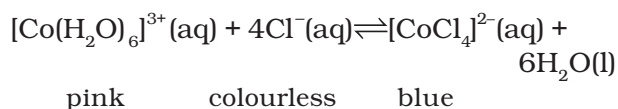formation of NO_2 and thus, the brown colour intensifies.

Effect of temperature can also be seen in an endothermic reaction,

$[Co(H_2O)_6]^{3+}$(aq) + 4Cl⁻(aq)$\rightleftharpoons$$[CoCl_4]^{2-}$(aq) + $6H_2O$(l)

    pink   colourless   blue

At room temperature, the equilibrium mixture is blue due to $[CoCl_4]^{2-}$. When cooled in a freezing mixture, the colour of the mixture turns pink due to $[Co(H_2O)_6]^{3+}$.

7.8.5 Effect of a Catalyst

A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products. It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium. Catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression.

Let us consider the formation of NH_3 from dinitrogen and dihydrogen which is highly exothermic reaction and proceeds with decrease in total number of moles formed as compared to the reactants. Equilibrium constant decreases with increase in temperature. At low temperature rate decreases and it takes long time to reach at equilibrium, whereas high temperatures give satisfactory rates but poor yields.

German chemist, Fritz Haber discovered that a catalyst consisting of iron catalyse the reaction to occur at a satisfactory rate at temperatures, where the equilibrium concentration of NH_3 is reasonably favourable. Since the number of moles formed in the reaction is less than those of reactants, the yield of NH_3 can be improved by increasing the pressure.

Optimum conditions of temperature and pressure for the synthesis of NH_3 using catalyst are around 500 °C and 200 atm.

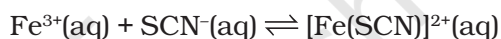Similarly, in manufacture of sulphuric acid by *contact process*,

$2SO_2$(g) + O_2(g) $\rightleftharpoons$ $2SO_3$(g); K_c = 1.7 × 10²⁶

though the value of K is suggestive of reaction going to completion, but practically the oxidation of SO_2 to SO_3 is very slow. Thus, platinum or divanadium penta-oxide (V_2O_5) is used as catalyst to increase the rate of the reaction.

Note: If a reaction has an exceedingly small K, a catalyst would be of little help.

7.9 IONIC EQUILIBRIUM IN SOLUTION

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

Fe^{3+}(aq) + SCN⁻(aq) $\rightleftharpoons$ $[Fe(SCN)]^{2+}$(aq)

There are numerous equilibria that involve ions only. In the following sections we will study the equilibria involving ions. It is well known that the aqueous solution of sugar does not conduct electricity. However, when common salt (sodium chloride) is added to water it conducts electricity. Also, the conductance of electricity increases with an increase in concentration of common salt. Michael Faraday classified the substances into two categories based on their ability to conduct electricity. One category of substances conduct electricity in their aqueous solutions and are called *electrolytes* while the other do not and are thus, referred to as *non-electrolytes*. Faraday further classified electrolytes into *strong* and *weak* electrolytes. Strong electrolytes on dissolution in water are ionized almost completely, while the weak electrolytes are only partially dissociated. For example, an aqueous solution of sodium chloride is comprised entirely of sodium ions and chloride ions, while that of acetic acid mainly contains unionized acetic acid molecules and only some acetate ions and hydronium ions. This is because there is almost 100% ionization in case of sodium chloride as compared to less than 5% ionization of acetic acid which is a weak electrolyte. It should be noted that in weak electrolytes, equilibrium is

established between ions and the unionized molecules. This type of equilibrium involving ions in aqueous solution is called **ionic equilibrium**. Acids, bases and salts come under the category of electrolytes and may act as either strong or weak electrolytes.

7.10 ACIDS, BASES AND SALTS

Acids, bases and salts find widespread occurrence in nature. Hydrochloric acid present in the gastric juice is secreted by the lining of our stomach in a significant amount of 1.2-1.5 L/day and is essential for digestive processes. Acetic acid is known to be the main constituent of vinegar. Lemon and orange juices contain citric and ascorbic acids, and tartaric acid is found in tamarind paste. As most of the acids taste sour, the word "acid" has been derived from a latin word "*acidus*" meaning sour. Acids are known to turn blue litmus paper into red and liberate dihydrogen on reacting with some metals. Similarly, bases are known to turn red litmus paper blue, taste bitter and feel soapy. A common example of a base is washing soda used for washing purposes. When acids and bases are mixed in the right proportion they react with each other to give *salts*. Some commonly known examples of salts are sodium chloride, barium sulphate, sodium nitrate. Sodium chloride (common salt) is an important component of our diet and is formed by reaction between hydrochloric acid and sodium hydroxide. It

exists in solid state as a cluster of positively charged sodium ions and negatively charged chloride ions which are held together due to electrostatic interactions between oppositely charged species (Fig.7.10). The electrostatic forces between two charges are inversely proportional to dielectric constant of the medium. Water, a universal solvent, possesses a very high dielectric constant of 80. Thus, when sodium chloride is dissolved in water, the electrostatic interactions are reduced by a factor of 80 and this facilitates the ions to move freely in the solution. Also, they are well-separated due to hydration with water molecules.
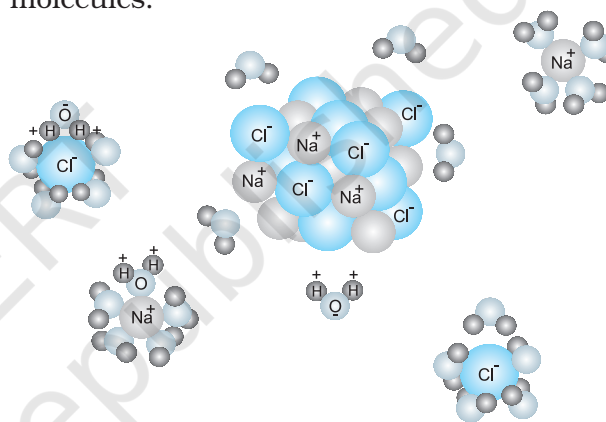

Fig.7.10 *Dissolution of sodium chloride in water. Na^+ and Cl^- ions are stablised by their hydration with polar water molecules.*

Comparing, the ionization of hydrochloric acid with that of acetic acid in water we find that though both of them are polar covalent
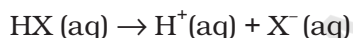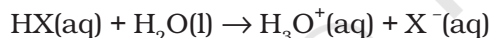
molecules, former is completely ionized into its constituent ions, while the latter is only partially ionized (< 5%). The extent to which ionization occurs depends upon the strength of the bond and the extent of solvation of ions produced. The terms dissociation and ionization have earlier been used with different meaning. Dissociation refers to the process of separation of ions in water already existing as such in the solid state of the solute, as in sodium chloride. On the other hand, ionization corresponds to a process in which a neutral molecule splits into charged ions in the solution. Here, we shall not distinguish between the two and use the two terms interchangeably.

7.10.1 Arrhenius Concept of Acids and Bases

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

$$HX\ (aq) \rightarrow H^+(aq) + X^-\ (aq)$$
$$or$$
$$HX(aq) + H_2O(l) \rightarrow H_3O^+(aq) + X^-(aq)$$

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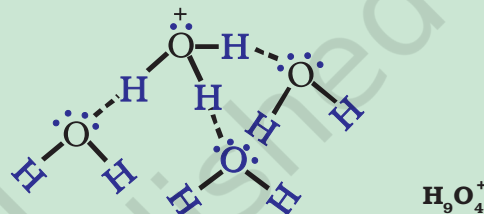
Similarly, a base molecule like MOH ionizes in aqueous solution according to the equation:

$$MOH(aq) \rightarrow M^+(aq) + OH^-(aq)$$

The hydroxyl ion also exists in the hydrated form in the aqueous solution. Arrhenius concept of acid and base, however, suffers from the limitation of being applicable only to aqueous solutions and also, does not account for the basicity of substances like, ammonia which do not possess a hydroxyl group.
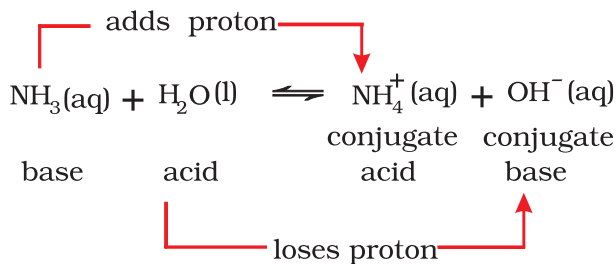

Hydronium and Hydroxyl Ions

Hydrogen ion by itself is a bare proton with very small size ($\sim 10^{-15}$ m radius) and intense electric field, binds itself with the water molecule at one of the two available lone pairs on it giving H_3O^+. This species has been detected in many compounds (e.g., $H_3O^+Cl^-$) in the solid state. In aqueous solution the hydronium ion is further hydrated to give species like $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$. Similarly the hydroxyl ion is hydrated to give several ionic species like $H_3O_2^-$, $H_5O_3^-$ and $H_7O_4^-$ etc.

$H_9O_4^+$

7.10.2 The Brönsted-Lowry Acids and Bases

The Danish chemist, Johannes Brönsted and the English chemist, Thomas M. Lowry gave a more general definition of acids and bases. According to Brönsted-Lowry theory, *acid is a substance that is capable of donating a hydrogen ion H^+ and bases are substances capable of accepting a hydrogen ion, H^+*. In short, acids are proton donors and bases are proton acceptors.

Consider the example of dissolution of NH_3 in H_2O represented by the following equation:

The basic solution is formed due to the presence of hydroxyl ions. In this reaction, water molecule acts as proton donor and ammonia molecule acts as proton acceptor and are thus, called Lowry-Brönsted acid and
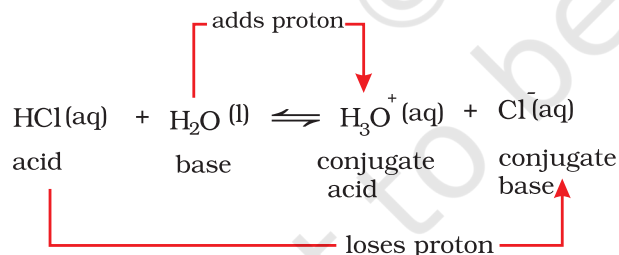
Arrhenius was born near Uppsala, Sweden. He presented his thesis, on the conductivities of electrolyte solutions, to the University of Uppsala in 1884. For the next five years he travelled extensively and visited a number of research centers in Europe. In 1895 he was appointed professor of physics at the newly formed University of Stockholm, serving its rector from 1897 to 1902. From 1905 until his death he was Director of physical chemistry at the Nobel Institute in Stockholm. He continued to work for many years on electrolytic solutions. In 1899 he discussed the temperature dependence of reaction rates on the basis of an equation, now usually known as Arrhenius equation.

Svante Arrhenius (1859-1927)

        He worked in a variety of fields, and made important contributions to immunochemistry, cosmology, the origin of life, and the causes of ice age. He was the first to discuss the 'green house effect' calling by that name. He received Nobel Prize in Chemistry in 1903 for his theory of electrolytic dissociation and its use in the development of chemistry.

base, respectively. In the reverse reaction, H^+ is transferred from NH_4^+ to OH^-. In this case, NH_4^+ acts as a Bronsted acid while OH^- acted as a Brönsted base. The acid-base pair that differs only by one proton is called a **conjugate acid-base pair**. Therefore, OH^- is called the conjugate base of an acid H_2O and NH_4^+ is called conjugate acid of the base NH_3. If Brönsted acid is a strong acid then **its conjugate base is a weak base and *vice-versa.*** It may be noted that conjugate acid has one extra proton and each conjugate base has one less proton.

Consider the example of ionization of hydrochloric acid in water. HCl(aq) acts as an acid by donating a proton to H_2O molecule which acts as a base.

$$\text{HCl(aq)} + \underset{\text{base}}{\text{H}_2\text{O (l)}} \rightleftharpoons \underset{\text{conjugate acid}}{\text{H}_3\text{O}^+\text{(aq)}} + \underset{\text{conjugate base}}{\text{Cl}^-\text{(aq)}}$$

It can be seen in the above equation, that water acts as a base because it accepts the proton. The species H_3O^+ is produced when water accepts a proton from HCl. Therefore, Cl^- is a conjugate base of HCl and HCl is the conjugate acid of base Cl^-. Similarly, H_2O is a conjugate base of an acid H_3O^+ and H_3O^+ is a conjugate acid of base H_2O.

It is interesting to observe the dual role of water as an acid and a base. In case of reaction with HCl water acts as a base while in case of ammonia it acts as an acid by donating a proton.

Problem 7.12

What will be the conjugate bases for the following Brönsted acids: HF, H_2SO_4 and HCO_3^- ?

Solution

The conjugate bases should have one proton less in each case and therefore the corresponding conjugate bases are: F^-, HSO_4^- and CO_3^{2-} respectively.

Problem 7.13

Write the conjugate acids for the following Brönsted bases: NH_2^-, NH_3 and $HCOO^-$.

Solution

The conjugate acid should have one extra proton in each case and therefore the corresponding conjugate acids are: NH_3, NH_4^+ and HCOOH respectively.

Problem 7.14

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

Solution

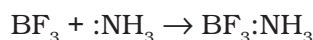The answer is given in the following Table:

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

7.10.3 Lewis Acids and Bases

G.N. Lewis in 1923 defined an *acid as a species which accepts electron pair and base which donates an electron pair*. As far as bases are concerned, there is not much difference between Brönsted-Lowry and Lewis concepts, as the base provides a lone pair in both the cases. However, in Lewis concept many acids do not have proton. A typical example is reaction of electron deficient species BF_3 with NH_3.

BF$_3$ does not have a proton but still acts as an acid and reacts with NH_3 by accepting its lone pair of electrons. The reaction can be represented by,

$$BF_3 + :NH_3 \rightarrow BF_3:NH_3$$

Electron deficient species like $AlCl_3$, Co^{3+}, Mg^{2+}, etc. can act as Lewis acids while species like H_2O, NH_3, OH^- etc. which can donate a pair of electrons, can act as Lewis bases.
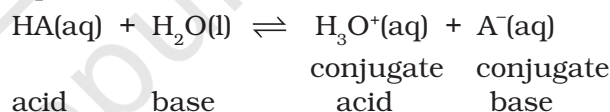

Problem 7.15

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

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

Solution

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

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

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

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

7.11 IONIZATION OF ACIDS AND BASES

Arrhenius concept of acids and bases becomes useful in case of ionization of acids and bases as mostly ionizations in chemical and biological systems occur in aqueous medium. Strong acids like perchloric acid ($HClO_4$),

hydrochloric acid (HCl), hydrobromic acid (HBr), hyrdoiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) are termed *strong* because they are almost completely dissociated into their constituent ions in an aqueous medium, thereby acting as proton (H^+) donors. Similarly, strong bases like lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), caesium hydroxide (CsOH) and barium hydroxide $Ba(OH)_2$ are almost completely dissociated into ions in an aqueous medium giving hydroxyl ions, OH^-. According to Arrhenius concept they are strong acids and bases as they are able to completely dissociate and produce H_3O^+ and OH^- ions respectively in the medium. Alternatively, the strength of an acid or base may also be gauged in terms of Brönsted-Lowry concept of acids and bases, wherein a strong acid means a good proton donor and a strong base implies a good proton acceptor. Consider, the acid-base dissociation equilibrium of a weak acid HA,

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

	conjugate	conjugate
acid	base	acid	base

In section 7.10.2 we saw that acid (or base) dissociation equilibrium is dynamic involving a transfer of proton in forward and reverse directions. Now, the question arises that if the equilibrium is dynamic then with passage of time which direction is favoured? What is the driving force behind it? In order to answer these questions we shall deal into the issue of comparing the strengths of the two acids (or bases) involved in the dissociation equilibrium. Consider the two acids HA and H_3O^+ present in the above mentioned acid-dissociation equilibrium. We have to see which amongst them is a stronger proton donor. Whichever exceeds in its tendency of donating a proton over the other shall be termed as the stronger acid and the equilibrium will shift in the direction of weaker acid. Say, if HA is a stronger acid than H_3O^+, then HA will donate protons and not H_3O^+, and the solution will mainly contain A^- and H_3O^+ ions. The equilibrium moves in the direction of formation of weaker acid and weaker base
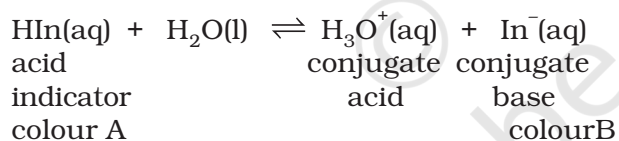
because **the stronger acid donates a proton to the stronger base**.

It follows that as a strong acid dissociates completely in water, the resulting base formed would be very weak i.e., **strong acids have very weak conjugate bases.** Strong acids like perchloric acid ($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) will give conjugate base ions ClO_4^-, Cl, Br^-, I^-, NO_3^- and HSO_4^-, which are much weaker bases than H_2O. Similarly a very strong base would give a very weak conjugate acid. On the other hand, a weak acid say HA is only partially dissociated in aqueous medium and thus, the solution mainly contains undissociated HA molecules. Typical weak acids are nitrous acid (HNO_2), hydrofluoric acid (HF) and acetic acid (CH_3COOH). It should be noted that the *weak acids have very strong conjugate bases*. For example, NH_2^-, O^{2-} and H^- are very good proton acceptors and thus, much stronger bases than H_2O.
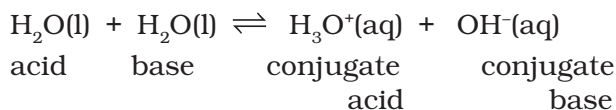
Certain water soluble organic compounds like phenolphthalein and bromothymol blue behave as weak acids and exhibit different colours in their acid (HIn) and conjugate base (In^-) forms.

HIn(aq) + H_2O(l) $\rightleftharpoons$ H_3O^+(aq) + In^-(aq)
acid   conjugate conjugate
indicator   acid   base
colour A   colourB

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

7.11.1 The Ionization Constant of Water and its Ionic Product

Some substances like water are unique in their ability of acting both as an acid and a base. We have seen this in case of water in section 7.10.2. In presence of an acid, HA it accepts a proton and acts as the base while in the presence of a base, B^- it acts as an acid by donating a proton. In pure water, one H_2O molecule donates proton and acts as an acid and another water molecules accepts a proton and acts as a base at the same time. The following equilibrium exists:

H_2O(l) + H_2O(l) $\rightleftharpoons$ H_3O^+(aq) + OH^-(aq)
acid   base   conjugate   conjugate
                       acid   base

The dissociation constant is represented by,

$$K = [H_3O^+] [OH^-] / [H_2O] \tag{7.26}$$

The concentration of water is omitted from the denominator as water is a pure liquid and its concentration remains constant. $[H_2O]$ is incorporated within the equilibrium constant to give a new constant, K_w, which is called the **ionic product of water**.

$$K_w = [H^+][OH^-] \tag{7.27}$$

The concentration of H^+ has been found out experimentally as 1.0×10^{-7} M at 298 K. And, as dissociation of water produces equal number of H^+ and OH^- ions, the concentration of hydroxyl ions, $[OH^-] = [H^+] = 1.0 \times 10^{-7}$ M. Thus, the value of K_w at 298K,

$$K_w = [H_3O^+][OH^-] = (1 \times 10^{-7})^2 = 1 \times 10^{-14} \text{ M}^2 \tag{7.28}$$

The value of K_w is temperature dependent as it is an equilibrium constant.

The density of pure water is 1000 g / L and its molar mass is 18.0 g /mol. From this the molarity of pure water can be given as,

$[H_2O]$ = (1000 g /L)(1 mol/18.0 g) = 55.55 M.

Therefore, the ratio of dissociated water to that of undissociated water can be given as:

10^{-7} / (55.55) = 1.8×10^{-9} or $\sim$ 2 in 10^{-9} (thus, equilibrium lies mainly towards undissociated water)

We can distinguish acidic, neutral and basic aqueous solutions by the relative values of the H_3O^+ and OH^- concentrations:

Acidic: $[H_3O^+] > [OH^-]$

Neutral: $[H_3O^+] = [OH^-]$

Basic : $[H_3O^+] < [OH^-]$

7.11.2 The pH Scale

Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the **pH scale**. The pH of a solution is defined as the negative logarithm to base 10 of the activity $\left(a_{H^+}\right)$ of hydrogen

ion. In dilute solutions (< 0.01 M), activity of hydrogen ion (H^+) is equal in magnitude to molarity represented by $[H^+]$. It should be noted that activity has no units and is defined as:

$$= [H^+] / mol\ L^{-1}$$

From the definition of pH, the following can be written,

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

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

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

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

Acidic solution has pH < 7

Basic solution has pH > 7

Neutral solution has pH = 7

Now again, consider the equation (7.28) at 298 K

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

Taking negative logarithm on both sides of equation, we obtain

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

$$pK_w = pH + pOH = 14 \qquad (7.29)$$

Note that although K_w may change with temperature the variations in pH with temperature are so small that we often ignore it.

pK_w is a very important quantity for aqueous solutions and controls the relative concentrations of hydrogen and hydroxyl ions as their product is a constant. It should be noted that as the pH scale is logarithmic, a

change in pH by just one unit also means change in $[H^+]$ by a factor of 10. Similarly, when the hydrogen ion concentration, $[H^+]$ changes by a factor of 100, the value of pH changes by 2 units. Now you can realise why the change in pH with temperature is often ignored.

Measurement of pH of a solution is very essential as its value should be known when dealing with biological and cosmetic applications. The pH of a solution can be found roughly with the help of pH paper that has different colour in solutions of different pH. Now-a-days pH paper is available with four strips on it. The different strips have different colours (Fig. 7.11) at the same pH. The pH in the range of 1-14 can be determined with an accuracy of ~0.5 using pH paper.
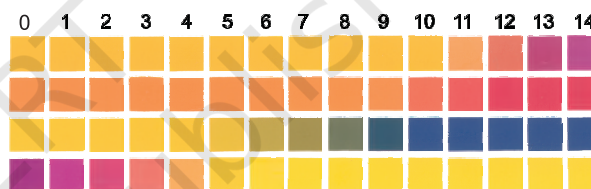

Fig.7.11 pH-*paper with four strips that may have different colours at the same* pH

For greater accuracy pH meters are used. pH meter is a device that measures the pH-dependent electrical potential of the test solution within 0.001 precision. pH meters of the size of a writing pen are now available in the market. The pH of some very common substances are given in Table 7.5 (page 212).

Problem 7.16

The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3}M. what is its pH ?

Solution

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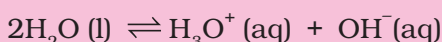$$= - \{(0.58) + (- 3.0)\} = - \{- 2.42\} = 2.42$$

Therefore, the pH of the soft drink is 2.42 and it can be inferred that it is acidic.

Problem 7.17

Calculate pH of a 1.0×10^{-8} M solution of HCl.

Table 7.5 The pH of Some Common Substances

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

Solution

$2H_2O\ (l) \rightleftharpoons H_3O^+\ (aq)\ +\ OH^-(aq)$

$K_w = [OH^-][H_3O^+]$

$\quad = 10^{-14}$

Let, $x = [OH^-] = [H_3O^+]$ from H_2O. The H_3O^+ concentration is generated (i) from the ionization of HCl dissolved i.e.,

$HCl(aq)\ +\ H_2O(l) \rightleftharpoons H_3O^+\ (aq)\ +\ Cl^-(aq),$

and (ii) from ionization of H_2O. In these very dilute solutions, both sources of H_3O^+ must be considered:

$[H_3O^+] = 10^{-8} + x$

$K_w = (10^{-8} + x)(x) = 10^{-14}$

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

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

So, pOH = 7.02 and pH = 6.98

7.11.3 Ionization Constants of Weak Acids

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

$HX(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + X^-(aq)$

Initial
concentration (M)

c 0 0

Let α be the extent of ionization

Change (M)

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

Equilibrium concentration (M)

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

Here, c = initial concentration of the undissociated acid, HX at time, t = 0. α = extent up to which HX is ionized into ions. Using these notations, we can derive the equilibrium constant for the above discussed acid-dissociation equilibrium:

$K_a = c^2\alpha^2\ /\ c(1-\alpha) = c\alpha^2\ /\ 1-\alpha$

K_a is called the **dissociation or ionization constant** of acid HX. It can be represented alternatively in terms of molar concentration as follows,

$K_a = [H^+][X^-]\ /\ [HX]$ \hfill (7.30)

At a given temperature T, K_a is a measure of the strength of the acid HX i.e., larger the value of K_a, the stronger is the acid. K_a is a dimensionless quantity with the understanding that the standard state concentration of all species is 1M.

The values of the ionization constants of some selected weak acids are given in Table 7.6.
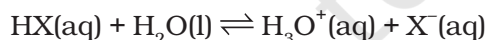
Table 7.6 The Ionization Constants of Some Selected Weak Acids (at 298K)

Acid	Ionization Constant, K_a
Hydrofluoric Acid (HF)	3.5×10^{-4}
Nitrous Acid (HNO_2)	4.5×10^{-4}
Formic Acid (HCOOH)	1.8×10^{-4}
Niacin (C_5H_4NCOOH)	1.5×10^{-5}
Acetic Acid (CH_3COOH)	1.74×10^{-5}
Benzoic Acid (C_6H_5COOH)	6.5×10^{-5}
Hypochlorous Acid (HClO)	3.0×10^{-8}
Hydrocyanic Acid (HCN)	4.9×10^{-10}
Phenol (C_6H_5OH)	1.3×10^{-10}

The pH scale for the hydrogen ion concentration has been so useful that besides pK_w, it has been extended to other species and

quantities. Thus, we have:

$pK_a = -\log(K_a)$ (7.31)

Knowing the ionization constant, K_a of an acid and its initial concentration, c, it is possible to calculate the equilibrium concentration of all species and also the degree of ionization of the acid and the pH of the solution.

A general step-wise approach can be adopted to evaluate the pH of the weak electrolyte as follows:

Step 1. The species present before dissociation are identified as Brönsted-Lowry acids / bases.

Step 2. Balanced equations for all possible reactions i.e., with a species acting both as acid as well as base are written.

Step 3. The reaction with the higher K_a is identified as the primary reaction whilst the other is a subsidiary reaction.

Step 4. Enlist in a tabular form the following values for each of the species in the primary reaction

(a) Initial concentration, c.

(b) Change in concentration on proceeding to equilibrium in terms of α, degree of ionization.

(c) Equilibrium concentration.

Step 5. Substitute equilibrium concentrations into equilibrium constant equation for principal reaction and solve for α.

Step 6. Calculate the concentration of species in principal reaction.
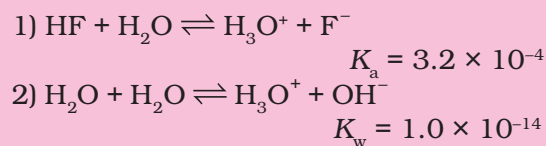
Step 7. Calculate pH = $-\log[H_3O^+]$

The above mentioned methodology has been elucidated in the following examples.
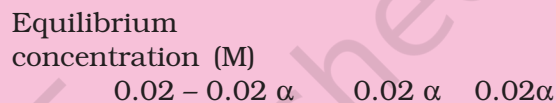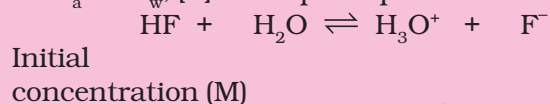

Problem 7.18

The ionization constant of HF is 3.2×10^{-4}. Calculate the degree of dissociation of HF in its 0.02 M solution. Calculate the concentration of all species present (H_3O^+, F^- and HF) in the solution and its pH.

Solution

The following proton transfer reactions are possible:

1) $HF + H_2O \rightleftharpoons H_3O^+ + F^-$
                              $K_a = 3.2 \times 10^{-4}$

2) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$
                              $K_w = 1.0 \times 10^{-14}$

As $K_a >> K_w$, [1] is the principle reaction.

	HF	+	H_2O	$\rightleftharpoons$	H_3O^+	+	F^-
Initial concentration (M)	0.02				0		0
Change (M)	−0.02α				+0.02α		+0.02α
Equilibrium concentration (M)	0.02 − 0.02 α				0.02 α		0.02α

Substituting equilibrium concentrations in the equilibrium reaction for principal reaction gives:

$K_a = (0.02α)^2 / (0.02 - 0.02α)$

$= 0.02\ α^2 / (1 - α) = 3.2 \times 10^{-4}$

We obtain the following quadratic equation:

$α^2 + 1.6 \times 10^{-2}α - 1.6 \times 10^{-2} = 0$

The quadratic equation in α can be solved and the two values of the roots are:

α = + 0.12 and − 0.12

The negative root is not acceptable and hence,

α = 0.12

This means that the degree of ionization, α = 0.12, then equilibrium concentrations of other species viz., HF, F^- and H_3O^+ are given by:

$[H_3O^+] = [F^-] = cα = 0.02 \times 0.12$

                   $= 2.4 \times 10^{-3}$ M

$[HF] = c(1 - α) = 0.02 (1 - 0.12)$

$= 17.6 \times 10^{-3}$ M

$pH = -\log[H^+] = -\log(2.4 \times 10^{-3}) = 2.62$

Problem 7.19

The pH of 0.1M monobasic acid is 4.50. Calculate the concentration of species H^+,

A$^-$ and HA at equilibrium. Also, determine the value of K_a and pK_a of the monobasic acid.

Solution

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

Therefore, $[H^+] = 10^{-pH} = 10^{-4.50}$

$$= 3.16 \times 10^{-5}$$

$[H^+] = [A^-] = 3.16 \times 10^{-5}$

Thus, $K_a = [H^+][A^-] / [HA]$

$[HA]_{eqlbm} = 0.1 - (3.16 \times 10^{-5}) \simeq 0.1$

$K_a = (3.16 \times 10^{-5})^2 / 0.1 = 1.0 \times 10^{-8}$

$pK_a = - \log(10^{-8}) = 8$

Alternatively, "Percent dissociation" is another useful method for measure of strength of a weak acid and is given as:

Percent dissociation

$= [HA]_{dissociated}/[HA]_{initial} \times 100\%$ (7.32)

Problem 7.20

Calculate the pH of 0.08M solution of hypochlorous acid, HOCl. The ionization constant of the acid is 2.5×10^{-5}. Determine the percent dissociation of HOCl.

Solution

$HOCl(aq) + H_2O (l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$

Initial concentration (M)

  0.08   0   0

Change to reach
equilibrium concentration
(M)

   – x   + x   +x

equilibrium concentartion (M)

0.08 – x   x   x

$K_a = \{[H_3O^+][ClO^-] / [HOCl]\}$

$\quad = x^2 / (0.08 - x)$

As x << 0.08, therefore $0.08 - x \simeq 0.08$

$x^2 / 0.08 = 2.5 \times 10^{-5}$

$x^2 = 2.0 \times 10^{-6}$, thus, $x = 1.41 \times 10^{-3}$

$[H^+] = 1.41 \times 10^{-3}$ M.

Therefore,

Percent dissociation

$= \{[HOCl]_{dissociated} / [HOCl]_{initial}\} \times 100$

$= 1.41 \times 10^{-3} \times 10^2 / 0.08 = 1.76$ %.

$pH = -\log(1.41 \times 10^{-3}) = 2.85.$

7.11.4 Ionization of Weak Bases

The ionization of base MOH can be represented by equation:

$MOH(aq) \rightleftharpoons M^+(aq) + OH^-(aq)$

In a weak base there is partial ionization of MOH into M$^+$ and OH$^-$, the case is similar to that of acid-dissociation equilibrium. The equilibrium constant for base ionization is called **base ionization constant** and is represented by K_b. It can be expressed in terms of concentration in molarity of various species in equilibrium by the following equation:

$K_b = [M^+][OH^-] / [MOH]$ (7.33)

Alternatively, if c = initial concentration of base and α = degree of ionization of base i.e. the extent to which the base ionizes. When equilibrium is reached, the equilibrium constant can be written as:
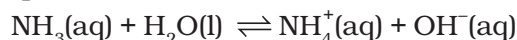
$K_b = (c\alpha)^2 / c(1-\alpha) = c\alpha^2 / (1-\alpha)$

The values of the ionization constants of some selected weak bases, K_b are given in Table 7.7.

Table 7.7   **The Values of the Ionization Constant of Some Weak Bases at 298 K**

Base	K_b
Dimethylamine, $(CH_3)_2NH$	5.4×10^{-4}
Triethylamine, $(C_2H_5)_3N$	6.45×10^{-5}
Ammonia, NH_3 or NH_4OH	1.77×10^{-5}
Quinine, (A plant product)	1.10×10^{-6}
Pyridine, C_5H_5N	1.77×10^{-9}
Aniline, $C_6H_5NH_2$	4.27×10^{-10}
Urea, $CO(NH_2)_2$	1.3×10^{-14}

Many organic compounds like *amines* are weak bases. Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by another group. For example, methylamine, codeine, quinine and

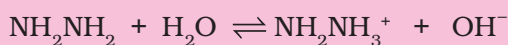nicotine all behave as very weak bases due to their very small K_b. Ammonia produces OH^- in aqueous solution:

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

The pH scale for the hydrogen ion concentration has been extended to get:

$pK_b = -\log (K_b)$ (7.34)

Problem 7.21

The pH of 0.004M hydrazine solution is 9.7. Calculate its ionization constant K_b and pK_b.

Solution

$NH_2NH_2 + H_2O \rightleftharpoons NH_2NH_3^+ + OH^-$

From the pH we can calculate the hydrogen ion concentration. Knowing hydrogen ion concentration and the ionic product of water we can calculate the concentration of hydroxyl ions. Thus we have:

$[H^+] = $ antilog ($-pH$)

$= $ antilog (-9.7) = 1.67×10^{-10}

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

The concentration of the corresponding hydrazinium ion is also the same as that of hydroxyl ion. The concentration of both these ions is very small so the concentration of the undissociated base can be taken equal to 0.004M.

Thus,

$K_b = [NH_2NH_3^+][OH^-] / [NH_2NH_2]$

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

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

Problem 7.22

Calculate the pH of the solution in which 0.2M NH_4Cl and 0.1M NH_3 are present. The pK_b of ammonia solution is 4.75.
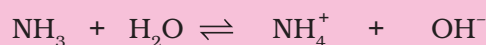
Solution

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

The ionization constant of NH_3,

$K_b = $ antilog ($-pK_b$) i.e.

$K_b = 10^{-4.75} = 1.77 \times 10^{-5}$ M

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

Initial concentration (M)

    0.10   0.20   0

Change to reach

equilibrium (M)

    $-x$ $+x$ $+x$

At equilibrium (M)

    $0.10 - x$ $0.20 + x$ x

$K_b = [NH_4^+][OH^-] / [NH_3]$

$= (0.20 + x)(x) / (0.1 - x) = 1.77 \times 10^{-5}$

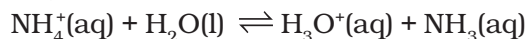As K_b is small, we can neglect x in comparison to 0.1M and 0.2M. Thus,

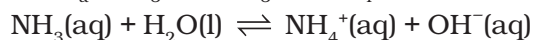$[OH^-] = x = 0.88 \times 10^{-5}$

Therefore, $[H^+] = 1.12 \times 10^{-9}$

$pH = -\log[H^+] = 8.95.$

7.11.5 Relation between K_a and K_b

As seen earlier in this chapter, K_a and K_b represent the strength of an acid and a base, respectively. In case of a conjugate acid-base pair, they are related in a simple manner so that if one is known, the other can be deduced. Considering the example of NH_4^+ and NH_3 we see,

$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$

$K_a = [H_3O^+][NH_3] / [NH_4^+] = 5.6 \times 10^{-10}$

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$K_b = [NH_4^+][OH^-] / NH_3 = 1.8 \times 10^{-5}$

Net: $2 H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ M

Where, K_a represents the strength of NH_4^+ as an acid and K_b represents the strength of NH_3 as a base.

It can be seen from the net reaction that the equilibrium constant is equal to the product of equilibrium constants K_a and K_b for the reactions added. Thus,

$K_a \times K_b = \{[H_3O^+][NH_3] / [NH_4^+]\} \times \{[NH_4^+]$
$[OH^-] / [NH_3]\}$

$= [H_3O^+][OH^-] = K_w$

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

This can be extended to make a generalisation. **The equilibrium constant for a net reaction obtained after adding two (or more) reactions equals the product of the equilibrium constants for individual reactions:**
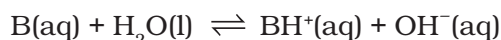
$$K_{NET} = K_1 \times K_2 \times \ldots \ldots \qquad (3.35)$$

Similarly, in case of a conjugate acid-base pair,

$$K_a \times K_b = K_w \qquad (7.36)$$

Knowing one, the other can be obtained. It should be noted that a *strong acid will have a weak conjugate base and vice-versa.*

Alternatively, the above expression $K_w = K_a \times K_b$, can also be obtained by considering the base-dissociation equilibrium reaction:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_b = [BH^+][OH^-] / [B]$$

As the concentration of water remains constant it has been omitted from the denominator and incorporated within the dissociation constant. Then multiplying and dividing the above expression by $[H^+]$, we get:

$$K_b = [BH^+][OH^-][H^+] / [B][H^+]$$

$$= \{[OH^-][H^+]\}\{[BH^+] / [B][H^+]\}$$

$$= K_w / K_a$$

or $K_a \times K_b = K_w$

It may be noted that if we take negative logarithm of both sides of the equation, then pK values of the conjugate acid and base are related to each other by the equation:
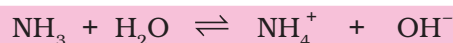
$$pK_a + pK_b = pK_w = 14 \text{ (at 298K)}$$

Problem 7.23

Determine the degree of ionization and pH of a 0.05M of ammonia solution. The ionization constant of ammonia can be taken from Table 7.7. Also, calculate the ionization constant of the conjugate acid of ammonia.

Solution

The ionization of NH_3 in water is represented by equation:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

We use equation (7.33) to calculate hydroxyl ion concentration,

$$[OH^-] = c\,\alpha = 0.05\,\alpha$$

$$K_b = 0.05\,\alpha^2 / (1 - \alpha)$$

The value of α is small, therefore the quadratic equation can be simplified by neglecting α in comparison to 1 in the denominator on right hand side of the equation,

Thus,

$$K_b = c\,\alpha^2 \text{ or } \alpha = \sqrt{(1.77 \times 10^{-5} / 0.05)}$$

$$= 0.018.$$

$$[OH^-] = c\,\alpha = 0.05 \times 0.018 = 9.4 \times 10^{-4}M.$$

$$[H^+] = K_w / [OH^-] = 10^{-14} / (9.4 \times 10^{-4})$$

$$= 1.06 \times 10^{-11}$$

$$pH = -\log(1.06 \times 10^{-11}) = 10.97.$$

Now, using the relation for conjugate acid-base pair,

$$K_a \times K_b = K_w$$

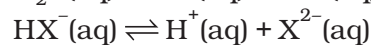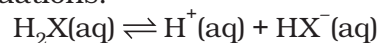using the value of K_b of NH_3 from Table 7.7.

We can determine the concentration of conjugate acid NH_4^+

$$K_a = K_w / K_b = 10^{-14} / 1.77 \times 10^{-5}$$

$$= 5.64 \times 10^{-10}.$$

7.11.6 Di- and Polybasic Acids and Di- and Polyacidic Bases

Some of the acids like oxalic acid, sulphuric acid and phosphoric acids have more than one ionizable proton per molecule of the acid. Such acids are known as polybasic or polyprotic acids.

The ionization reactions for example for a *dibasic acid* H_2X are represented by the equations:

$$H_2X(aq) \rightleftharpoons H^+(aq) + HX^-(aq)$$

$$HX^-(aq) \rightleftharpoons H^+(aq) + X^{2-}(aq)$$

And the corresponding equilibrium constants are given below:

$$K_{a_1} = \{[H^+][HX^-]\} / [H_2X] \text{ and}$$

$K_{a_2} = \{[H^+][X^{2-}]\} / [HX^-]$

Here, K_{a_1} and K_{a_2} are called the first and second ionization constants respectively of the acid H_2X. Similarly, for tribasic acids like H_3PO_4 we have three ionization constants. The values of the ionization constants for some common polyprotic acids are given in Table 7.8.

Table 7.8 The Ionization Constants of Some Common Polyprotic Acids (298K)

Acid	K_{a_1}	K_{a_2}	K_{a_3}
Oxalic Acid	5.9×10^{-2}	6.4×10^{-5}	
Ascorbic Acid	7.4×10^{-4}	1.6×10^{-12}	
Sulphurous Acid	1.7×10^{-2}	6.4×10^{-8}	
Sulphuric Acid	Very large	1.2×10^{-2}	
Carbonic Acid	4.3×10^{-7}	5.6×10^{-11}	
Citric Acid	7.4×10^{-4}	1.7×10^{5}	4.0×10^{-7}
Phosphoric Acid	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}

It can be seen that higher order ionization constants (K_{a_2}, K_{a_3}) are smaller than the lower order ionization constant (K_{a_1}) of a polyprotic acid. The reason for this is that it is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces. This can be seen in the case of removing a proton from the uncharged H_2CO_3 as compared from a negatively charged HCO_3^-. Similarly, it is more difficult to remove a proton from a doubly charged HPO_4^{2-} anion as compared to $H_2PO_4^-$.

Polyprotic acid solutions contain a mixture of acids like H_2A, HA^- and A^{2-} in case of a diprotic acid. H_2A being a strong acid, the primary reaction involves the dissociation of H_2A, and H_3O^+ in the solution comes mainly from the first dissociation step.

7.11.7 Factors Affecting Acid Strength

Having discussed quantitatively the strengths of acids and bases, we come to a stage where we can calculate the pH of a given acid solution. But, the curiosity rises about why should some acids be stronger than others? What factors are responsible for making them stronger? The answer lies in its being a complex phenomenon. But, broadly speaking we can say that the extent of dissociation of an acid depends on the **strength** and **polarity** of the H-A bond.

In general, when strength of H-A bond decreases, that is, the energy required to break the bond decreases, HA becomes a stronger acid. Also, when the H-A bond becomes more polar i.e., the electronegativity difference between the atoms H and A increases and there is marked charge separation, cleavage of the bond becomes easier thereby increasing the acidity.

But it should be noted that while comparing elements in the same *group* of the periodic table, H-A bond strength is a more important factor in determining acidity than its polar nature. As the size of A increases down the group, H-A bond strength decreases and so the acid strength increases. For example,

Size increases
→
HF << HCl << HBr << HI
→
Acid strength increases
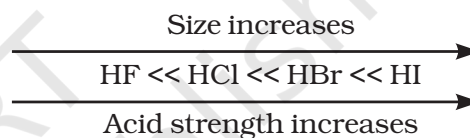
Similarly, H_2S is stronger acid than H_2O.

But, when we discuss elements in the same *row* of the periodic table, H-A bond polarity becomes the deciding factor for determining the acid strength. As the electronegativity of A increases, the strength of the acid also increases. For example,

Electronegativity of A increases
→
$CH_4 < NH_3 < H_2O < HF$
→
Acid strength increases
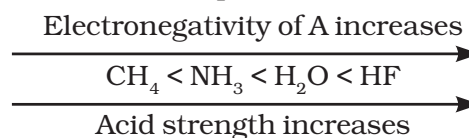
7.11.8 Common Ion Effect in the Ionization of Acids and Bases

Consider an example of acetic acid dissociation equilibrium represented as:

$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

or $HAc(aq) \rightleftharpoons H^+(aq) + Ac^-(aq)$

$K_a = [H^+][Ac^-] / [HAc]$
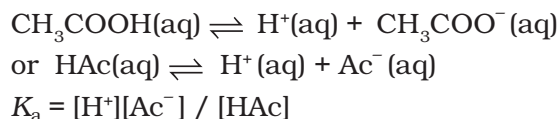
Addition of acetate ions to an acetic acid solution results in decreasing the concentration of hydrogen ions, $[H^+]$. Also, if H^+ ions are added from an external source then the equilibrium moves in the direction of undissociated acetic acid i.e., in a direction of reducing the concentration of hydrogen ions, $[H^+]$. This phenomenon is an example of