen that water can act as a very weak acid and also as a very weak base. In a sample of water a small number of water molecules undergo auto ionisation. Half of them acting as an acid while the other half acting as a base. As a consequence small concentration of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are formed in water. The self ionisation of water can be represented as



The corresponding equilibrium constant expression can be written as

$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} \quad (12.38)$$

Since the concentration of  $\text{H}_2\text{O}$  is constant we can rearrange the expression and define a new constant  $K_w$ , as

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_{\text{eq}} \times [\text{H}_2\text{O}]^2 = K_w \text{ (a new constant)} \quad (12.39)$$

This constant,  $K_w$ , is called the dissociation constant or **ionic product constant of water**. The value of  $K_w$  at 298 K has been determined from the measurement of electrical conductivity of carefully purified water and has been found to be  $1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ .

Since the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions is equal we may write

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

$$K_w = [\text{H}_3\text{O}^+]^2 = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

$$\Rightarrow [\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$$

$$\text{and similarly, } [\text{OH}^-] = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$$

Thus in pure water and in neutral solutions

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ mol dm}^{-3} \text{ at } 298 \text{ K} \quad (12.40)$$



## Notes

## 12.5.1 Acidic, Basic and Neutral Solutions

An acidic solution is defined as one in which the hydrogen ion ( or 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  $[\text{H}_3\text{O}^+]$  and a neutral solution is one in which  $[\text{OH}^-]$  equals  $[\text{H}_3\text{O}^+]$ .

Neutral solution	$[\text{H}_3\text{O}^+] = [\text{OH}^-]$	
Acidic solution	$[\text{H}_3\text{O}^+] > [\text{OH}^-]$	
Basic solution	$[\text{H}_3\text{O}^+] < [\text{OH}^-]$	(12.41)

Since the product  $[\text{H}_3\text{O}^+][\text{OH}^-]$  is constant, if the concentration of either of these increases, the other one would decrease. In other words the concentrations of  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  are not independent but are linked by the relationship

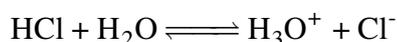
$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w \quad (12.42)$$

This provides an easy way to calculate concentration of one of these if we know that of the other.

You must note that the self ionisation equilibrium discussed above 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 every aqueous solution, and they are always in equilibrium with water molecules. Let us try to calculate the concentration of these ions in some simple solutions.

**Example 12.3 :** Calculate the concentrations of  $\text{OH}^-$  and  $\text{H}_3\text{O}^+$  ions in 0.01 M solution of HCl.

**Solution:** In an aqueous solution of HCl, the following two processes would occur simultaneously



The ionisation of HCl goes to completion and that of water to a very limited extent. In addition according to Le-Chatlier principle, the  $\text{H}_3\text{O}^+$  from the ionization of HCl will shift the position of the equilibrium of the self-ionization reaction to the left. As a consequence the concentration of the  $\text{OH}^-$  ions would reduce further. Suppose concentration of  $\text{OH}^-$  is 'x' mol  $\text{dm}^{-3}$ , then concentration of  $\text{H}_3\text{O}^+$  from the self-ionization of water must also be x mol  $\text{dm}^{-3}$ . The concentration of  $\text{H}_3\text{O}^+$  from ionization of HCl is 0.010 mol  $\text{dm}^{-3}$ . Therefore, total concentration of  $\text{H}_3\text{O}^+$  (aq) = (0.010 + x) mol  $\text{dm}^{-3}$ .

Thus Equilibrium Concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions would be (0.01 + x) and x mol  $\text{dm}^{-3}$  respectively.

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

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (0.01 \times x)(x) \text{ mol}^2 \text{ dm}^{-6} = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

Since  $x$  must be very small, we can assume that  $x \ll 0.01$  and therefore we may assume that the equilibrium concentration of  $\text{H}_3\text{O}^+$  is equal to 0.01 M

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

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

or

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

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

$$[\text{OH}^-] = 1.0 \times 10^{-12} \text{ mol dm}^{-3} \text{ and}$$

$$[\text{H}_3\text{O}^+] = 0.01 + 1.0 \times 10^{-12} \text{ mol dm}^{-3} = 0.01 \text{ mol dm}^{-3}$$

Since the value of  $x$  ( $1.0 \times 10^{-12}$  the hydronium ions obtained from the self ionisation of water) is far smaller than 0.01, our assumption is justified. Thus you may note that in case of aqueous solutions of strong acids it is reasonable to assume that the concentration of  $\text{H}_3\text{O}^+$  ions equals the concentration of the acid itself.

### 12.5.2 pH Scale

In aqueous solutions of acids and bases the concentration of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions may vary from about 10 M to  $10^{-14}$  M. It is quite inconvenient to express these concentrations by using powers of 10. In 1909 a Danish botanist S.P.L. Sorensen proposed a logarithmic scale (called pH scale) for expressing the concentrations of  $\text{H}^+$  ions. He defined pH as the negative logarithm of the molar concentration of hydrogen ions. That is,

$$\text{pH} = -\log_{10}[\text{H}^+] \quad (12.43)$$

We now a days it is represented as

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] \quad (12.44)$$

For neutral solutions (or pure water)

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1 \times 10^{-7}$$

$$\Rightarrow \text{pH} = -\log 1 \times 10^{-7} = 7.0$$

For acidic solutions

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

$$\Rightarrow [\text{H}_3\text{O}^+] > 1 \times 10^{-7}$$



Notes



## Notes

$$\Rightarrow \text{pH} = -\log (>1 \times 10^{-7}) = < 7.0$$

For basic solutions

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

$$\Rightarrow [\text{H}_3\text{O}^+] < 1 \times 10^{-7}$$

$$\Rightarrow \text{pH} = -\log (< 1 \times 10^{-7})$$

$$\Rightarrow > 7.0$$

A strongly acidic solution can have a pH of less than zero (i.e., negative) and a strongly alkaline solution can have a pH value greater than 14. However the pH range normally observed is between 0 to 14.

The notation p is used in a number of places. It carries the meaning, 'the negative logarithm of'. It has been extended to  $\text{OH}^-$ (aq) and equilibrium constants like,  $K_a$ ,  $K_b$  and  $K_w$ , etc.

$$\begin{aligned} \text{pOH} &= -\log_{10}[\text{OH}^-] \\ \text{p}K_a &= -\log_{10} K_a \\ \text{p}K_b &= -\log_{10} K_b \\ \text{p}K_w &= -\log_{10} K_w \end{aligned} \quad (12.45)$$

This gives us an important relation. You would recall (eq 12.42)

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

Taking logs on both sides, we get

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

Multiplying through out by  $-1$

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

$$\text{p}K_w = \text{pH} + \text{pOH}$$

Since the value of  $K_w = 1.0 \times 10^{-14}$   $\text{p}K_w = 14$

$$\text{i.e., } \text{pH} + \text{pOH} = 14 \quad (12.46)$$

If we know the value of pH of a given solution we can find its pOH and vice versa.

Let us take up some examples to understand the application of these important formulae.

**Example 12.4:** What is the pH of a 0.01 M aqueous solution of HCl?

**Solution:** Since HCl is a strong acid it would ionize completely.

Therefore,  $[\text{H}_3\text{O}^+]$  in 0.01 M HCl = 0.01 M

$$\begin{aligned} \text{pH} &= -\log_{10}[\text{H}_3\text{O}^+] = -\log 10^{-2} \\ &= -(-2.0) = 2.0. \end{aligned}$$

**Example 12.5 :** Calculate the pH of 0.010 M aqueous solution of NaOH.

**Solution:** Since NaOH is a strong base, it is fully ionized to give  $\text{Na}^+$  and  $\text{OH}^-$

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

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

$$\text{So, } [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{1.00 \times 10^{-2} \text{ mol dm}^{-3}}$$

$$= 1.00 \times 10^{-12} \text{ mol dm}^{-3}$$

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

**Example 12.6 :** The pH of a sample of rain water at 25 °C is 5. What is the concentration of hydronium ions ?

**Solution:**  $\text{pH} = -\log [\text{H}_3\text{O}^+]$

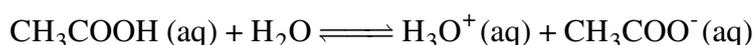
$$\text{or } 5 = -\log [\text{H}_3\text{O}^+] \Rightarrow \log [\text{H}_3\text{O}^+] = -5$$

Taking antilogs, we get

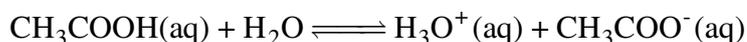
$$[\text{H}_3\text{O}^+] = 10^{-5} \text{ mol dm}^{-3}.$$

**Example 12.7:** Calculate the pH of 0.1 M aqueous solution of acetic acid. The dissociation constant,  $K_a = 1.85 \times 10^{-5}$ ,  $\alpha = 0.0134$ .

**Solution:** The following equilibrium exists in this solution



If  $\alpha$  be the degree of dissociation of acetic acid in this solution, the equilibrium concentrations of various species would be



$$c(1 - \alpha) \qquad \qquad \qquad c\alpha \qquad \qquad c\alpha$$

Since  $c = 0.1 \text{ M}$

$$0.1(1 - \alpha) \qquad \qquad \qquad 0.1\alpha \qquad \qquad 0.1\alpha$$

$$[\text{H}_3\text{O}^+] = c \alpha$$

$$\Rightarrow [\text{H}_3\text{O}^+] = 0.1 \times 0.0134 = 0.00134$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log [0.00134] = -\log [1.34 \times 10^{-3}] = -(-2.87) = 2.87$$



Notes



Notes

12.5.3 Effect of Common-Ions on the Dissociation of Weak Acids and Bases

In the previous lesson you have learnt about Le Chatelier's principle. According to this principle the presence of common ions in a solution of a weak acid or a base will affect its dissociation. This in fact would suppress the dissociation of the acid or base.

In a solution containing a weak acid HA and its salt NaA, the following equilibria exists:



Here  $\text{A}^-(\text{aq})$  is the common-ion

and in case of a weak base BOH and its salt BX the equilibria are



Here,  $\text{B}^+$  is the common-ion. According to Le-Chatelier principle, the presence of common ions would make the equilibrium to go to the left. It is said that the common ions suppress the equilibrium.

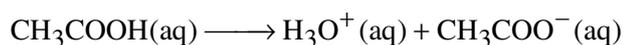
Let us take an example to understand the effect of common ions on such equilibria.

**Example 12.8 :** Calculate the pH, degree of dissociation and concentration of various species in a solution of 0.1 M acetic acid which also contains 0.1 M sodium acetate ( $K_a$  (for acetic acid) =  $1.85 \times 10^{-5} \text{ mol dm}^{-3}$ ).

**Solution :** In the given solution the following two equilibria exist simultaneously.



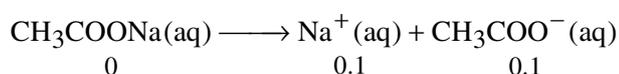
Let  $\alpha$  be the degree of dissociation of acetic acid in this solution, the equilibrium concentrations of various species would be



$$c(1 - \alpha) \qquad c\alpha \qquad c\alpha$$

Since  $c = 0.1 \text{ M}$

$$0.1(1 - \alpha) \qquad 0.1\alpha \qquad 0.1\alpha$$



$$\text{CH}_3\text{COOH} = 0.1(1 - \alpha)$$

$$\text{CH}_3\text{COO}^- = 0.1 + 0.1\alpha = 0.1(1 + \alpha)$$

$$\text{H}_3\text{O}^+ = 0.1\alpha$$

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

rearranging the expression we get,

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

Substituting the values, we get

$$[\text{H}_3\text{O}^+] = 1.85 \times 10^{-5} \times \frac{0.1(1 - \alpha)}{0.1(1 + \alpha)}$$

Since acetic acid is a weak acid, its degree of dissociation further decreases in presence of acetate (ions the common ion). Therefore it is reasonable to assume that

$$\alpha \ll 1; \text{ and } (1 - \alpha) \sim 1; \text{ also } (1 + \alpha) \sim 1$$

This gives

$$[\text{H}_3\text{O}^+] = 1.85 \times 10^{-5} \times 0.1 / 0.1 = 1.85 \times 10^{-5}$$

and  $\text{pH} = -\log(1.85 \times 10^{-5}) = 4.73$

Also since  $[\text{H}_3\text{O}^+] = 0.1\alpha$

$$\therefore \alpha = 1.85 \times 10^{-5} / 0.1 = 1.85 \times 10^{-4} = 0.000185$$

The concentration of different species at equilibrium will be

$$\text{CH}_3\text{COOH} = 0.1(1 - 0.000185) = 0.1$$

$$\text{CH}_3\text{COO}^- = 0.1(1 + 0.000185) = 0.1$$

$$\text{H}_3\text{O}^+ = 0.1 \times \alpha = 0.1 \times 0.000185 = 1.85 \times 10^{-5}$$

⇒ the concentration of acid = initial concentration of acid

⇒ the concentration of  $\text{CH}_3\text{COO}^-$  ions = initial concentration of the salt



### INTEXT QUESTIONS 12.2

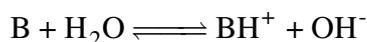
1. HF is a weak acid in water. Write down the expression for  $K_a$  for the dissociation of HF.
2. Consider a weak base BOH which partially dissociates in its aqueous solutions as per the following equilibrium



Notes



## Notes



- A sample of lime juice has a hydronium ion concentration of  $6.3 \times 10^{-2}$  M. Calculate its pH.
- Calculate the pH of 1.0 M aqueous solution of amino acid glycine – a weak acid. The  $K_a = 1.67 \times 10^{-10}$ .

### 12.6 BUFFER SOLUTIONS

The example discussed above leads us to a very important conclusion that the extent of dissociation of a weak acid can be decreased by adding a salt containing a common ion. Further, it can be shown that the change in the extent of dissociation can also be varied by changing the concentration of the common ion. The mixture of a weak base and a salt of common ion also behave in the same way. These aqueous solutions containing weak acids / bases and a salt of common ion are important in a yet another way. These act as **buffer solutions**.

**Buffer solutions are the ones that resist a change in its pH on adding a small amount of an acid or a base.**

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.

There are two kinds of commonly used buffer-solutions

- A weak acid and a soluble ionic salt of the weak acid e.g. acetic acid and sodium acetate;  $CH_3COOH + CH_3COONa$  and,
- A weak base and a soluble ionic salt of the weak base e.g. ammonium hydroxide and ammonium chloride ;  $NH_4OH + NH_4Cl$ .

The buffers with pH less than 7 are called *acidic buffers* and those with pH above 7 are called *basic buffers*. Acetic acid - sodium acetate buffer is an example of *acidic buffer* while Ammonium hydroxide - ammonium chloride is a basic buffer.

#### 12.6.1 Buffer Action

A buffer system contains a conjugate acid- base pair and the concentrations of these two are quite high as compared to that of the hydronium ions. These are called as the acid reserve and the base reserve respectively. The added acid or base reacts with these reserves and gets consumed without significantly altering

the hydronium ion concentration and therefore the pH does not change significantly. Let us consider a buffer solution containing acetic acid,  $\text{CH}_3\text{COOH}$  and sodium acetate  $\text{CH}_3\text{COONa}$  to understand the buffer action.

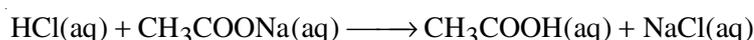
In acetic acid - sodium acetate buffer  $\text{CH}_3\text{COOH}$  is the acid reserve while  $\text{CH}_3\text{COONa}$  ( or  $\text{CH}_3\text{COO}^-$  ions ) is the base reserve. In the solution mixture the added components dissociate as follows. The weak acid dissociates partially while the salt undergoes complete dissociation.



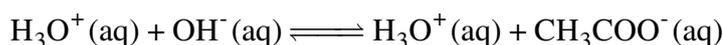
If we add a strong acid such as HCl to this solution, it produces  $\text{H}_3\text{O}^+$ . These added  $\text{H}_3\text{O}^+$  (acid) react with an equivalent amount of the base reserve [ $\text{CH}_3\text{COO}^-$ ] to generate undissociated acetic acid. The reaction being



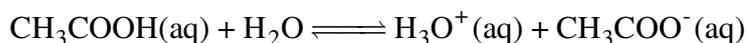
The net effect of this reaction is that there is a slight increase in the concentration of the acid reserve and an equivalent decrease in the concentration of the base reserve. The effective reaction being



Similarly, when small amounts of a strong base like NaOH is added, it generates  $\text{OH}^-$  ions. These additional  $\text{OH}^-$  neutralize some of the  $\text{H}_3\text{O}^+$  ions present in the solution,



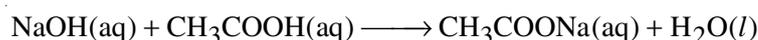
Since one of the products of the acid dissociation equilibrium (eq) is used up, there is some more ionisation of  $\text{CH}_3\text{COOH}$  to re-establish the equilibrium.



The net result is the neutralization of  $\text{OH}^-$  by  $\text{CH}_3\text{COOH}$ . In other words we can say that the added  $\text{OH}^-$  ions ( base ) react with the acid reserve to produce  $\text{CH}_3\text{COO}^-$  ions



The effective reaction being the reaction of the added base with acid reserve.



The net effect of this reaction is that there is a slight increase in the concentration of the base reserve and an equivalent decrease in the concentration of the acid reserve.

You may note here that the added acid or the base only cause minor changes in the concentrations of the weak acid and the salt. The concentration of the



Notes

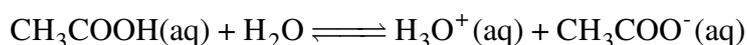


## Notes

hydronium ions and thereby the pH does not change significantly. Let us derive a mathematical expression for determining the pH of a buffer solution.

### 12.6.2 Henderson-Hasselbalch Equation

This equation relates the pH of a given buffer solution to the concentrations of its components viz. weak acid / salt or weak base / salt. Let us derive the expression for an acidic buffer system that we have discussed above. In acetic acid – sodium acetate buffer the central equilibrium is



which is characterized by the acid dissociation constant,

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

rearranging, we get

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

The concentration of undissociated acetic acid can be taken as total acid concentration [Acid] and that of sodium acetate as the total salt concentration [Salt]. In the light of this the above equation may be re written as

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{Acid}]}{[\text{Salt}]}$$

Taking logarithm and multiplying through out by (-1) we get

$$-\log [\text{H}^+] = -\log K_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

Recall that  $\text{pH} = -\log [\text{H}_3\text{O}^+]$  and  $\text{p}K_a = -\log K_a$ . This gives the desired equation.

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

This equation is known as **Henderson-Hasselbalch equation**. A similar expression can be derived for a basic buffer ( e.g., ammonium hydroxide and ammonium chloride) . The expression is

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Let us take up some examples to see the application of this equation.

**Example 12.9 :** Calculate the pH of acetic acid – sodium acetate buffer containing 0.1 M acetic acid and 0.1 M sodium acetate. ( $K_a = 1.85 \times 10^{-5} \text{ mol dm}^{-3}$ ).

**Solution:** Here, [ Acid ] = 0.1 M and [Salt] = 0.1 M

Since  $K_a = 1.85 \times 10^{-5} \text{ mol dm}^{-3}$  ;

$$pK_a = -\log K_a = -\log 1.85 \times 10^{-5}$$

$$\Rightarrow pK_a = 4.73$$

According to Henderson equation,  $pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

Substituting the values in Henderson equation, we get

$$pH = 4.73 + \log ( 0.1 / 0.1 ) = 4.73 + \log 1 = 4.73.$$

**Example 12.10 :** Calculate the pH of ammonium hydroxide – ammonium chloride buffer solution that is 0.1 M in ammonium hydroxide and 0.01 M in ammonium chloride. (  $pK_b$  of  $\text{NH}_4\text{OH} = 9.25$  ).

**Solution:** Here, [ Base ] = 0.1 M and [ Salt ] = 0.01 M

Since  $pK_b = 9.25$  ;

According to Henderson equation,  $pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$

Substituting the values in Henderson equation, we get

$$pOH = 9.25 + \log ( 0.01 / 0.1 ) = 9.25 + \log 0.1 = 9.25 - 1.0 = 8.25$$

## 12.7 SALT HYDROLYSIS

The aqueous solutions of certain salts also behave as acids or bases. They do so because of the hydrolysis of the cation or anion or both. As you know, hydrolysis is a reaction with water. Depending on the behaviour towards hydrolysis there are four different types of salts.

Salt of strong acid + strong base (eg. HCl + NaOH)	NaCl
Salt of strong acid + weak base ( e.g. HCl + $\text{NH}_4\text{OH}$ )	$\text{NH}_4\text{Cl}$
Salt of weak acid + strong base ( e.g. $\text{CH}_3\text{COOH}$ + NaOH)	$\text{CH}_3\text{COONa}$
Salt of weak Acid + weak Base (e.g. $\text{CH}_3\text{COOH}$ + $\text{NH}_4\text{OH}$ )	$\text{CH}_3\text{COONH}_4$

Let us learn about the acid- base behaviour of the different types of salts.

**Salt of strong acid + strong base :** the cations of the strong bases and the anions of the strong acids do not get hydrolysed. Therefore the salts of this category do not show any acid-base behaviour and are neutral.

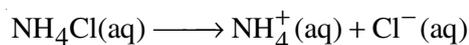


Notes



## Notes

**Salt of strong acid + weak base:** the salts of this type dissociate in aqueous solutions to give a cation of a weak base and the anion belonging to strong acid. For example,  $\text{NH}_4\text{Cl}$  dissociates as :



As mentioned above, the anion does not get hydrolysed but the cation does get hydrolysed as per the following equation.



since it generates  $\text{H}^+(\text{aq})$  ions, the solution is acidic in nature.

**Salt of weak acid and strong base:** the salts of this type dissociate in aqueous solutions to give a anion of a weak acid and the cation belonging to strong base. for example,  $\text{CH}_3\text{COONa}$  dissociates as :

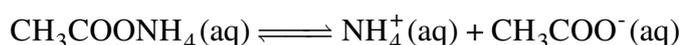


in this case the cation does not get hydrolysed but the anion does get hydrolysed as per the following equation.



Since it generates hydroxyl ions the solution is basic in nature.

**Salt of weak Acid and weak Base :** the salts of this type dissociate in aqueous solutions to give a anion of a weak acid and the cation belonging to a weak base. for example, ammonium acetate,  $\text{CH}_3\text{COONH}_4$  dissociates as :



In this case both the cation as well as the anion would undergo hydrolysis and the nature of the solution, whether acidic, basic or neutral would depend on the relative strength of the weak acid and the weak base.

## 12.8 THE SOLUBILITY EQUILIBRIUM

When we try to dissolve a solid into water, if it dissolves, there are three possibilities:

1. The solid is a non-electrolyte and it dissolves as neutral molecules.
2. The solid is a highly soluble electrolyte; it dissolves almost completely.
3. The solid is a sparingly soluble electrolyte; it dissolves to a limited extent.

It is the third possibility that interests us here. Let us take the example of dissolution of  $\text{AgCl}$  to understand the equilibria in such cases. When silver chloride is added to water, the following equilibrium is established.



This is an example of a heterogeneous equilibrium because it involves both a solid and a solution. This equilibrium is known as the *solubility equilibrium* for which the equilibrium constant expression is

$$K = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl(s)}]}$$

As a matter of convention the concentration of the undissolved solid is taken as one. We can rewrite the equilibrium as

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$

The equilibrium constant now is the product of the concentrations of the ions. It is called *solubility product constant* or simply *solubility product*. A new symbol,  $K_{\text{sp}}$ , has been assigned to this constant. The mass expression on the right, is called, ion product or ionic product. The solubility product constant of a given salt is constant at a given temperature.

### 12.8.1 Relationship between Solubility and Solubility Product Constant

The *solubility product constant* for a substance is related to its solubility. The nature of relationship depends on the nature of the salt.

**Salt of AB type:** ( For example AgCl, CaSO<sub>4</sub>). In such cases the solubility equilibrium can be represented as

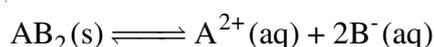


and  $K_{\text{sp}} = [\text{A}^+][\text{B}^-]$

If the solubility of salt is 's' mol dm<sup>-3</sup> then the concentrations of the cations and the anions would be 's' mol dm<sup>-3</sup> each. Substituting the values in the expression of  $K_{\text{sp}}$  we get,

$$K_{\text{sp}} = ['s' \text{ mol dm}^{-3}] \times ['s' \text{ mol dm}^{-3}] = s^2 \text{ mol}^2 \text{ dm}^{-6}$$

**Salt of AB<sub>2</sub> type:** (For example CaF<sub>2</sub>). In such cases the solubility equilibrium can be represented as



and  $K_{\text{sp}} = [\text{A}^{2+}][\text{B}^-]^2$

If the solubility of salt is 's' mol dm<sup>-3</sup> then the concentration of the cations and the anions would be 's' mol dm<sup>-3</sup> and '2s' mol dm<sup>-3</sup> respectively. Substituting the values in the expression of  $K_{\text{sp}}$  we get,

$$K_{\text{sp}} = ['s' \text{ mol dm}^{-3}] \times ['2s' \text{ mol dm}^{-3}]^2 = 4s^3 \text{ mol}^3 \text{ dm}^{-9}$$



Notes



Notes

**Salt of A<sub>2</sub>B type:** (For example Ag<sub>2</sub>CrO<sub>4</sub>). In such cases the solubility equilibrium can be represented as



and  $K_{sp} = [A^+]^2 [B^{2-}]$

If the solubility of salt is 's' mol dm<sup>-3</sup> then the concentrations of the cations and the anions would be '2s' mol dm<sup>-3</sup> and 's' mol dm<sup>-3</sup> respectively. Substituting the values in the expression of K<sub>sp</sub> we get,

$$K_{sp} = ['2s' \text{ mol dm}^{-3}]^2 \times ['s' \text{ mol dm}^{-3}] = 4s^3 \text{ mol}^3 \text{ dm}^{-9}$$

**Salt of A<sub>3</sub>B<sub>2</sub> type:** (For example Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>). In such cases the solubility equilibrium can be represented as



and  $K_{sp} = [A^{2+}]^3 [B^{3-}]^2$

If the solubility of salt is 's' mol dm<sup>-3</sup> then the concentrations of the cations and the anions would be '3s' mol dm<sup>-3</sup> and '2s' mol dm<sup>-3</sup> respectively. Substituting the values in the expression of K<sub>sp</sub> we get,

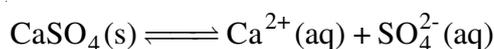
$$K_{sp} = ['3s' \text{ mol dm}^{-3}]^3 \times ['2s' \text{ mol dm}^{-3}]^2 = 108 s^5 \text{ mol}^5 \text{ dm}^{-15}$$

In general for a salt with the formula A<sub>x</sub>B<sub>y</sub> and a solubility of s mol dm<sup>-3</sup> the relationship between the solubility and K<sub>sp</sub> can be given as

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y = (xs)^x (ys)^y = x^x y^y s^{x+y}$$

**Example 12.11:** The solubility of calcium sulphate in water is 4.9 × 10<sup>-3</sup> mol dm<sup>-3</sup> at 298K. Calculate the value of K<sub>sp</sub> for CaSO<sub>4</sub> at this temperature.

**Solution:** The following equilibrium would exist in this case



For this reaction;  $K_{sp} = [Ca^{2+}] [SO_4^{2-}]$

From the equation we see that when 4.9 × 10<sup>-3</sup> mol of CaSO<sub>4</sub> dissolves to make 1 dm<sup>-3</sup> of a saturated solution, the ionic concentration are

$$[Ca^{2+}] = 4.9 \times 10^{-3} \text{ mol dm}^{-3}; [SO_4^{2-}] = 4.9 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\begin{aligned} K_{sp} &= [Ca^{2+}] [SO_4^{2-}] = [4.9 \times 10^{-3} \text{ mol dm}^{-3} \times 4.9 \times 10^{-3} \text{ mol dm}^{-3}] \\ &= 2.4 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6} \end{aligned}$$

**Example 12.12:** Solubility product of silver iodide, AgI is  $8.5 \times 10^{-17}$  at  $25^\circ\text{C}$ . What is the molar solubility of AgI in water at this temperature?

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



Let the solubility of AgI be is 's' mol dm<sup>-3</sup> the concentrations of silver and iodide ions would be is 's' mol dm<sup>-3</sup> each.

At equilibrium,  $K_{\text{sp}} = [\text{Ag}^+][\text{I}^-]$  ; Substituting the values, we get

$$['s' \text{ mol dm}^{-3}]['s' \text{ mol dm}^{-3}] = s^2 \text{ mol}^2 \text{ dm}^{-6} = 8.5 \times 10^{-17} \text{ mol}^2 \text{ dm}^{-6}$$

This gives , solubility (s) =  $[8.5 \times 10^{-17} \text{ mol}^2 \text{ dm}^{-6}]^{1/2}$

$$= 9.2 \times 10^{-9} \text{ mol dm}^{-3}.$$

The solubility of AgI in water is therefore  $9.2 \times 10^{-9} \text{ mol dm}^{-3}$  at 298 K.

### 12.8.2 Effect of Common Ion on Solubility Equilibria

What will happen if we add a soluble salt containing a common-ion to a solution of a sparingly soluble salt? You may reason out that according to Le Chatelier's principle, the common-ion will shift the equilibrium in backward direction which would reduce its solubility still further. This actually is the case. Let us understand it with the help of an example.

**Example 12.13:** Calculate the molar solubility of AgI in a solution containing  $0.1 \text{ mol dm}^{-3} \text{ AgNO}_3$ . The solubility product of silver iodide, AgI is  $8.5 \times 10^{-17} \text{ mol}^2 \text{ dm}^{-6}$  at 298 K.

**Solution:** Silver nitrate is a strong electrolyte ionising as



and for AgI the solubility equilibrium is



If we take the solubility of AgI to be 's' mol dm<sup>-3</sup>, then the total concentration of Ag<sup>+</sup> ions in the solution would be  $[0.1 + s] \text{ mol dm}^{-3} \sim [0.1] \text{ mol dm}^{-3}$  because the value of 's' is very small. And the concentration of I<sup>-</sup> ions would be 's' mol dm<sup>-3</sup>.

Substituting in the expression for  $K_{\text{sp}} = [\text{Ag}^+][\text{I}^-]$  ; we get

$$[0.1] \text{ mol dm}^{-3} [ 's' \text{ mol dm}^{-3} ] = 0.1 s \text{ mol}^2 \text{ dm}^{-6} = 8.5 \times 10^{-17} \text{ mol}^2 \text{ dm}^{-6}$$



Notes



## Notes

$$\begin{aligned} \text{This gives, solubility (s)} &= [8.5 \times 10^{-17}] / [0.1] \text{ mol dm}^{-3} \\ &= 8.5 \times 10^{-16} \text{ mol dm}^{-3}. \end{aligned}$$

(The value of 's' is clearly negligible in comparison with 0.10 and thus justifies our assumption)

The solubility of AgI in 0.1M AgNO<sub>3</sub> is therefore 8.5 × 10<sup>-16</sup> mol dm<sup>-3</sup> at 298 K. Compare this value with the solubility of AgI in water as determined in the previous example

Solvent	Water	0.1M AgNO <sub>3</sub>
Solubility	9.2 × 10 <sup>-9</sup> mol dm <sup>-3</sup>	8.5 × 10 <sup>-16</sup> mol dm <sup>-3</sup> .

Thus we see that the solubility of a sparingly soluble 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**.



## INTEXT QUESTIONS 12.3

1. Calculate the pH of a solution containing 0.05 M benzoic acid and 0.025 M sodium benzoate. Benzoic acid has a pK<sub>a</sub> of 4.2.
2. Calculate the solubility product for Ag<sub>2</sub>SO<sub>4</sub> if [SO<sub>4</sub><sup>2-</sup>] = 2.5 × 10<sup>-2</sup> M.

## 12.8.3 Application of Solubility Product in Qualitative Analysis

The qualitative analysis of cations is carried out by dividing them into several groups. This group separation of cations is based upon **selective precipitation** of some cations out of many that are present in a solution. This is achieved by adjusting the solution conditions in such a way that the K<sub>sp</sub> of specific salts of some cations is exceeded and they precipitate out. The remaining cations remain in the solution. A typical example is the use of H<sub>2</sub>S. The dissociation of H<sub>2</sub>S can be written as



Since the equilibrium involves hydrogen ions, the acidity of the solution would play an important role in controlling the concentration of sulphide ions.

You are aware, that in the separation of group II sulphides, the medium of the solution is kept acidic. In this medium the concentration of the S<sup>2-</sup> ions is very small and only the sulphides of group II are precipitated. On the other hand in the alkaline medium the concentration of sulphide ions is fairly high and the sulphides of group IV cations precipitate out.



### WHAT YOU HAVE LEARNT

- Electrolytes are compounds, which, when dissolved in water, produce ions.
- Strong electrolytes are almost completely dissociated while weak electrolytes are only partially dissociated in their solutions.
- There are three different concepts of acids and bases proposed by Arrhenius, Brønsted and Lowry and Lewis respectively.
- According to Arrhenius Concept an acid is a substance capable of producing hydrogen ions by dissociating in aqueous solution while a base is a substance capable of providing a hydroxyl ion. The neutralization reaction is basically the reaction between a proton and a hydroxyl ion to give a molecule of water.
- Since a hydrogen ion  $H^+$  is very small with high charge density it does not exist free in a polar solvent like water. It binds itself to a water molecule and form a hydronium ion ( $H_3O^+$ ).
- According to Brønsted and Lowry, an acid is defined as a proton ( $H^+$ ) donor, and a base is defined as a proton acceptor. An acid-base reactions can be thought of as a proton-transfer from an acid to a base. In this concept, acids and bases can be either ions or molecular substances.
- According to Brønsted and Lowry definition the species in either side of the acid-base equilibrium, differ by the gain or loss of a proton. These are called a conjugate acid-base pair. In such a pair a strong acid has a weak conjugate base while a weak acid has a strong conjugate base.
- Lewis definition is quite broad, according to him, an acid is defined as, 'any atom, molecule or ion that can accept an electron pair from any other atom, molecule or ion, while a base is 'any atom, molecule or ion that can donate a pair of electron'. The product of a reaction between an acid and a base is called an adduct.
- Strong Arrhenius acids and bases dissociate completely in aqueous solutions where as the weak acids and bases undergo partial ionisation. Higher the extent of ionisation stronger the acid or the base.
- In Brønsted- Lowry concept, the relative strength of an acid is defined as its relative tendency to lose/donate a proton to water.
- The ionisation equilibria of weak acids and bases are characterized by equilibrium constants called ionisation constants. The values of these constants is a measure of their relative strength.
- Water can act both as a weak acid as well a weak base. In a sample of water a small number of water molecules undergo autoionisation, in which half the ions act as an acid while the other half acts as a base.



Notes



## Notes

- In aqueous solutions the concentration of  $\text{H}_3\text{O}^+$  can be expressed in terms of a logarithmic scale called pH scale. The pH of a solution is defined as  $\text{pH} = -\log_{10}[\text{H}^+]$  or  $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$ .
- A neutral solution has a pH of 7 ; any solution with a pH less than 7 is acidic while the ones with a pH of greater than 7 are basic in nature.
- The presence of common ions in a solution of a weak acid or a weak base suppress its dissociation. Such solutions act as buffer solutions which resist a change in their pH on addition of small amount of an acid or a base. The pH of buffer solutions depend on their composition and can be found by using a simple equation called **Henderson Hasselbalch equation**.
- The aqueous solutions of certain salts also behave as acids or bases due to the hydrolysis of their cation or anion or both.
- In an aqueous solution of a sparingly soluble salt an equilibrium exists between the undissolved salt and the ions obtained from the dissolved salt. This is called **solubility equilibrium**.
- The product of the concentration of the ions in the solubility equilibrium is a constant called **solubility product** ( $K_{\text{sp}}$ ) and is proportional to the solubility of the sparingly soluble salt.
- The presence common ions decreases the solubility of a sparingly soluble salt. This is called common ion effect and has widespread applications in qualitative analysis.



## TERMINAL EXERCISE

1. What is degree of dissociation? What are factors upon which it depends.
2. Write the equilibrium constant expression for the following reaction.  

$$\text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})$$
3. Explain why does a strong Bronsted – Lowry acid has a weak conjugate base?
4. What do you understand by the term ‘amphoteric’? Show with the help of equations that water is amphoteric in nature.
5. Calculate the pH of  $1 \times 10^{-3}$  M solution of  $\text{NH}_4\text{OH}$ . The dissociation constant of  $\text{NH}_4\text{OH}$  is  $1.85 \times 10^{-5} \text{ mol dm}^{-3}$ .
6. The pH of an aqueous solution of HCl is 2.301. Find out the concentration of hydrogen ions in this solution.
7. What is a buffer solution? What are its main constituents?
8. Solubility of lead iodide  $\text{PbI}_2$  is  $1.20 \times 10^{-3} \text{ mol dm}^{-3}$  at 298K. Calculate its solubility product constant.

- Calculate the solubility of  $\text{Bi}_2\text{S}_3$  in water at 298K if its  $K_{\text{sp}} = 1.0 \times 10^{-97} \text{ mol}^5 \text{ dm}^{-15}$ .
- Calculate the solubility of AgI in 0.10M NaI at 298 K.  $K_{\text{sp}}$  for AgI is  $8.5 \times 10^{-7}$  at this temperature.



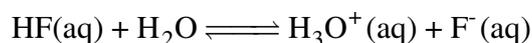
## ANSWERS TO INTEXT QUESTIONS

## 12.1

- According to Arrhenius concept an acid is defined as a substance that is capable of producing hydrogen ion ( $\text{H}^+$ ) by ionisation in aqueous solution. For example, HCl and  $\text{CH}_3\text{COOH}$ .
- Arrhenius definition has the following drawbacks:
  - It is limited to only aqueous solutions and requires ionisation of the substance.
  - It does not explain the acidic or basic behaviour of some substances which lack a hydrogen (or a hydroxide) ion. For example,  $\text{AlCl}_3$  and  $\text{Na}_2\text{CO}_3$  which lack a hydroxide.
- In the Brnsted-Lowry concept, any molecule or ion that can accept a proton is a base whereas in Arrhenius concept a base is the one which provides hydroxide ions in solution.
- Acids             $\text{HCl}, \text{H}_3\text{O}^+$   
Bases             $\text{NH}_3, \text{CN}^-$
- X is a weak electrolyte and Y is a strong electrolyte.

## 12.2

- The ionisation of weak acid, HF, can be represented as



The expression for  $K_a$  would be,  $K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$

- For a weak base BOH which partially dissociates in aqueous solutions, and has a degree of dissociation as  $\alpha$  we can write



Initial concentrations	c	~55	0	0
Equilibrium concentrations	$c(1 - \alpha)$	~55	$c\alpha$	$c\alpha$

The equilibrium constant expression or base dissociation constant can be written as



Notes



Notes

$$K = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{H}_2\text{O}][\text{B}]} = \frac{[c\alpha][c\alpha]}{c[1-\alpha]55}$$

rearranging we get,

$$\Rightarrow 55K = K_b = \frac{[c\alpha][c\alpha]}{c[1-\alpha]} = \frac{c^2\alpha^2}{c[1-\alpha]} = \frac{c\alpha^2}{(1-\alpha)}$$

Since the acid B is very weak,  $\alpha \ll 1$ ; we can neglected in comparison to 1 in the denominator to get

$$K_b \approx c\alpha^2 \quad \text{or} \quad \alpha^2 = \frac{K_b}{c} \quad \text{or} \quad \alpha = \sqrt{\frac{K_b}{c}}$$

3. Given hydronium ion concentration,  $[\text{H}_3\text{O}^+] = 6.3 \times 10^{-2}\text{M}$

As per definition  $\text{pH} = -\log [\text{H}_3\text{O}^+]$

$$\Rightarrow \text{pH} = -\log 6.3 \times 10^{-2}$$

$$\Rightarrow \text{pH} = -(0.7993 - 2.0000)$$

$$\Rightarrow \text{pH} = -(-1.2007) = \mathbf{1.2007}$$

4. Given: Concentration of glycine = 1.0M

$$K_a = 1.67 \times 10^{-10}$$

$$\text{For a weak acid } \alpha = \sqrt{\frac{K_a}{c}} = \alpha = \sqrt{1.67 \times 10^{-10}} = 1.29 \times 10^{-5}$$

$$\Rightarrow [\text{H}_3\text{O}^+] = 1 \times 1.29 \times 10^{-5} = 1.29 \times 10^{-5}\text{M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [1.29 \times 10^{-5}] = -(-4.8894) = \mathbf{4.8894}$$

12.3

1. Here, [Acid] = 0.05M and [Salt] = 0.025M; and  $\text{p}K_a = 4.2$

Substituting the values in Handerson equation, we get

$$\text{pH} = 4.2 + \log (0.05/0.025) = 4.2 + \log 2 = 4.2 + 0.3010 = \mathbf{4.5010}$$

2. Let the solubility of  $\text{Ag}_2\text{SO}_4$  be 's' mol  $\text{dm}^{-3}$

The concentrations of the  $\text{Ag}^+$  and the  $\text{SO}_4^{2-}$  would be '2s' mol  $\text{dm}^{-3}$  and 's' mol  $\text{dm}^{-3}$  respectively, and  $K_{sp} = [\text{Ag}^+]^2 [\text{SO}_4^{2-}]$

$$\text{Given } [\text{SO}_4^{2-}] = 2.5 \times 10^{-2}\text{M} \Rightarrow [\text{Ag}^+] = 2 \times 2.5 \times 10^{-2}\text{M} = 5 \times 10^{-2}\text{M}$$

Substituting the values in the expression of  $K_{sp}$  we get,

$$\mathbf{K_{sp} = [5 \times 10^{-2}]^2 \times [2.5 \times 10^{-2}] = 6.25 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}}$$