16 ACID-BASE EQUILIBRIA

The understanding of acid-base equilibria in solutions constitute an important part of Physical Chemistry. Many analytical as well as biological processes are dependent on such equilibria. The dissociation of weak acids and weak bases constitute an important group of ionic equilibria. In acid-base equilibria all the ions are dissolved in solvent medium, and so they are *homogeneous equilibria.*

16.1 Acids and Bases: the Arrhenius concept

The uses of acids and bases were known since time immemorial, although a concise definition was not given until 1884 when Svante Arrhenius proposed his theory of acids and bases. According to Arrhenius,

An acid is a compound that yields hydrogen ion (H^+) in aqueous solution and a base is a compound that gives hydroxyl (OH^-) ions in aqueous solution.

Neutralization of a base by an acid was considered essentially to be the reaction:

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l) \qquad (16.1)$$

in which the hydrogen and hydroxyl ions combine to form water. Arrhenius' definition of acids and bases proved to be inadequate for several reasons.

(i) It was recognized that acid-base reactions took place in solvents other than water.

(ii) Compounds which do not contain hydrogen could release H^+ ion by reacting with water :

$$SO_3(g) + H_2O(l) \rightleftharpoons H_2SO_4(aq) \rightleftharpoons H^+(aq) + HSO_4^-(aq) \qquad (16.2)$$

(iii) Some bases do not contain OH^- ions. For examples, NH_3, CaO etc.

It was also believed that a H^+ ion cannot exist in free state in any solvent because of its high charge density. A hydrogen ion would combine with one or more molecules of the solvent. In the case of water as solvent H^+ ion would combine with water molecules to form what is usually known as a hydronium, hydroxonium or oxonium ion (H_3O^+).

$$H^+ + H_2O(l) \rightleftharpoons H_3O^+(aq)$$

These facts together with the studies on catalysis by acids and bases suggested that the ideas of Arrhenius were inadequate and had to be modified.

16.2 Bronsted-Lowry concept

In 1923, J. N. Bronsted and J. M. Bjerrum in Denmark and T. M. Lowry in England independently proposed a theory known as '*the proton theory of acids and bases*'. According to this theory:

> *An acid is a substance - a molecule or an ion - which can* ***donate*** *a proton.*
>
> *A base is a substance - a molecule or an ion - which can* ***accept*** *a proton.*

A proton is a hydrogen atom which has lost its electron. An acid A ionizes as

$$A\,(aq) \rightleftharpoons H^{+}(aq) + B(aq) \tag{16.3}$$

B is said to be the *conjugate base* of the acid, while A is the *conjugate acid* of the base B. A and B are termed *conjugate acid-base pair. The conjugate acid and base differ only by a proton*. Examples of a few conjugate acid-base pairs are:

Acid	*Base*
$H_2O\,(aq)$	$OH^-\,(aq)$
$HCl\,(aq)$	$Cl^-\,(aq)$
$H_2SO_4\,(aq)$	$HSO_4^-\,(aq)$
$HSO_4^-\,(aq)$	$SO_4^{2-}\,(aq)$
$NH_4^+\,(aq)$	$NH_3\,(aq)$
$HCO_3^-\,(aq)$	$CO_3^{2-}\,(aq)$
$CH_3COOH\,(aq)$	$CH_3COO^-(aq)$
$H_2S\,(aq)$	$HS^-\,(aq)$
$H_2NO_3^+(aq)$	$HNO_3\,(aq)$
$CH_3COOH_2^+(aq)$	$CH_3COOH(aq)$

It may be seen that according to this concept a base or an acid may be a neutral molecule or an ion. Hydrogen chloride acts as an acid in solution because it can donate a proton. If the solvent is water H^+ ion forms the hydronium ion, H_3O^+. Water here acts as a proton acceptor, a base. This can be represented as

Conjugate acid-base pair

$$HCl\,(aq) + H_2O(l) \rightleftharpoons H_3O^+\,(aq) + Cl^-(aq) \tag{16.4}$$

Conjugate acid-base pair

Ammonia in water acts as a base because it can accept a proton from water. As a result an OH^- ion is produced,

Conjugate acid-base pair

$$NH_3(g) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq) \tag{16.5}$$

Conjugate acid-base pair

Water acts as an acid in this reaction. Following the definition it may be said that in equation (16.4) Cl^- ion is the conjugate base of the acid HCl, while water is the conjugate base of the acid H_3O^+. In equation (16.5) NH_3 is the conjugate base of the acid NH_4^+, while OH^- is the conjugate base of the acid H_2O. It can be clearly seen that *conjugate acid-base pairs* differ only by a *single proton*. In general, we may write

$$\begin{array}{ccccccc} A_1 & + & B_2 & \rightleftharpoons & B_1 & + & A_2 \\ Acid_1 & & Base_2 & & Base_1 & & Acid_2 \end{array}$$

Note that depending on the relative *proton donating* and *proton accepting* ability the same compound, such as water in the two examples given above, can act either as acid or as a base.

The Bronsted – Lowry concept may also be applied to reactions between HCl and NH_3, both dissolved in benzene. In benzene none of these two compounds are ionized. They react, however, to form NH_4Cl.

Conjugate acid-base pair

$$HCl + NH_3 \rightarrow Cl^- + NH_4^+$$

Conjugate acid-base pair

Advantages of the Bronsted – Lowry theory:

(a) It includes all substances described as acids and bases by Arrhenius.

(b) The acid – base reactions are not limited to aqueous solutions only.

(c) The theory provides a method of comparing the strengths of the '*strong*' acids and '*strong*' bases.

The usefulness of the Bronsted-Lowry concept in determining the relative strengths of acids and bases can be shown by the following considerations.

The strength of an acid is a measure of its tendency to give up a proton and the strength of a base is a measure of its tendency to accept a proton. It may be noted that since a strong acid dissociates completely to give protons its conjugate base cannot keep the proton and hence it must be very weak. Similarly, the conjugate acid of a strong base must be very weak.

(i) *A strong acid has a weak conjugate base*

(ii) *A strong base has a weak conjugate acid.*

The relative strengths of acids like HCl, HNO_3, $HClO_4$, HBr, H_2SO_4 cannot be determined in aqueous solutions as they appear to be equally strong in water. This is because the acids are completely dissociated in water which acts as a strong base. Water here is said to exert a '*Levelling effect*'. If, however, these acids are dissolved in a solvent like glacial ethanoic acid, which is not a good proton acceptor, the relative proton donating tendencies become apparent and can be determined by measuring the molar conductance. The strengths of the above mentioned acids have been found to be in the order

$$HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$$

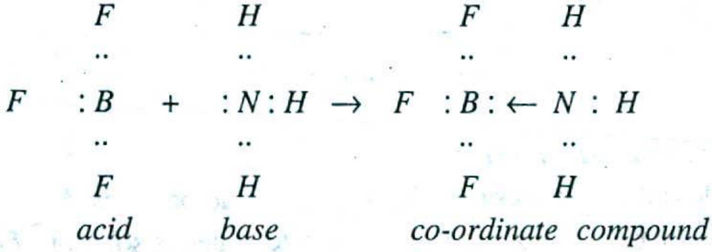
16.3 The Lewis Concept

The Bronsted-Lowry theory is actually a special case of a more general theory of acids and bases as proposed by G. N. Lewis in 1932. Lewis pointed out that substances like SO_3, BF_3 which behave as acids in solution do not contain any proton. According to the Lewis theory,

"*An acid is a species (molecule, ion or radical) which can* ***accept a pair of electrons*** *from another species*".

"*A base is a species (molecule, ion or radical) which can* ***donate a pair of electrons*** *to another species.*"

In Lewis theory the *neutralization* reaction leads to the formation of co-ordinate covalent link between an acid and a base. An example is given below:



$$\begin{array}{ccccccccc} & F & & H & & & F & & H \\ & \cdot\cdot & & \cdot\cdot & & & \cdot\cdot & & \cdot\cdot \\ F & :B & + & :N:H & \rightarrow & F & :B:\leftarrow & N & :\ H \\ & \cdot\cdot & & \cdot\cdot & & & \cdot\cdot & & \cdot\cdot \\ & F & & H & & & F & & H \\ & \text{acid} & & \text{base} & & & \text{co-ordinate} & & \text{compound} \end{array}$$

Lewis concept of acids and bases is more general than other definitions, since many reactions that do not involve Bronsted-Lowry acid–base reactions are included in the Lewis' definition. Some examples are given below :

$$H^+ + :OH_2 \rightarrow H \leftarrow :OH_2$$

$$F_3B + :F^- \rightarrow [F_3B \leftarrow :F]^-$$

$$Cu^{2+} \quad + \quad 4(:NH_3) \quad \rightarrow \quad [Cu(\leftarrow:NH_3)_4]^{2+}$$

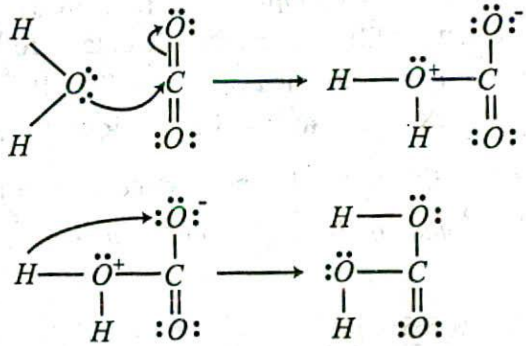
$$Fe^{3+} \quad + \quad 6(:C \equiv N:)^- \quad \rightarrow \quad [Fe(\leftarrow:C \equiv N:)_6]^{3-}$$

Lewis acid Lewis base

The formation of carbonic acid from gaseous carbon dioxide and water is a Lewis acid-base reaction.

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$$

The hydration of gaseous carbon dioxide takes place in two steps as shown below,



In the first step a lone pair of electrons on the oxygen atom in water is donated to the carbon atom of carbon dioxide. Therefore water is a Lewis base, and carbon dioxide is a Lewis acid. In the second step, a proton is transferred onto the O atom bearing a negative charge to form H_2CO_3.

16.4 Self-Ionization (or auto ionization) of Water

Water is known to be a non-electrolyte (non-conductor of electricity), although precise measurements indicate that water is a weak conductor of electricity. The conductivity of water arises due to a phenomenon known as *self-ionization*. In water two molecules of water may react to give ions as shown below:

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

The equilibrium constant for self-ionization of water is given by,

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \tag{16.6}$$

Since the concentration of the ions formed by self-ionization is very small, the concentration of H_2O remains practically constant and equation (16.6) can be rewritten as,

$$[H_2O]^2 \times K_c \;=\; [H_3O^+] \times [OH^-] \tag{16.7}$$

The quantities on the left hand side of equation (16.7) are constants, and may be replaced by a new constant term K_w, known as the ***ionic product of water***.

$$K_w = [H_3O^+] \times [OH^-] \tag{16.8}$$

K_w is a very important quantity for water. In all ionic equilibrium in water K_w is constant as long as the temperature is constant. In pure water

$$[H_3O^+]\ (\text{or simply } [H^+]) = [OH^-]$$

so that $K_w = [H^+]^2 = [OH^-]^2$ (16.9)

The value of K_w has been carefully determined at different temperatures by various methods. The value of K_w at 298 K is about $1.0\times10^{-14}\ mol^2\ L^{-6}$. Whether the solution is acidic or alkaline the value of $[H^+]\times[OH^-]$ will always be 1.0×10^{-14} at 298 K. The ionic product K_w of water may be calculated from conductance data as follows:

The specific conductance of pure water at 298 K is $5.50 \times 10^{-8}\ ohm^{-1}\ cm^{-1}$. The ion conductances $\lambda^0_{H^+}$ and $\lambda^0_{OH^-}$ at 298 K and at infinite dilutions are 349.8 $cm^2ohm^{-1}mol^{-1}$ and 198.0 $cm^2ohm^{-1}\ mol^{-1}$ respectively. So the molar conductance is $\Lambda^0 = \lambda^0_{H^+} + \lambda^0_{OH^-}$ = 349.8 $cm^2ohm^{-1}mol^{-1}$ + 198 $cm^2ohm^{-1}mol^{-1}$ = 547.8 $cm^2ohm^{-1}mol^{-1}$.

Using equation (14.8)

$$c = \frac{1000\kappa}{\Lambda^0} = \frac{1000 \times 5.5 \times 10^{-8}}{547.8}$$
$$= 1.00 \times 10^{-7}$$

where c is the concentration of ionized water. As each molecule of H_2O gives one H^+ ion and one OH^- ion we can write

$$c = [H^+] = [OH^-]$$

That is to say that in pure water the concentrations of H^+ and OH^- are equal.

Hence $K_w = [H^+]^2 = (1.0 \times 10^{-7})^2$
$= 1.0 \times 10^{-14}$

The ionic product of water at various temperatures is given in Table 16.2.

Table 16.2 Values of K_w at different temperatures

Temperature (K)	273	288	298	308
$K_w \times 10^{14}$	0.113	0.450	1.008	2.08

16.5 Hydrogen ion concentration –The pH Scale

An accurate knowledge of the hydrogen ion concentration and its control is of utmost importance in many chemical, analytical, industrial and biological processes.The hydrogen ion concentration generally found in many chemical and biological systems are very small, and often in the range of 10^{-2} –10^{-12} $mol\ L^{-1}$. It is rather difficult to always deal with such small numbers. In order to avoid this inconvenience Soren Peter Lauritz

Sorensen (1909), a Danish biochemist, proposed a more practical measure of the concentration of hydrogen ion in solutions. He introduced the term *pH* and defined it as

'pH of a solution is the negative logarithm(to the base 10) of the hydrogen ion (strictly speaking H_3O^+) concentration (in mol L^{-1})'.

$$pH = -\ log_{10}\ [H_3O^+] = \ log \frac{1}{[H^+]} \tag{16. 10}$$

For example the *pH* of a solution having a hydrogen ion concentration of 10^{-3} *mol* L^{-1} is

$$pH = -\ log_{10}\ (10^{-3}) = 3$$

[***Note :*** With the introduction of the concept of activity the correct definition is

$$pH = -\ log\ a_{H+}$$

where a_{H+} is the activity of hydrogen ion in solution and this should be used in accurate work. For ordinary purposes the definition of Sorensen is adequate and in all descriptions concentration will be used in defining *pH*.]

The *pH* is a dimensionless quantity and its values indicate acidity, basicity and neutral nature of any medium. At 298 K the *pH scale* ranges from 0 – 14.

Acidic solution	$[H^+] > 1.0 \times 10^{-7}$ mol L^{-1}	$pH < 7.00$
Basic solution	$[H^+] < 1.0 \times 10^{-7}$ mol L^{-1}	$pH > 7.00$
Neutral solution	$[H^+] = 1.0 \times 10^{-7}$ mol L^{-1}	$pH = 7.00$

The *pH* values of some common fluids are given in Table 16.3.

Table 16.3 pH of some common fluids at 298 K

Fluids	*pH*
Pure water	7.0
Sea water	7.0-8.3
Water exposed to air	5.5
Pure milk	6.5
Orange juice	3.5
Lemon juice	2.2-2.4
Grapefruit juice	3.2
Vinegar	2.4-3.4
Soda water	3.9
Blood	7.35-7.45
Gastric juice in the stomach	1.0-3.0
Tears	7.4
Urine	4.8-7.5
Saliva	6.4-6.9
Milk of magnesia	10.6

It can be seen from Table 16.3, the *pH* of body fluids varies greatly depending on the locations and metabolic functions that a particular body - part performs. The low *pH* (*high acidity*) in the stomach helps in digestion, enhances the activity of certain digestive enzymes and transport of H^+ ions across the cell membrane. The high *pH* (*basicity*) is required for active transport of oxygen.

Example 16.1: Calculate the *pH* of a solution in which the hydrogen ion concentration is 1.82×10^{-5} *mol* L^{-1}.

Solution: We know,

$$\begin{aligned} pH &= -\log_{10}[H^+] \\ &= -\log_{10}(1.82 \times 10^{-5}) \\ &= 5 - 0.26 \quad = 4.74 \end{aligned}$$

Example 16.2 If the *pH* of a solution is 8.45, what is the hydrogen ion concentration of the solution?

Solution:

$$\begin{aligned} pH = -\log_{10}[H^+] &= 8.45 \\ \log_{10}[H^+] &= -8.45 \\ [H^+] &= \text{anti } \log(-8.45) \\ &= 3.55 \times 10^{-9}\, mol\, L^{-1} \end{aligned}$$

Example 16.3: The *pH* of rain water collected in a certain area is 4.82. Calculate the $[H^+]$ of rain water.

Solution:

$$\begin{aligned} pH = -\log_{10}[H^+] &= 4.82 \\ \log_{10}[H^+] &= -4.82 \\ [H^+] &= \text{anti } \log \text{ of } (-4.82) \\ &= 1.5 \times 10^{-5}\, mol\, L^{-1} \end{aligned}$$

Example 16.4: 100 *mL* of 0.05 *mol* L^{-1} *HCl* solution is mixed with 150 *mL* of 0.04 *mol* L^{-1} HNO_3 solution. Calculate the *pH* of the resulting solution.

Solution: Both the acids are strong. So the concentrations of the acids are the same as the concentrations of H^+ ions. They do not react with each other

$$\text{Moles of } H^+ \text{ in 100 } mL \text{ of } HCl \text{ solution } = \frac{0.05 \times 100}{1000} = 0.005$$

$$\text{Moles of } H^+ \text{ in 150 } mL \text{ of } HNO_3 \text{ solution} = \frac{0.04 \times 150}{1000} = 0.006$$

Total moles of H^+ ions in 250 *mL* of solution = 0.005 + 0.006 = 0.011

Total volume of solution = 250 *mL*

$$\text{Concentration of } H^+ \text{ ions } = \frac{0.011 \times 1000}{250} = 0.044\, mol\, L^{-1}$$

$$\text{Hence } \quad pH = -\log_{10}[H^+] = -\log_{10}(0.044) = 1.36$$

16.6 Some useful relationship

Analogous to the definition of *pH* other *p* functions have been defined. Examples are :

$$pOH = -\ log_{10}\, [OH^-] \qquad pK_w = -\ log_{10}\, K_w$$
$$pCu = -\ log_{10}\, [Cu^{2+}]$$
$$pAg = -\ log_{10}\, [Ag^+] \qquad pK_a = -\ log_{10}\, K_a$$

We know from equation (16. 8) that

$$K_w = [H^+]\, [OH^-]$$

Taking logarithm and changing signs on both sides of this equation

We obtain, $-\ log\ K_w = -\ log\ [H^+] - log\ [OH^-]$

Using the definition of *pOH* and pK_w as shown above, we have

$$pK_w = pH + pOH \tag{16.11}$$

or

$$pH + pOH = pK_w \tag{16.11a}$$

Since $K_w = 1.00 \times 10^{-i4}$ at 298 *K*, $pK_w = 14$

and $pH + pOH = 14$ at 298 *K* for any aqueous solution.

If the hydroxyl ion concentration of a solution is given the *pH* of the solution can then be calculated from equation (16.11).

Example16.5: Calculate the *pH* of a solution of *NaOH* of concentration 5.0×10^{-4} $mol\ L^{-1}$.

Solution: Since *NaOH* is a strong base $[NaOH] = [OH^-]$

$$pOH \text{ of the solution} = -\ log_{10}\, (5.0 \times 10^{-4})$$
$$= 4 - 0.698$$
$$= 3.30$$

Hence $pH = 14 - 3.30 = 10.7$

Example 16.6: Calculate the *pH* of a solution of $Ba(OH)_2$ of concentration 3.2×10^{-3} $mol\ L^{-1}$.

Solution: In aqueous solution $Ba(OH)_2$ exists as

$$Ba(OH)_2\, (aq) \rightarrow Ba^{2+}\, (aq) + 2\ OH^-(aq)$$

As $Ba(OH)_2$ is a strong electrolyte $[OH^-] = 2\ Ba(OH)_2\, (aq)$

$$= 2 \times 3.2\ x10^{-4}\ mol\ L^{-1}$$

Therefore, $pOH = -\ \log_{10}\, (6.4 \times 10^{-3}) = 3 - 0.79$

$$= 2.21$$

Hence, $pH = 14 - 2.21 = 11.8$

The *pH* and *pOH* values of solutions with different hydrogen ion concentrations are given in Table 16.4.

Table 16.4 $[H^+]$, pH and pOH of solutions

$[H^+]$ /mol L^{-1}	pH	pOH	Condition
1.0	0	14	Acidic
1.0×10^{-1}	1	13	
1.0×10^{-2}	2	12	
1.0×10^{-3}	3	11	
1.0×10^{-4}	4	10	
1.0×10^{-5}	5	9	
1.0×10^{-6}	6	8	
1.0×10^{-7}	7	7	Neutral
1.0×10^{-8}	8	6	Alkaline
1.0×10^{-9}	9	5	
1.0×10^{-11}	11	3	
1.0×10^{-14}	14	0	

It is clear that solutions having $pH < 7.0$ are acidic and those with $pH > 7.0$ are alkaline. pH value of 0 and negative pH values are also possible. For example, a solution of $pH = -1.0$ corresponds to a $[H^+] = 10.0\ mol\ L^{-1}$.

16.7 Measurement of pH

The methods of determination of pH of a solution are broadly divided into two groups:

(a) the indicator method and

(b) the *e.m.f.* method (see Section 15)

(a) Indicator method: This method is based on the fact that indicators have different colours in solutions of different pH. From previous knowledge of the *colour-pH* match one can directly determine the pH of a solution by adding one or two drops of the indicator solution. A suitable mixture of different indicators, known as *universal indicator*, can help determine the pH of a solution over a wide range of values. Nowadays, special papers, known as *pH-papers*, are also available for approximate determination of pH of a solution. The indicator method is simple and easy to use, but provides approximate value only of pH of the solution.

***(b) The e.m.f. method*:** This is based on the use of an electrode whose potential is dependent on H^+ ion concentration in solution. Three such electrodes are usually used. These are (i) the hydrogen electrode, (ii) the quinhydrone electrode and (iii) the glass electrode. Each of these electrodes is combined with a reference *calomel electrode* to set up a cell and the emf of the cell is determined to evaluate accurately the pH of the solution.

(i) The hydrogen electrode

The hydrogen electrode has been discussed in *Section (15.16)*. The Nernst equation for hydrogen electrode is

$$E_{H^+/H_2} = 0.0591 \log[H^+] \text{ at 298 K.}$$

or $$E_{H^+/H_2} = -\,0.0591\,pH \qquad (16.12)$$

The following cell is set up with a reference calomel electrode:

$$Pt,\ \mathrm{H_2}\ (1\ atm) \mid \mathrm{H}^+\ (test\ solution) \parallel KCl\ (Satd.) \mid Hg_2Cl_2(s) \mid Hg$$

The emf of the cell is, $E_{cell} = E_{R(R)} - E_{R(L)}$

$$= 0.2415 - (-\,0.0591\ pH)$$

$$= 0.2415 + (\,0.0591\ pH)$$

$$pH = \frac{E_{cell} - 0.2145}{0.0591} \qquad \textbf{(16.13)}$$

In the above equation 0.02145 is the *standard electrode potential* of the calomel electrode. Thus, if the E_{cell} of the cell is determined potentiometrically, *pH* of the solution can be accurately determined.

(ii) Quinhydrone electrode

Quinhydrone *(Q)* is an equimolar mixture of hydroquinone and quinone *(H_2Q)*. **Both** are sparingly soluble in water. When dissolved in water they form an oxidation-reduction system as shown below:

$$\underset{Quinone(Q)}{C_6H_4O_2\,(aq)} + 2H^+(aq) + 2e^- \rightleftharpoons \underset{Hydroquinone(H_2Q)}{C_6H_4(OH)_2\,(aq)}$$

If a *Pt* wire is dipped into this solution, an electrode *Pt*, $Q \mid H_2Q$ is formed and the Nernst equation for this electrode is given by,

$$E_{Q/H_2Q} = E^0_{Q/H_2Q} - \frac{RT}{2F} \ln \frac{[H_2Q]}{[Q][H^+]^2}$$

$$= E^0_{Q/H_2Q} - \frac{RT}{2F} In \frac{1}{[H^+]^2},$$

Since $\frac{[H_2Q]}{[Q]} = 1$ (as these are solids)

$$E_{Q/H_2Q} = E^0_{Q/H_2Q} + \frac{RT}{2F} In[H^+]^2$$

$$= E^0_{Q/H_2Q} + \frac{RT}{F} In[H^+]$$

$$\text{At } T = 298\text{ K} \quad = E^0_{Q/H_2Q} + 0.0591\log_{10}[H^+]$$
$$= E^0_{Q/H_2Q} - 0.0591\,pH$$
$$= 0.6996 - 0.0591\,pH \qquad (16.14)$$

In order to determine the pH of an unknown solution, the following cell is set up.

$$Hg \mid Hg_2Cl_2(s) \mid KCl(satd.) \parallel H^+\,(Test\ solution) \mid Q \mid H_2Q \mid Pt$$

The emf of this cell is given by

$$E_{cell} = E_{R(R)} - E_{R(L)}$$
$$= 0.6996 - 0.0591\,pH - E_{cal}$$

$$\text{Therefore, } pH = \frac{0.6996 - E_{cal} - E_{cell}}{0.0591} \qquad (16.15)$$

Thus the pH of an unknown solution can be determined.

(iii) The glass electrode

Glass electrode has become the most useful and convenient electrode in determining the pH of solutions, particularly with the commercially built pH meters. A glass electrode consists of a glass tube with a thin-walled bulb at the end (Figure 16.1). The bulb is filled with 1 $mol\ L^{-1}$ HCl solution. One end of a silver wire is coated with $AgCl$ and sealed into the glass bulb in such a way that the $AgCl$-coated end dips into the HCl solution. The entire assembly forms an electrode known as glass electrode. This is represented as

$$Ag \mid AgCl \mid HCl(1.0\ mol\ L^{-1}) \mid Glass \mid$$

If the glass electrode is placed in a solution of H^+ ions, a potential is developed across the glass membrane due to the difference of the H^+ ion concentration on the two sides of the membrane. The potential is given by,

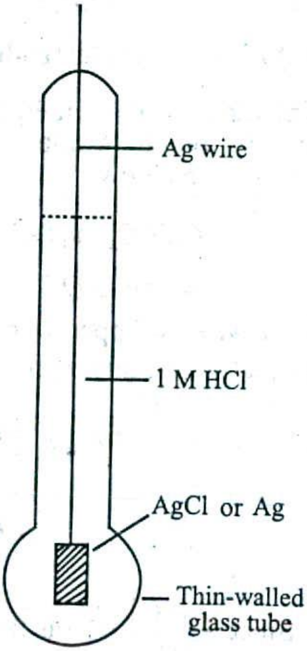


Figure 16.1 Glass electrode

$$E_{Glass} = E^0_{Glass} - \frac{RT}{F}ln[H^+] \qquad (16.16)$$
$$= E^0_{Glass} + 0.0591\,pH \qquad (16.17)$$

In order to determine the *pH* of an unknown solution the glass electrode is combined with calomel electrode to set up the following cell :

$$Glass\ Electrode|\ Solution\ of\ unknown\ pH|\ Calomel\ Electrode$$

The emf of the cell is given by,

$$E_{cell} = E_{Cal} - E_{Glass} \tag{16.18}$$

Substituting equation (16.17) into (16.18) we get,

$$E_{cell} = E_{Cal} - E^0_{Glass} - 0.0591\,pH \tag{16.19}$$

$$pH = \frac{E_{Cal} - E^0_{Glass} - E_{cell}}{0.0591} \tag{16.20}$$

Thus the *pH* of an unknown solution can be easily determined by measuring the *e.m.f* of the cell, since E_{Cal} *and* E^0_{Glass} are known. Glass electrodes are commercially available. These have the following advantages:

(i) simple to use
(ii) not affected by oxidizing and reducing agents
(iii) not easily poisoned
(iv) can be used for small quantity of solutions

However, glass electrodes are very delicate, and should be handled carefully. The glass electrode is an essential part of the *pH*-meters which are widely used in biological studies, in industries and in analysis.

16.8 Dissociation of weak acids and weak bases: Ostwald's Dilution Law

Weak electrolytes are incompletely dissociated into ions. Consider the equilibrium involving the dissociation of the binary electrolyte *MA*:

$$MA(aq) \rightleftharpoons M^+(aq) + A^-(aq)$$

The equilibrium constant, K_c, is given by,

$$K_c = \frac{M^+][A^-]}{[MA]} \tag{16.21}$$

If the concentration of the electrolyte is $c\ mol\ L^{-1}$ and α is the degree of dissociation, then

$$[M^+] = [A^-] = \alpha c$$

and $$[MA] = (1-\alpha)c$$

These on substitution in equation (16.21) give

$$K_c = \frac{\alpha^2 c}{1-\alpha} \tag{16.22}$$

At a constant temperature K_c has a constant value. Hence when the concentration c is changed α must change in order to keep the value of K_c constant. Equation (16.22) is called the '*Ostwald Dilution Law*'. The higher the value of K_c, the stronger the electrolyte. This equation represents the variation of the degree of dissociation with concentration.

16.9 Dissociation constants of weak acids and weak bases

The dissociation of weak acid, HA, in water may be represented by the equation

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

The equilibrium constant K *for this reaction* may be written as,

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \tag{16.23}$$

Equation (16.23) may be written as

$$K \times [H_2O] = \frac{[H_3O^+][A^-]}{[HA]} \tag{16.23a}$$

When the solution is dilute the concentration of water remains practically constant. Under this condition equation (16.23a) takes the form

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{16.24}$$

where $K_a = K \times [H_2O]$. The constant K_a is known as the *dissociation constant* or *acid dissociation constant* of the acid. The hydronium ion, H_3O^+, in equation (16.24) may be replaced by H^+ and one can write

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{16.25}$$

The equilibrium constants K_a varies with temperature. Whatever be the other ions present the constancy of K_a will be maintained.

Similarly for the dissociation of a weak base B we can write,

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

and the base dissociation constant K_b may be shown to be,

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{16.25a}$$

16.10 pH of solutions of very weak acids

If the acid is very weak then the extent of dissociation will be very small and for all practical purposes *[HA]* in equation (16.25) may be taken as the initial concentration of the acid. As $[H^+] = [A^-]$ equation(16.25) reduces to

$$[H^+]^2 = K_a[HA] \tag{16.26}$$

so that

$$[H^+] = \sqrt{(K_a[HA])} \tag{16.27}$$

This relation may be used to make approximate calculations of *pH* of solutions of very weak and moderately weak acids. If the *pH* of the solution of a weak acid is known an approximate value of its K_a may be calculated. The value of K_a may also be determined from a titration curve (*Section 16.16*)

Example 16.7: Calculate the *pH* of a solution of *n*- butyric acid of concentration 0.12 $mol\ L^{-1}$; (K_a of the acid = $1{\cdot}515 \times 10^{-5}\ mol\ L^{-1}$)

Solution: Using the relation (16.27),

$$\begin{aligned}[H^+] &= \sqrt{(K_a[HA])}\\ &= \sqrt{(0.12 \times 1.515 \times 10^{-5})}\\ &= 1.66 \times 10^{-3}\\ pH &= -\log\ (1.66 \times 10^{-3})\\ &= 2.78\end{aligned}$$

Example 16.8: The *pH* of 0.10 $mol\ L^{-1}$ solution of an acid is 2.58. Calculate the K_a of the acid.

Solution:

$$\begin{aligned}pH &= -\log\ [H^+] = 2.58\\ [H^+] &= \text{anti}\log(-2.58)\\ &= 2.62 \times 10^{-3}\end{aligned}$$

Again

$$[H^+] = \sqrt{(K_a[HA])}$$

or

$$K_a = \frac{[H^+]^2}{[HA]}$$

$$= \frac{(2.62 \times 10^{-3})^2}{0.10} = 6.86 \times 10^{-5}\ mol\ L^{-1}$$

A more accurate value of K_a may be calculated if the degree of dissociation of the acid in solution is known. If α is the degree of dissociation of the acid when the concentration is $c\ mol\ L^{-1}$, then

$$[H^+] = \alpha c;\ [A^-] = \alpha c \text{ and } [HA] = (1-\alpha)c$$

Hence

$$K_a = \frac{\alpha^2 c}{(1-\alpha)} \tag{16.28}$$

When α is small $(1-\alpha) \approx 1$ and equation (16.28) reduces to

$$K_a = \alpha^2 c \tag{16.29}$$

This relation enables one to make an approximate calculation of α if K_a is known, and *vice versa.*

Example 16.9: Ethanoic acid solution of concentration 0.05 $mol\ L^{-1}$ is 1.88% dissociated. Calculate the K_a of the acid.

Solution: Here $\alpha = 0.0188$. From equation (16.29) we get,

$$K_a = \alpha^2 \times c = (0.0188)^2\,(0.05) = 1.76 \times 10^{-5}\ mol\ L^{-1}$$

The dissociation constants of acids are measures of their relative strengths. The dissociation constants of a number of acids are quoted in Table 16.5

Table 16.5 Dissociation constants of acids at 25°C

Acid	K_a	pK_a
Formic	$1\cdot772 \times 10^{-4}$	3·75
Acetic	$1\cdot754 \times 10^{-5}$	4·76
Propionic	$1\cdot336 \times 10^{-5}$	4·87
Chloroacetic	$1\cdot379 \times 10^{-3}$	2·36
n-Butyric	$1\cdot515 \times 10^{-5}$	4·82
Benzoic	$6\cdot310 \times 10^{-5}$	4·20
Phenol	$1\cdot200 \times 10^{-10}$	9·50

Polyprotic acids

Acids	K_1	K_2	K_3
Oxalic	6.5×10^{-2}	6.1×10^{-5}	-----
Citric	8.7×10^{-4}	1.8×10^{-5}	4.0×10^{-6}
Phosphoric	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}

In Table 16.5 the dissociation constants have also been expressed as pK_a which is defined as

$$pK_a = -\log_{10} K_a \tag{16.30}$$

It should be recognized that higher is the dissociation, the higher is the concentration of H^+ ion produced in solution; and consequently larger is the value of K_a. It means that acids with higher K_a values are stronger acids. pK_a is a logarithmic quantity with negative sign. The higher pK_a value corresponds to lower K_a value as may be observed in Table. 16.5.

The dissociation constants of some polyprotic acids are also included in Table 16.5. These acids contain two or more ionizable hydrogen atoms per molecule. Experiments show that such acids always ionize in steps. For example, carbonic acid ionizes in two steps:

(i) $H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$

(ii) $HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$

The equilibrium constants for these steps are:

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.3 \times 10^{-7} \text{ at } 25°C$$

$$K_2 = \frac{[H^+][CO_3^-]}{[HCO_3^-]} = 5.6 \times 10^{-11} \text{ at } 25°C$$

Although both ionizations occur simultaneously, in all cases K_2 (or K_3) is found to be much smaller than K_1 (See Table 16.5).

16.11 pH of solutions of very weak bases

A treatment similar to the one used for weak acids may be given for the dissociation of weak bases. For a weak base B in aqueous solution the following equilibrium exists:

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

The equilibrium constant K_b, called the base dissociation constant, is given by

$$K_b = \frac{[BH^+]\times[OH^-]}{[B]} \tag{16.31}$$

Water being the solvent its concentration is taken as constant. As the base is very weak, $[B]$ does not change very much and may be considered constant for all practical purposes. Since $[BH^+] = [OH^-]$ equation (16.31) may be written as

$$[OH^-]^2 = K_b\,[B] \tag{16.32}$$

So $[OH^-] = \sqrt{(K_b\,[B])}$

Example 16.10: Calculate the *pH* of a 0.10 $mol\ L^{-1}$ solution of ethylamine at 25°C. The dissociation constant of the organic base is $5.1\times10^{-4}\ mol\ L^{-1}$.

Solution: When ethylamine dissociates in solution we have

$$CH_3CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^+ + OH^-$$

and $$K_b = \frac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2]}$$

As $$[OH^-] = [CH_3CH_2NH_3^+]$$

we can write $$[OH^-]^2 = K_b([CH_3CH_2NH_2])$$

hence $$[OH^-] = \sqrt{(K_b)(CH_3CH_2NH_2)}$$

Substituting the values $$[OH^-] = \sqrt{(5.1\times10^{-4})(0.10)}$$

$$= 7.14\times10^{-3}\ mol\ L^{-1}$$

$$pOH = -\log\ 7.14\times10^{-3} = 2.15$$

$$pH = 14 - pOH = 14 - 2.15$$

$$= 11.85$$

Example 16.11 : An aqueous solution of dimethylamine of concentration 0.020 $mol\ L^{-1}$ has a pH of 7.78. Calculate K_b, the base dissociation constant, of dimethylamine.

Solution : Dimethylamine dissociates as follows in aqueous solution:

$$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$$

Now $$pOH = 14 - pH = 14 - 7.78$$

$$= 6.22$$

Hence $[OH^-] = -\ anti\ log\ 6.22 = 6.18\times10^{-7}\ mol\ L^{-1}$

Then $$K_b = \frac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]}$$

$$= \frac{[OH^-]^2}{[(CH_3)_2NH]}$$

$$= \frac{(6.18\times10^{-7})^2}{0.020}$$

$$= 1.91\times10^{-11}\ mol\ L^{-1}$$

A more accurate estimation of K_b may be made if the degree of dissociation α is known. As in the case of weak acids if the degree of dissociation of the base is α then at equilibrium

$$[BH^+] = \alpha c \qquad [OH^-] = \alpha c$$

and $$[B] = (1-\alpha)c$$

where c is the initial concentration of the base. The base dissociation constant of B will be given by

$$K_b = \frac{\alpha^2 c}{(1-\alpha)} \tag{16.33}$$

For dilute solutions

$$K_b = \alpha^2 \times c \tag{16.34}$$

Example16.12: In a solution of concentration 0.020 $mol\ L^{-1}$ ammonia is only 3.0% dissociated. Find the K_b of ammonia.

Solution: Here $\alpha = 0.030$, $K_b = \alpha^2 c = (0\ .030)^2(0.020) = 1.8 \times 10^{-5}\ mol\ L^{-1}$

Table 16.6 Dissociation constants of some bases in aqueous solution at 25°C

Substance	Formula	K_b
Ammonia	NH_3	1.8×10^{-5}
Methylamine	CH_3NH_2	4.4×10^{-4}
Ethylamine	$CH_3CH_2NH_2$	4.7×10^{-4}
Dimethylamine	$(CH_3)_2NH$	1.91×10^{-11}
Hydrazine	H_2NNH_2	1.7×10^{-6}
Aniline	$C_6H_5NH_2$	4.2×10^{-10}
Hydroxylamine	NH_2OH	1.1×10^{-8}

16.12 The Common Ion Effect

The dissociation of an electrolyte may be depressed by adding another electrolyte having an ion (cation or anion) in common with the dissolved electrolyte.

'The phenomenon in which the dissociation of a weak electrolyte is suppressed due to the presence of another electrolyte having an ion in common with the dissolved weak electrolyte is known as 'The Common Ion Effect'.

This may be illustrated with ethanoic acid and sodium ethanoate. In solution the following equilibrium is established:

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

If CH_3OONa is added to the solution of ethanoic acid, it dissociates completely, since it is a strong electrolyte.

$$CH_3COONa(s) + aq \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

According to *Le Châtelier's principle* addition of the common ion CH_3COO^- from CH_3COONa to the solution of CH_3COOH will shift the equilibrium to the left and thereby suppress the dissociation of CH_3COOH. As a result the solution will be less acidic than the solution having the same concentration of CH_3COOH. The common ion effect plays an important role in determining the pH of a solution as well as the solubility of sparingly soluble salts.

Example 16.13: Calculate the hydrogen ion concentration and the degree of dissociation of 0.20 $mol\ L^{-1}$ solution of acetic acid in water at 298 K. What is the degree of dissociation of acid if sodium acetate is added to this solution so that its concentration is 0.05 $mol\ L^{-1}$. The dissociation constant of the acid is 1.8×10^{-5}.

Solution: From equation (16.29) we get for a solution of the acid,

$$K_a = \alpha^2 c$$

$$\text{or} \quad \alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1{\cdot}8 \times 10^{-5}}{0{\cdot}20}} = 0{\cdot}0095$$

Hence $[H^+] = \alpha c = 0{\cdot}0095 \times 0{\cdot}2 = 1{\cdot}9 \times 10^{-3}\ mol\ L^{-1}$

Also $[CH_3COO^-] = \alpha c = 1{\cdot}9 \times 10^{-3}\ mol\ L^{-1}$.

In presence of CH_3COONa the dissociation of the acid will be diminished. Let the degree of dissociation be α' in presence of the salt. So $[CH_3COO^-]$ from dissociation of the acid is $\alpha' c$. Since the salt is completely in the form of ions

$$\text{Total } [CH_3COO^-] = 0.2\alpha' + 0.05$$

But $[H^+] = 0.2\alpha'$, as it is derived only from the dissociation of CH_3COOH. Hence $[CH_3COOH] = (1 - \alpha')(0.2)$. Substituting these values in the expression (equation (16.23a) for the dissociation constant,

$$1.8 \times 10^{-5} = \frac{(0.2\alpha')(0.2\alpha' + 0.05)}{0.2(1 - \alpha')} = \frac{\alpha'(0.2\alpha + 0.05)}{1 - \alpha'}$$

Considering that $\alpha' << 1$, α' can be neglected from the denominator.
Solving the quadratic equation we get,

$$1.8 \times 10^{-5} = \frac{0.2\alpha'(0.2\alpha' + 0.05)}{0.2}$$

$$0.2(\alpha')^2 + 0.05\alpha' - 1.8 \times 10^{-5} = 0,$$

$$\alpha' = 0.003$$

So we find that on the addition of the salt the degree of dissociation of the acid dropped from 0.0095 to 0.003.

16.13 Indicators in Acid - Base Titrations

Indicators, as the name implies, are substances which indicate, generally by their colour change, the equivalence point or end point of a titration. There are different types of indicators used in chemical analysis. Here only acid – base indicators will be dealt with.

Acid-base indicators are usually complex organic compounds which are weak acids or bases. They change their colour over a small range of *pH*. The undissociated form of the indicator has one colour and the dissociated form (the anion in the case of an acid indicator and cation in the case of a base indicator) has a different colour. As the indicator is used only in very small quantities the colour of one form must be quite distinct from that of the other. The colour of the solution will depend on the relative proportion of the dissociated and undissociated forms.

Taking the common indicator phenolphthalein as a weak acid, HIn, its dissociation may be represented by

$$\underset{\text{colourless}}{HIn} \rightleftharpoons \underset{\substack{\text{reddish}\\ \text{purple}}}{In^-} + H^+ \tag{16.35}$$

The equilibrium constant for this equilibrium is given by

$$K_{In} = \frac{[H^+][In^-]}{[HIn]} \tag{16.36}$$

K_{In} is the dissociation constant of the indicator and is called the ***indicator constant***.

In an acid solution the equilibrium will lie to the left as the ionization is repressed (common ion effect) due to the presence of H^+ ion in large concentration. The colour will be that of HIn. In an alkaline solution, on the other hand, the equilibrium will be shifted towards the right as more HIn will dissociate when the H^+ ions are removed by OH^- ions from the alkali. There will be large concentration of In^- ions and the colour will be that of In^-. If the acidic and basic forms have two different colours the neutral colour is obtained at the pH where the concentration of HIn and In^- are equal.

Our eyes are not very sensitive to small colour changes. As a result it is often difficult to detect the colour change until about 10% of the indicator is neutralized (when it is mostly in the HIn form) and the change does not appear to be complete until about 90 per cent of the indicator is neutralized (when it is mostly in the In^- form). Taking logarithm to the base 10 of both sides of equation (16.36) and multiplying both sides of the obtained equation by –1 one gets,

$$-\log K_{In} = -\log [H^+] - \log \frac{[In^-]}{[HIn]} \tag{16.37}$$

Using the definition of pH and pK_{In}

$$pK_{In} = pH - \log \frac{[In^-]}{[HIn]} \tag{16.38}$$

Rearrangement of equation (16.38) gives the relation

$$pH = pK_{In} + \log \frac{[In^-]}{[HIn]} \tag{16.38a}$$

When the ratio $\frac{[In^-]}{[HIn]}$ is large, say about 90% of the indicator is dissociated,

$$pH = pK_{In} + \log\left(\frac{90}{10} \text{ or nearly } 10\right)$$

or,
$$pH = pK_{In} + 1 \qquad (16.39)$$

Again when the ratio $\frac{[In^-]}{[HIn]}$ is small, say about 10% of the indicator is dissociated,

$$pH = pK_{In} + \log\left(\frac{10}{90} \text{ or nearly } 0.1\right)$$

$$pH = pK_{In} - 1 \qquad (16.40)$$

It can be seen from these considerations that our eyes can detect sharp change of colour of the indicator only if during the titration the *pH* changes over the range $pH = pK_{In} \pm 1$; i.e. over a range of about 1 *pH* unit on either side of pK_{In}. It is obvious from this discussion that different indicators indicate neutralization points at different *pH* values. Table 16.7 gives the *pH* range of colour change for a number of commonly used indicators.

Table 16.7 *pH* range of acid-base indicators

Indicator	Colour		*pH* range of colour change	pK_{In}
	Acid form	Alkaline form		
Thymol blue	*Red*	*Yellow*	1.2 - 2.8	1.65
Methyl orange	*Red*	*Orange*	3.1- 4.4	3.46
Methyl red	*Red*	*Yellow*	4.2 - 6.3	5.00
Litmus	*Red*	*Blue*	5.0 - 8.0	7.0
Bromothymol blue	*Yellow*	*Blue*	6.0 – 7.6	
Phenol red	*Yellow*	*Red*	6.8 - 8.4	8.00
Phenolphthalein	*Colourless*	*Reddish- purple*	8.3 -10.0	9.10

16.14 Acid -Base Titrations: Choice of Indicator for Titrations

Titrations are used to determine concentrations of solutions. The titration is carried out by adding a solution of a reagent (*titre*) from the burette to a solution taken in a conical flask (*titrant*). *An acid-base titration is a procedure for determining the concentration of an acid (or base) in a solution in a given volume taken in a conical flask by determining the volume of a base (or acid) of known concentration required for complete reaction, the titre being added from a burette.*

When the solutions are mixed such that the titrant and titre are in the proportion shown in the stoichiometric equation the *equivalence point* is said to have been reached and the reaction is complete. In a volumetric titration the equivalence point is determined with the help of an indicator. The completion of the reaction is indicated by the colour change of the indicator and when this happens the titration is said to have reached '*the end point*'. Ideally the equivalence point and the end point should be the same.

The equivalence point of an acid-base titration may also be determined by measuring the *pH* of the solution in the conical flask after each addition of the titre and by plotting the *pH* values against the volume of titre added. The curves obtained in such graphs are called *neutralization curves*.

The *pH* at the equivalence point of acid-base titrations varies with the relative strengths of the acid and base. As the indicator changes colour in a small range of *pH*, for use in indicating the end point of titrations the selection of proper indicator is important. This can be best discussed by considering the *pH* changes of the solution occurring in acid–base reactions during titration and plotting such changes as neutralization curves.

Figures 16.2 to 16.5 illustrate schematically the different possible types of neutralization curves.

16.15 Titration of a Strong Acid with a Strong Base

Figure 16.2 shows a curve for the titration of 25.0 mL of 0.100 $mol\ L^{-1}\ HCl$ solution in the conical flask by 0.100 $mol\ L^{-1}\ NaOH$ solution added from the burette. The pH can be calculated after each addition of base. Sample calculation is shown:

Before any $NaOH$ is added the pH of the solution = $-\log\,[H_3O^+] = -\log\ 0.1 = 1.0$.
On adding 5.0 mL of $NaOH$ solution the moles of acid left is

$$\frac{(25.0-5.0)(0.1)}{1000} = 0.002$$

Volume of the solution is (25.0 + 5.0 =) 30.0 mL.

The concentration of acid left = $\dfrac{0.002\times1000}{30.0} = 0.067\ mol\ L^{-1} = [H_3O^+]$

Hence
$$pH = -\log\ 0.067$$
$$= 1.48$$

Similar calculations can be carried out after addition of each volume of the titre.

On addition of 25.0 mL of the base the solution becomes neutral and its pH is 7.0.

On adding excess $NaOH$, say 25.1 mL,

the moles of excess $NaOH = \dfrac{(25.1-25.0)(0.1)}{1000} = \dfrac{0.01}{1000}$

$$= 1.0\times10^{-5}\ mol\ L^{-1}$$

and $[OH^-] = \dfrac{(1.0\times10^{-5})(1000)}{50.1} = 0.0002\ mol\ L^{-1}$.

Hence $pOH = -\log 0.0002 = 3.70$

And $pH = 14 - 3.70$

$= 10.30$

Similar calculations for addition up to about 50.0 *mL* of the base can be done.

Values of *pH* as calculated when plotted against the volume of *NaOH* solution added yield a curve like the one shown in Figure 16.2

It can be noted that the *pH* changes slowly at first until the molar amount of base added is close to the molar amount of *HCl*, i.e. until the titration is close to the equivalence point. At the equivalence point the pH is 7.0 as the acid is completely neutralized by the base and the solution contains only Na^+ and Cl^- ions.

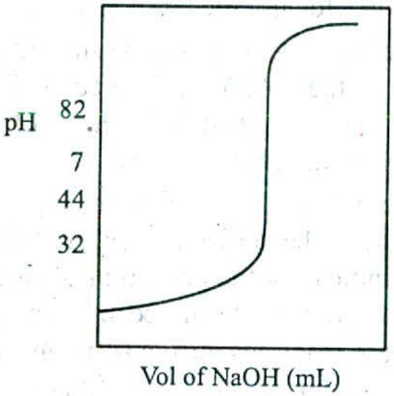


Figure 16.2 Acid-base neutralization curve for strong acid with strong base

However,as the equivalence point is approached the *pH* changes rapidly and the value rises sharply from about 3 to 11 close to the equivalence point. Beyond this point on addition of more *NaOH* the value of *pH* changes slowly. The volume of *NaOH* solution where a sharp rise in the *pH* occurs is the equivalence point.

'The equivalence point of a titration may be found with the help of an indicator ***only if*** *it changes colour in the pH range in the vertical portion of the neutralization curve'.*

In this case the *pH* range in the vertical part is from 3 to 11. The exact range of *pH* depends on the concentration of the acid and base.

It was noted that an indicator changes colour approximately within a $pH = pK_{In} \pm 1$. So for this titration an indicator which has pK_{In} lying between 4 and 10 would be suitable. From Table 16.7 we can see that methyl orange, methyl red, bromothymol blue or phenolphthalein can be used.

16.16 Titration of a Weak Acid with a Strong Base

The titration of 25.0 *mL* of 0.100 $mol\ L^{-1}$ of ethanoic acid with a solution of *NaOH* of concentration 0.10 $mol\ L^{-1}$ may be considered. When no *NaOH* has been added the *pH* of the solution is 2.87. After addition of 20.0 *mL* of the *NaOH* solution,

$$\text{Moles of salt formed} = \frac{20.0\times0.1}{1000} = 0.002.$$

$$\text{Moles of acid remaining} = \frac{(25.0-20.0)(0.1)}{1000} = 0.0005.$$

$$\text{Volume of the solution} = 20.0 + 25.0 = 45.0\ mL$$

$$\text{Hence } [CH_3COOH] = \frac{0.002 \times 1000}{45} = 0.0444\ mol\ L^{-1}$$

$$\text{And } [CH_3COO^-] = \frac{0.0005 \times 1000}{45} = 0.0011\ mol\ L^{-1}$$

The concentration of H^+ ion may be calculated approximately from the relation

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$\text{And} \quad [H^+] = \frac{(K_a)[CH_3COOH]}{[CH3COO^-]}$$

$$= \frac{(1.8 \times 10^{-5})(0.0444)}{0.0011}$$

$$= 7.265 \times 10^{-4}\ mol\ L^{-1}$$

$$pH = 3.14$$

These calculations give only approximate values of H^+ ion concentration because of hydrolysis of CH_3COO^- (*Section 16.21*). When similar calculations are carried out for further additions of *NaOH* solution and the data plotted in a graph, a curve of the type shown in Figure 16.3 is obtained.

Titration curves for titration of a strong acid with a weak base and a weak acid with a weak base are shown in Figures 16.3 and 16.4

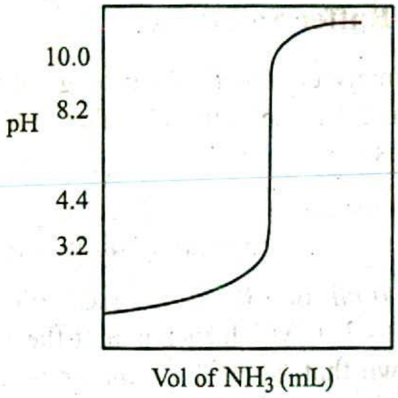


Figure 16.3 Acid – base neutralization curve for strong acid with weak base

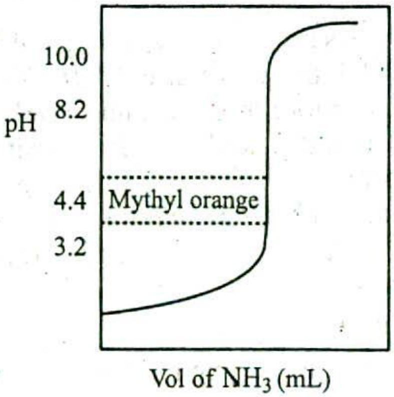


Figure 16.4 Acid – base neutralization curve for weak acid with weak base

Figure 16.5 shows the titration curve for the titration of a weak acid (in the conical flask) with a strong base added from the burette.

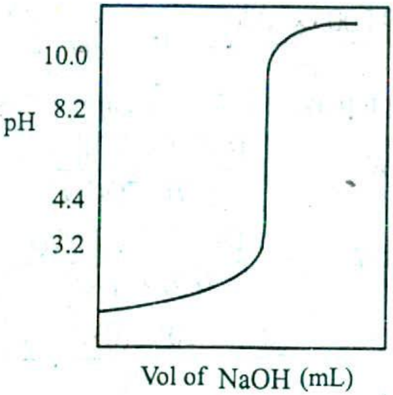


Figure 16.5 Acid – base neutralization curve for weak acid with strong base

16.17 Buffer Solutions

In many chemical and biological processes it is necessary to maintain the *pH* of the medium fairly at constant value. Solutions used for this purpose are known as buffer solutions.

> *'Buffer solution is defined as a solution that resists change in pH upon addition of small quantities of strong acids or strong bases to it'.*

If 1.0 *mL* of 1.0 $mol\ L^{-1}$ *HCl* solution is added to 1 *L* of water the *pH* changes from 7.0 to 3.0, which means that the *pH* changes by 4 units. On the other hand it can be shown that when the same amount of acid is added to 1 *L* of an appropriate buffer solution the *pH* changes only slightly, by 0.1 unit or so.

16.17.1 Uses of buffer solutions

Strict control of *pH* is necessary for many biological systems. For example, blood *pH* is maintained at about 7.4 by a mixture of H_2CO_3 and HCO_3^- and protein – phosphate buffers. A change of more than 0.1 unit of *pH* of blood brings about serious pathological problems. Other body fluids, such as tears, have to be maintained at specific values of *pH* for normal functioning. Buffering action is necessary to do the job. In many analytical procedures *pH* is maintained at optimum value with help of buffers. Buffers have applications in many industrial processes, particularly in pharmaceutical industries.

There are two types of buffer solutions:

(i) A weak acid and its salt with a strong base. For example, a mixture of CH_3COOH and CH_3COONa acts as a buffer. In this case CH_3COONa is a salt of ethanoic acid with *NaOH* which is a strong base. This is an *acid buffer.*

(ii) A weak base and its salt with a strong acid. For example, a mixture of NH_4OH and NH_4Cl acts as a buffer. In this case, NH_4OH is a weak base and NH_4Cl is its salt with HCl which is a strong acid. This is a *basic buffer*.

16.17.2 Mechanism of buffer action

The way in which a buffer solution acts may be illustrated by considering a buffer solution made up of CH_3COOH and CH_3COONa. A buffer solution may be prepared by mixing comparable molar amounts of ethanoic acid and sodium ethanoate in water. In solution we have the following situation:

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

$$CH_3COONa(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

The salt exists completely as ions.

Thus the buffer contains both acid (CH_3COOH) and its conjugate base (CH_3COO^-). When a small quantity of an acid is added the hydrogen ions are removed by the conjugate base CH_3COO^- as follows:

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

Since ethanoic acid is only slightly dissociated and in the form CH_3COOH it does not contribute any H^+ ion, the pH of the resulting solution will remain practically constant. If, however, a strong base is added, the added OH^- ions are neutralized by the reaction with the acid in the buffer,

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

One may also consider that the added OH^- ion reacts with the H^+ ion to produce water. The added OH^- ions are removed and the acid equilibrium shifts to the right to replace the H^+ ions used up.

In either case the effect of the added acid or base is effectively balanced so that the pH of the solution remains approximately constant. Similarly, the mechanism of basic buffers can be explained.

16.17.3 The Henderson-Hasselbalch equation

The pH of an acidic or basic buffer can be calculated by using the Henderson-Hasselbalch equation. The Henderson-Hasselbalch equation can also be used to prepare a buffer solution of specific pH. In order to derive this equation let us consider the pH of a buffer solution containing a weak acid HA and a soluble salt NaA of the weak acid. In solution the dissociation of weak acid HA can be written as

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

The acid dissociation constant K_a is given by

$$K_a = \frac{[H^+]\,[A^-]}{[HA]} \tag{16.41}$$

$$\text{or} \quad [H^+] = \frac{K_a[HA]}{[A^-]} \tag{16.42}$$

Taking logarithm of both sides of equation (16.42) and multiplying by –1 we obtain,

$$-\log\,[H^+] = -\log K_a - \log\frac{[HA]}{[A]} \tag{16.43}$$

or

$$-\log\,[H^+] = -\log K_a + \log\frac{[A^-]}{[HA]} \tag{16.44}$$

or

$$pH = pK_a + \log\frac{[A^-]}{[HA]} \tag{16.44}$$

Equation (16.45) is known as the **Henderson-Hasselbalch equation.**

In this equation *[HA]* can be considered to be equal to the initial concentration of *HA* as this is a weak acid. The added salt further diminishes its dissociation because of the presence of the common ion A^- (*common ion effect*), making it undissociated for all practical purposes. Also $[A^-]$ may be considered to be the concentration of the added salt which is completely in the form of ions, and because the dissociation of the acid being very small A^- ion is contributed almost entirely by the salt *NaA*. Equation (16.45) can then be written as

$$pH = pK_a + \log\frac{[salt]}{[acid]} \tag{16.46}$$

If the concentrations of the salt and acid are equal $pH = pK_a$.

If, however, a buffer is made by mixing a weak base *BOH* and its soluble salt *BCl*, then similar arguments as above lead to

$$pOH = pK_b + \log\frac{[B^+]}{[BOH]} \tag{16.47}$$

We know, $\quad pK_w = pH + pOH$

and $\quad pOH = pK_w - pH$

$$pK_w - pH = pK_b + \log\frac{[B^+]}{[BOH]}$$

or

$$pH = pK_w - pK_b - \log\frac{[B^+]}{[BOH]}$$

or

$$pH = pK_w - pK_b - \log\frac{[salt]}{[base]} \tag{16.48}$$

The *pH* of acidic or basic buffers can be calculated by using equation (16.46) or (16.48) as the case may be.

Example 16.14: Calculate the *pH* of a buffer solution containing 0.10 $mol\ L^{-1}$ ethanoic acid and 0.15 $mol\ L^{-1}$ sodium ethanoate. K_a of ethanoic acid is $1.77 \times 10^{-5}\ mol\ L^{-1}$

Solution: Using equation (16.46) we get,

$$pH = pK_a + log \frac{[salt]}{[acid]}$$

$$= -\ log\ K_a + log \frac{[salt]}{[acid]}$$

$$= 4.75 + \log \frac{[0.15]}{[0.10]}$$

$$pH = 4.75 + 0.18$$

$$= 4.93$$

16.17.4 Examples of buffer action

The effect of addition of a small amount of acid or alkali on the *pH* (= 4.93) of the buffer solution mentioned in example 16.14 will illustrate its buffering action.

(a) Let us calculate the change in *pH* of this buffer when 1.0 ml of 1.0 $mol\ L^{-1}$ *HCl* solution is added to 1.0 *L* of buffer. The number of moles of *HCl* added is

$$\frac{1.0 \times 1.0}{1000} = 0.001$$

This amount of acid will combine with CH_3COO^- ion to form CH_3COOH. Hence the concentration of CH_3COOH increases by 0.001 to 0.101 $mol\ L^{-1}$ and the concentration of CH_3COO^-, i.e. the concentration of salt decreases by 0.001 mol to (0.15 – 0.001 =) 0.149 $mol\ L^{-1}$. Using these values in the equation (16.46) we get

$$pH = pK_a + log \frac{0.149}{0.101}$$

$$= 4.75 + log\ 1.475$$

$$= 4.75 + 0.168$$

$$= 4.92$$

(b) Now let us calculate the change in the *pH* of this buffer when 1.0 *mL* of 1.0 $mol\ L^{-1}$ of *NaOH* solution is added to this buffer. The number of moles of *NaOH* added is

$$\frac{1.0 \times 1.0}{1000} = 0.001$$

This amount will react with CH_3COOH to form water and CH_3COO^-. Hence the concentration of CH_3COOH will decrease by 0.001 to 0.099 $molL^{-1}$ and the concentration of CH_3COO^-, i.e. the concentration of salt increases by 0.001 mol to (0.15 + 0.001 =) 0.151 $mol\ L^{-1}$. Using these values in the equation (16.46) we get

$$pH = pK_a + log\frac{0.151}{0.099}$$

$$= 4.75 + log\ 1.525$$

$$= 4.75 + 0.18$$

$$= 4.93$$

So we see that the addition of 0.001 *mol* of *HCl* or 0.001 *mol NaOH* to 1.0 *L* of the buffer has insignicant effect on its *pH*.

Example 16.15: Calculate the ratio in which sodium ethanoate and ethanoic acid must be mixed in order to give a buffer solution of $pH = 4.90$, given that K_a is 1.80×10^{-5}.

Solution: $pK_a = -log\ K_a = -log\ (1.80 \times 10^{-5}) = 4.75$.

Using Henderson equation

$$4.90 = 4.75 + log\frac{[salt]}{[acid]}$$

$$log\frac{[salt]}{[acid]} = 4.90 - 4.75 = 0.15$$

Hence

$$\frac{[salt]}{[acid]} = 1.42$$

Example 16.16: A buffer solution was prepared by mixing 200 *mL* of 0.60 $mol\ L^{-1}$ of NH_3 and 300 *mL* of 0.30 $mol\ L^{-1}$ NH_4Cl. Calculate the *pH* of the solution. pK_b of ammonia = 4.75.

Solution: First we need to calculate the concentrations of NH_3 and NH_4^+(i.e salt) in the buffer.

No. of moles of NH_3 in 200 *mL* of the mixture = $0.60 mol\ L^{-1} \times 200 \times 10^{-3}\ L$

$= 0.12\ mol$

Since the total volume is 200 + 300 = 500 *mL*

$$[NH_3] = \frac{0.12 \times 1000}{500} = 0.24\ mol\ L^{-1}$$

No. of moles of NH_4Cl in 300 *mL* of the mixture = $0.30\ mol\ L^{-1} \times 300 \times 10^{-3}\ L$

$= 0.090\ mol$

$$[NH_4Cl] = \frac{0.090 \times 1000}{500} = 0.18\ mol\ L^{-1}$$

Using equation (16.48) we get, $pH = pK_w - pK_b - \log \frac{[NH_4^+]}{[NH_3]}$

$$= 14 - 4.75 - \log \frac{[0.18]}{[0.24]}$$

$$= 9.25 + 0.12$$

$$= 9.47$$

Example 16.17: Calculate the mass of sodium formate required to prepare 500 *mL* of a buffer solution of *pH* 4.00 from a solution of formic acid of concentration 0.130 $mol\ L^{-1}$. K_a for formic acid is 1.80×10^{-4}.

Solution: Using equation (16.46) we get,

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

$$pK_a \text{ for formic acid} = -\log (1.80 \times 10^{-4})$$

$$= 3.75$$

So $$4.00 = 3.75 + \log \frac{[salt]}{[acid]}$$

$$\log \frac{[salt]}{[acid]} = 4.00 - 3.75 = 0.25 = \log\ 1.774$$

or $$\frac{[salt]}{[acid]} = 1.774$$

or sodium formate and formic acid have to be mixed in a 500 *mL* solution of formic acid such that the ratio of their concentration is 1.774.

In 500 *mL* of the solution moles of formic acid is 0.130/2 = 0.065

Moles of sodium formate required = 0.065 × 1.774 = 0.1153

Relative formula mass of sodium formate = 60

So mass of sodium formate = 0.1153 × 60 = 6.92 g

16.17.5 Buffer capacity

The two most important characteristics of any buffer solution are its *pH* and *buffer capacity*. The buffer capacity of any buffer gives a measure of the amount of acid or base that the buffer can react with before changing the *pH* of the solution significantly. The buffer capacity depends on the amount of acid and its conjugate base (for acid buffer) or the amount of base and its conjugate acid (for basic buffer). The larger is the amounts of acid and its conjugate base or the base and its conjugate acid needed to change the *pH* of the buffer, the greater is the *buffer capacity*. Mixtures of solutions of the two components, e.g. salt and acid, which will give buffer of high capacity can be found from the neutralization curves for the titration of a weak acid with a strong base or a weak base with a strong acid. In Figure 16.5 the region of the curve left of the vertical portion of the graph where there is a mixture of the salt and acid (or base) indicates the buffer mixture. The region where the slope of the curve is very small gives compositions of the mixtures where the buffer capacity is high. In most cases the buffer capacity is maximum where the concentrations of the salt and acid are equal, i.e. the acid or the base is half neutralized (Figure 16.5).

16.18 Salt Hydrolysis

Salts are ionic compounds produced by the neutralization of acids with bases. Solutions of salts in water are expected to be neutral with a *pH* of 7.0, but in many cases, depending on the acid and base involved in the neutralization reaction, the solution is either acidic or basic. As will be shown below this happens because one or more of the ions which are present in such solutions react with water. Reactions of salts with water are known *salt hydrolysis.*

Salts prepared from strong acids and strong bases are neutral with a $pH = 7.0$. Salts from the neutralization of weak acids by strong bases give alkaline solution of $pH > 7.0$, while salts formed from strong acids and weak bases are acidic in nature, since $pH < 7.0$.

For understanding the phenomenon of salt hydrolysis use may be made of the Bronsted – Lowry concept of acids and bases which suggests that some ions act as acids or bases. For example when HCl gives ions in solution we write

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

Here Cl^- is the conjugate base of the acid HCl. It being a strong acid Cl^- is a very weak base. In CH_3COOH, however, CH_3COO^- is a relatively strong (conjugate) base as the acid is weak.

In a solution of a salt of a strong acid and a strong base, e.g., $NaCl$, Na^+ and Cl^- ions do not react with water as they are very weak acid and weak base respectively. It may be seen that it is the strong conjugate base of a weak acid and the strong conjugate acid of a weak base that hydrolyze, i.e., undergo reaction with water.

The hydrolysis of sodium ethanoate may now be explained. Ethanoate ion, CH_3COO^- react with water as follows:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

As OH^- is a stronger base and CH_3COOH is a weak acid a solution of sodium ethanoate is alkaline.

Another familiar example is that of a solution of Na_2CO_3. CO_3^{2-} is a strong conjugate base of the weak acid H_2CO_3. As a result in aqueous solution CO_3^{2-} ion reacts with water as follows:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

OH^- being a strong base and HCO_3^- a weak acid the solution of Na_2CO_3 is alkaline.

If we consider a solution of NH_4Cl we may note that NH_4^+ will react with water as follows:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq) + H^+(aq)$$

Since H^+ is a strong acid and NH_4OH is a weak base the solution of NH_4Cl is slightly acidic.

If the salt is formed from a weak acid and a weak base, for instance ammonium ethanoate, then both NH_4^+ and CH_3COO^- ions react with water as follows:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq) + H^+(aq)$$

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

The pH of the solution depends on the relative strengths of the acid and the base from which the salt is prepared. The results of these discussions may be summarized as below:

1. *A salt of a strong acid and a strong base* gives a neutral solution because it has no hydrolysable ion. Example, $NaCl$
2. *A salt of a strong acid and a weak base*. The cation of the salt is the conjugate acid of a weak base. It gives an acidic solution as the cation undergoes hydrolysis. Example, NH_4Cl of which NH_4^+ ion is hydrolysable.
3. *A salt of a weak acid and a strong base*. The anion of the salt is the conjugate base of a weak acid. It gives an alkaline solution as the anion undergoes hydrolysis. Example, $NaCN$ of which CN^- ion is hydrolysable.
4. *A salt of a weak acid and a weak base*. The cation is the conjugate acid of a weak base and the anion is the conjugate base of a weak acid. Both ions are hydrolysable. The pH of the solution will depend on the relative strengths of the acid and base from which the salt is made. If the acid is stronger the solution will be acidic, while if the base is stronger the solution will be basic. If the acid and base are of equal strength the solution will have a pH of 7.0.

16.19 The pH of Salt Solutions

As mentioned earlier the solutions of salts made from strong acids and strong bases are neutral with a pH of 7.0. The pH of other types of salts whose solutions are not neutral may be considered separately.

(a) Salt of a weak acid and a strong base

In a solution of the salt of a weak acid HA and a string base the ion A^- undergoes hydrolysis as follows:

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(\mathrm{aq})$$

The equilibrium constant is given by

$$K_h = \frac{[HA]\,[OH^+]}{[A^-]\,[H_2O]} \qquad (16.49)$$

Water is a solvent and is present in large quantities compared to the solute. So the concentration of H_2O is taken as constant, and equation (16.49) becomes

$$K_h = \frac{[HA]\,[OH^-]}{[A^-]} \tag{16.50}$$

The constant K_h is called the ***hydrolysis constant***. It should be noticed that K_h is the base dissociation constant K_b of the base A^-.

Writing the above equation as below

$$K_h = \frac{[HA][OH^-][H^+]}{[A^-][H^+]} \tag{16.51}$$

and using the ionic product of water $\quad K_w = [H^+]\,[OH^-]$

and dissociation constant of the acid HA as $\quad K_a = \dfrac{[H^+][A^-]}{[HA]}$

one can see that

$$K_h = \frac{[HA][OH^-][H^+]}{[A^-][H^+]} = \frac{K_w}{K_a} \tag{16.52}$$

It can be seen from equation (16.49) that one molecule of HA is produced for each OH^- ion ; hence

$$[HA] = [OH^-].$$

Substitution in equation (16.52) yields

$$[OH^-]^2 = \frac{K_w}{K_a}[A^-] \tag{16.53}$$

But from (16. 8)

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

The above two equations combined together gives,

$$\left(\frac{K_w}{[H^+]}\right)^2 = \frac{K_w}{K_a}\left[A^-\right]$$

Or,

$$\left[H^+\right]^2 = \frac{K_w^2\,K_a}{K_w\,[A^-]} = \frac{K_w\,K_a}{\left[A^-\right]}$$

Hence

$$[H^+]^2 = \frac{K_w K_a}{[A^-]}$$

Or

$$[H^+] = \sqrt{\frac{K_w K_a}{[A^-]}} \tag{16.53}$$

Taking logarithms of both sides and changing signs one obtains

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log[A^-] \tag{16.54}$$

Equation (16.54) may be used to calculate the pH of the solution of a salt of a weak acid and strong base if the concentration of the unhydrolyzed fraction of the salt is known, i.e., if the degree of hydrolysis is known. *The degree of hydrolysis is defined as the fraction of the amount of the salt which has undergone hydrolysis.*

If the degree of hydrolysis is α and the original concentration of the salt is c then

$$[HA] = [OH^-] = \alpha \times c$$

and

$$[A^-] = (1 - \alpha)c$$

Substituting in equation (16.52) we have

$$K_h = \frac{K_w}{K_a}$$

$$= \frac{(c\alpha)(c\alpha)}{(1-\alpha)c} = \frac{c\alpha^2}{1-\alpha} \tag{16.55}$$

If the degree of hydrolysis α is quite small then

$$K_h = \frac{K_w}{K_a} = c\,\alpha^2$$

Or

$$\alpha = \sqrt{K_w/cK_a} \tag{16.56}$$

Example 16.18: Calculate the degree of hydrolysis and pH of a 0.10 $mol\ L^{-1}$ $NaCN$ solution at 25°C. The value of K_a of $HCN = 4.9 \times 10^{-10}\ mol\ L^{-1}$.

Solution: Let α be the degree of hydrolysis. Assuming that the degree of hydrolysis is very small (since K_a is very small).

$$\alpha = \sqrt{K_w/cK_a} = \sqrt{\frac{1.0\times10^{-14}}{0.10\times4.9\times10^{-10}}}$$

from which

$$\alpha = 0.014$$

$$[OH^-] = \alpha \times c = (0.014)(0.10) = 1.4 \times 10^{-3}\ mol\ L^{-1}$$

So

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1.4 \times 10^{-3}}$$

$$= 7.15 \times 10^{-12}$$

Hence $pH = -\log [H^+] = 11.15$

Or using equation (16.56)

$$pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log [A^-]$$

$$pK_a = -\log (4.9 \times 10^{-10}) = 9.31 \text{ and } \log [A^-] = -1.01$$

$$pH = 7 + \frac{1}{2}(9.31 - 1.01) = 11.15$$

(b) Salt of a weak base and strong acid

In a solution of a salt of weak base and strong acid the ion B^+ hydrolyzes:

$$B^+(aq) + H_2O(l) \rightleftharpoons BOH(aq) + H^+ (aq) \tag{16.57}$$

The resulting solution is acidic. Similar argument as for the salt of weak acid and strong base leads to the following expressions for K_h and pH:

$$K_h = \frac{K_w}{K_b} = \frac{\alpha^2}{1-\alpha} \tag{16.58}$$

And
$$pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log [B^+] \tag{16.59}$$

Example 16.19: Calculate the degree of hydrolysis and pH of a solution of NH_4Cl of concentration 0.015 $mol\ L^{-1}$. Given, $K_b = 1.80 \times 10^{-5}\ mol\ L^{-1}$.

Solution: If the degree of hydrolysis α is small compared with 1 then from (16.56)

$$K_h = \frac{K_w}{K_b} = c\alpha^2$$

Hence
$$\alpha = \sqrt{\frac{1.0 \times 10^{-14}}{0.915 \times 1.8 \times 10^{-5}}}$$

$$= 1.92 \times 10^{-4}$$

$$[H^+] = c\alpha$$

$$= (0.015)(1.92 \times 10^{-4})$$

$$= 2.88 \times 10^{-6}$$

$$pH = -\log [H^+] = -\log (2.88 \times 10^{-6})$$

$$= 5.54$$

or using equation (16.59) we get,

$$pH = 7 - \frac{1}{2}(-\ log\ K_b + log\ [B^+]\ )$$

$$= 7 - \frac{1}{2}(-\ log\ 1.80 \times 10^{-5} + log\ (0.015))$$

$$= 7 - 1.46$$

$$= 5.54$$

(c) Salt of a weak acid and a weak base

In a solution of a salt of weak acid and weak base both the cation and anion undergo hydrolysis as follows:

$$B^+(aq) + A^-(aq) + H_2O(l) \rightleftharpoons BOH(aq) + HA(aq) \qquad (16.60)$$

The hydrolysis constant will be

$$K_h = \frac{[BOH][HA]}{[B^+][A^-]} \text{ as water is in large quantity} \qquad (16.61)$$

If α is the degree of dissociation $[B^+] = [A^-] = (1-\alpha)\,c$ and $[BOH] = [HA] = \alpha c$ Substitution in the above equation gives

$$K_h = \frac{(\alpha c)(\alpha c)}{[(1-\alpha)c][(1-\alpha)c]}$$

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

$$= \frac{\alpha^2}{(1-\alpha)^2} \qquad (16.62)$$

When α is very small we have $K_h = \alpha^2$

So that, $\alpha = \sqrt{K_h}$ (16.63)

Now equation (16.61) may be written as

$$K_h = \frac{[BOH][HA][H^+][OH^-]}{[B^+][A^-][H^+][OH^-]} \qquad (16.64)$$

Or,

$$K_h = \frac{K_w}{K_a K_b} \qquad (16.65)$$

Hence degree of hydrolysis α is given by

$$\alpha = \sqrt{\frac{K_w}{K_a K_b}} \qquad (16.66)$$

The pH of a solution of such a salt can be determined by use of the following relationship. Considering the dissociation of the acid as

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

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

Hence $$[H^+] = \frac{K_a[HA]}{[A^-]}$$

From hydrolysis of the salt,

$$[HA] = \alpha c$$

and $$[A^-] = (1-\alpha)c$$

$$[H^+] = K_a \frac{\alpha}{1-\alpha} \tag{16.67}$$

When α is very small (for very weak acids) $[H^+] = K_a \times \alpha$ (16.67a)

Substituting the expression for α from equation (16.66) in equation (16.67) we get

$$[H^+] = K_a\sqrt{\frac{K_w}{K_aK_b}}$$

$$= \sqrt{\left(\frac{K_w K_a^2}{K_a K_b}\right)}$$

$$= \sqrt{\left(\frac{K_w K_a}{K_b}\right)} \tag{16.68}$$

Taking logarithm on both sides and multiplying by -1 we obtain,

$$-\log[H^+] = \frac{1}{2}(-\log K_w - \log K_a + \log K_b)$$

or $$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b \tag{16.69}$$

Example 16.20: Calculate the degree of hydrolysis in a solution of ammonium ethanoate and the pH of a solution of the salt of concentration 0.15 $mol\ L^{-1}$. Given $K_a = K_b = 1.8 \times 10^{-5}$.

Solution: As the salt is of a weak acid and weak base equation (16.66) gives,

$$\alpha = \sqrt{\frac{K_w}{K_aK_b}} = \sqrt{\frac{10^{-14}}{(1.8\times10^{-5})^2}} = 5.5\times10^{-3}$$

$$[H^+] = K_a \times \alpha = 1.8\times10^{-5} \times 5.5\times10^{-3}$$
$$= 9.9\times10^{-8}$$

$$pH = -\log[H^+] = -\log(9.9\times10^{-8})$$
$$= 7.00$$

It can be seen that the hydrolysis constant of the salts can be found out by application of the appropriate equations.

Solutions of salts like $Al(NO_3)_3$, $Fe(NO_3)_3$, $FeSO_4$ etc. are acidic due to hydrolysis because the metal hydroxides from which these are prepared are weak bases and the acids are strong ones.

16.20 Amphoteric Electrolytes: Zwitter Ions

There are some substances which under one set of conditions act as base and under another set of conditions act as acid. Such substances are called *amphoteric electrolytes.* Notable among the amphoteric electrolytes are the amino acids. The simplest of the group is glycine which is written as H_2NCH_2COOH. The amino acids can be titrated both with alkalis and with acids, indicating that there are both acidic and basic groups in the molecule. From the known characteristics of the $-NH_2$ and $-COOH$ groups in other organic compounds it was formerly believed that the $-NH_2$ group was the basic group reacting with acid and $-$ COOH group reacted with alkali. From several evidences, such as the fact that these are solids at room temperature, x-ray crystal study of the amino acid crystal, titration in presence of formaldehyde etc., it is now strongly believed that the amino acid should be written as

$$^{+}NH_3.CH_2.COO^{-}$$

The $^{+}NH_3$ group acts as the acid part and the $-COO^{-}$ end acts as the basic part. Such a bipolar molecule is called a *Zwitter-ion.* It should be recalled that the molecule as a whole is neutral. The reaction with a strong acid should be written as

$$^{+}NH_3.CH_2.COO^{-} + H^{+} \rightleftharpoons {}^{+}NH_3.CH_2COOH \tag{16.70}$$

and the reaction with a strong base should be

$$^{+}NH_3.CH_2.COO^{-} + OH^{-} \rightleftharpoons NH_2.CH_2.COO^{-} + H_2O \tag{16.71}$$

Because these are ionic in acidic or basic medium, solutions of such substances are conductors of electricity. If at a certain pH the acid strength and basic strength become equal the particles do not move under an electrical field. That point it is said to be the *isoelectric point.*

QUESTIONS AND PROBLEMS

1. State the definition of acids given by (a) Arrhenius, (b) Bronsted and Lowry and (c) Lewis. Give examples of Lewis acids.
2. What is meant by conjugate acid – base pair? Give two examples.
3. Write the conjugate base of the acids : HNO_3, H_2O, HCO_3^{-}, HNO_2, HSO_4^{-}
4. Write the conjugate acid of the bases : CO_3^{2-}, H_2O, CH_3COOH, HNO_3, OH^{-}
5. Write expressions of the dissociation constants of the following acids and bases: CH_3COOH, NH_4OH, HSO_4^{-}, HCO_3^{-}, $C_2H_5NH_2$, $C_6H_5NH_2$, $H_2PO_4^{-}$
6. Give the definition of pH and pOH. Why is $pH + pOH = 14$ at 298 K?

7. Identify the following as representing acidic, basic or neutral solutions:
   (a) $pH = 3.45$; (b) $pH = 11.80$; (c) $pOH = 6.24$, (d) $pH = 8.54$; (e) $pOH = 4.35$.
   Arrange these solutions in the increasing order of acidity.
8. Calculate the $[H^+]$, $[OH^-]$ and pH of the following solutions:
   (a) 0.001 $mol\ L^{-1}$ HCl; (b) 0.0120 $mol\ L^{-1}$ HNO_3; (c) 0.0042 $mol\ L^{-1}$ $NaOH$;
   (d) 0.0143 $mol\ L^{-1}$ $Ba(OH)_2$; 2.1×10^{-4} $mol\ L^{-1}$ $HClO_4$; (e) 4.8×10^{-4} $mol\ L^{-1}$ KOH
9. Calculate the $[H^+]$, and $[OH^-]$ in a solution having a pH equal to:
   (a) 1.92; (b) 5.75; (c) 7.84; (d) 9.63; (e) 11.73; (f) 12.96; (g) 13.59
10. A 0.12 $mol\ L^{-1}$ solution of a monoprotic acid was observed to have a
    $pH = 1.35$. Calculate the K_a of this acid
11. A weak base was found to have a pH of 9.15 when its concentration is 0.10 $mol\ L^{-1}$. What is the K_b for the base?
12. A solution is prepared by mixing 200 mL of 0.010 $mol\ L^{-1}$ HCl solution and 300 mL of HNO_3 solution of concentration 0.025 $mol\ L^{-1}$. What will be the pH of the resulting solution?
13. To 500 mL of a 0.030 $mol\ L^{-1}$solution of HCl is added 250 mL of a solution of $NaOH$ of concentration 0.015 $mol\ L^{-1}$. Calculate the pH of the resulting solution.
14. 400 mL of a 0.015 $mol\ L^{-1}$ HCl solution is mixed with 600 mL of KOH solution of concentration 0.020 $mol\ L^{-1}$. What is the pH of the resulting mixture?
15. Sketch a titration curve for the titration of 20.0 mL of 0.05 $mol\ L^{-1}NaOH$ solution with HCl solution of concentration 0.10 $mol\ L^{-1}$ until 20.0 mL of the acid solution is added. Suggest a suitable indicator (use Table 16.7) for the titration.
16. Calculate the pH of a 0.0120 $mol\ L^{-1}$ solution of acetic acid. K_a of the acid $= 1.8 \times 10^{-5}$
17. What is the concentration of hydroxide ion in a 0.080 $mol\ L^{-1}$ aqueous solution of methylamine, CH_3NH_2 ? $K_b = 4.4 \times 10^{-4}$. What is the pH of the solution?
18. A chemist wanted to determine the concentration of lactic acid, $CH_3CH(OH)COOH$. He found that the pH of the solution was 2.51.What was the concentration of the solution? The K_a of lactic acid is 1.4×10^{-4}.
19. Calculate the pH of a solution obtained by mixing 35.0 mL of 0.15 $mol\ L^{-1}$ ethanoic acid with 25.0 mL of 0.10 $mol\ L^{-1}$ sodium ethanoate.
20. Define a buffer solution. Using an example of a mixture of ethanoic acid and sodium ethanoate in solution explain how this mixture will act as buffer solution.
21. Calculate the pH of a solution of 0.20 mole of ethanoic acid and 0.40 mole of sodium ethanoate in 1.0 L of solution. pK_a of ethanoic acid = 4.75.
22. A buffer solution is prepared by adding 115 mL of 0.30 $mol\ L^{-1}$ solution of NH_3 to 145 mL of 0.15 $mol\ L^{-1}$ of NH_4NO_3. What is the pH of the final solution?
    K_b of aq. $NH_3 = 1.78 \times 10^{-5}$
23. How many grams of sodium acetate must be added to 2.0 L of 0.10 $mol\ L^{-1}$ acetic acid solution to give a solution that has a pH of 5.00? K_a of the acid $= 1.8 \times 10^{-5}$.
24. What is meant by buffer capacity? What will be the pH of the buffer solution in Example 23 if 2.0 mL of 1.0 $mol\ L^{-1}$ HCl solution is added to it? Ignore the change in volume on addition of HCl solution.

25. For each of the following salts, indicate if the aqueous solution will be acidic, basic or neutral:
(a) Na_2CO_3 ; (b) NH_4NO_3 ; (c) $Fe(NO_3)_3$;(d) $CuSO_4$; (e) $Ca(CN)_2$

26. What is meant by salt hydrolysis? Calculate the *pH* of a 0.0125 $mol\ L^{-1}$ solution of sodium propionate, CH_3CH_2COONa. What is the concentration of propionic acid in the solution?

27. Calculate the OH^- ion concentration and *pH* of a 0.010 solution of sodium cyanide, *NaCN*. Determine the hydrogen ion, CN^- and *HCN* concentrations in this solution. K_a of $HCN = 4.9 \times 10^{-10}$.

28. Sketch a curve for the titration of 25.0 *mL* of 0.10 $mol\ L^{-1}$ ethanoic acid with 0.10 $mol\ L^{-1}$ *NaOH* solution until 40.0 *mL* of *NaOH* has been added.
(a) State what indicator you would use and explain your choice.
(b) Show in the sketch the region where the mixture would act as buffer.
(c) Show in the sketch in which part the buffer capacity will be maximum.
(d) Use the graph to determine the K_a of acetic acid.

29. Blood contains several acid – base systems to keep the *pH* constant at about 7.4. One of the most important buffer system involves carbonic acid and hydrogen carbonate ion. What must the ratio of $[HCO_3^-]$ to $[H_2CO_3]$ to keep the *pH* at 7.4?
K_a of carbonic acid = 4.3×10^{-7}.

30. What is meant by hydrolysis of salts? Calculate the *pH* of the following:
(a) 0.10 $mol\ L^{-1}$ solution of Na_2CO_3, K_a of $H_2CO_3 = 4.3 \times 10^{-7}$;
(b) 0.125 $mol\ L^{-1}$ solution of NH_4Cl; K_b of aqueous ammonia $= 1.78 \times 10^{-5}$;
(c) 0.12 $mol\ L^{-1}$ solution of *NaCN*; K_a of $HCN = = 4.9 \times 10^{-10}$;
(d) 0.20 $mol\ L^{-1}$ solution of NH_3OHCl; K_b of $NH_2OH = 1.1 \times 10^{-8}$.
In each case calculate the degree of hydrolysis.

31. Explain why a solution of an amino acid conducts electricity.
Write notes on: (a) zwitter ion, (b) isoelectric point.

32. Sketch a titration curve for the titration of 25.0 *mL* of a 0.10 $mol\ L^{-1}$ solution of ammonia with 0.10 $mol\ L^{-1}$ solution of *HCl* until 40.0 *mL* has been added. Choose an indicator for this titration and explain your choice

17 SOLUBILITY AND COMPLEX-ION EQUILIBRIA

Equilibria involving weak acids and bases have been discussed in the previous chapter. As indicated many analytical as well as biological processes are dependent on such equilibria. These equilibria exist in solution and the system is homogeneous. Another type of equilibria between slightly soluble compounds and their ions and equilibria involving formation of complex ions will be the subject matter of this chapter. There are many salts which are not completely soluble in water. These salts are what are called sparingly soluble or slightly soluble salts. When placed in water these salts reach an equilibrium between the part that has dissolved and the part which remains undissolved. In the part that dissolves the ions separate from each other and the equilibrium is between the ions in solution and the solid salt. These are examples of *heterogeneous equilibria*, since the components exist in more than one phase. Some sparingly soluble metal hydroxides are also considered in this category.

Some ions in solution are found to form complex ions with neutral molecules like ammonia or an excess of one of the ions and in all such cases equilibrium is found to exist between the complex ion and the components from which the complex is formed.

Both these types of equilibria are of importance in analytical and other fields.

17.1 Solubility and Solubility Product

When an ionic compound dissolves in water the ions get separated. If one keeps on adding more of the solute a situation is reached when no more solute can be dissolved. At that position the solution is said to be saturated. A saturated solution in contact with solid solute constitutes an equilibrium system. This has been shown to be a dynamic equilibrium -- ions from the solution being deposited as solid solute and solid solute moving to the solution in the form of separated ions, both proceeding at the same rate so that there is no change in concentration. The equilibrium can be shown as,

$$\text{Solute (in solution)} \rightleftharpoons \text{Solute (solid)}$$

The concentration of the saturated solution is its solubility. This is expressed as g L–1 or mol L–1. As long as the temperature is constant and no other compound is added the concentration of the solution remains constant.

When a sparingly soluble solute, say BaSO4, is dissolved in water the amount of solute in the solution is very little and the following equilibrium is established.

$$BaSO_4\,(s) + aq \rightleftharpoons Ba^{2+}\,(aq) + SO_4^{2-}\,(aq)$$

An equilibrium constant for this equilibrium can be written as below:

$$K_{eq} = \frac{[Ba^{2+}][SO_4^{2-}]}{BaSO_4} \tag{17.1}$$

Since $BaSO_4$ is in the solid state its concentration is taken as unity and we obtain

$$K_{eq} = [Ba^{2+}][SO_4^{2-}] = K_{sp} \tag{17.2}$$

This equilibrium constant is named *solubility product* and is represented by the symbol K_{sp}.

In general in a saturated solution of a sparingly soluble salt M_xA_y the following equilibrium is established:

$$M_xA_y \rightleftharpoons xM^{y+} + yA^{x-} \tag{17.3}$$

The thermodynamic equilibrium constant for this equilibrium is

$$K = \frac{\left(a_{M^{y+}}\right)^x \left(a_{A^{x-}}\right)^y}{\left(a_{M_xA_y}\right)} \tag{17.4}$$

Since the activity of the pure solid phase is taken as unity, the above expression reduces to

$$K_{sp} = \left(a_{M^{y+}}\right)^x \left(a_{A^{x-}}\right)^y \tag{17.5}$$

Since the salts are sparingly soluble the solutions are dilute. For all practical purposes the activities may be replaced by concentrations and equation (17.5) takes the form

$$K_{sp} = \left(c_{M^{y+}}\right)^x \left(c_{A^{x-}}\right)^y \tag{17.5a}$$

For a sparingly soluble salt the solubility product, K_{sp}, of a salt may, therefore, be defined as:

The solubility product is the product of the molar concentration of the constituent ions, each raised to the power equal to its co-efficient in the stoichiometric equation.

For example, silver chromate dissociates as follows:

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

Hence K_{sp} of silver chromate = $[Ag^+]^2[CrO_4^{2-}]$.

Calcium fluoride, CaF_2, ionizes as below:

$$CaF_2(s) \rightleftharpoons Ca^{++}(aq) + 2F^-(aq)$$

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$$\text{and} \quad K_{sp} \text{ of } CaF_2 = [Ca^{++}][F^-]^2$$

$Ca_3(PO_4)_2$ ionizes as below:

$$Ca_3(PO_4)_2\,(s) \rightleftharpoons 3\,Ca^{2+}\,(aq) + 2\,PO_4^{3-}(aq)$$

and K_{sp} *of* $Ca_3(PO_4)_2 = [Ca^{2+}]^3[PO_4^{3-}]^2$

In calculating the solubility products the concentrations of ions are expressed in *mol* L^{-1}. Like any equilibrium constant *solubility product,* K_{sp}*, depends on the temperature and remains constant even if other salts are added to the solution.* The solubility products of some compounds are given in Table 17.1

Table 17.1 Solubility product of some compounds at 25°C

Compound	K_{sp}	Compound	K_{sp}
$Al(OH)_3$	4.6×10^{-33}	$Mg(OH)_2$	1.8×10^{-11}
$BaCO_3$	8.1×10^{-9}	$Mn(OH)_2$	4.5×10^{-14}
$BaCrO_4$	1.2×10^{-10}	MnS	1.4×10^{-15}
BaF_2	1.0×10^{-6}	Hg_2Cl_2	1.3×10^{-18}
$BaSO_4$	1.1×10^{-10}	HgS	1.6×10^{-52}
CdS	1.4×10^{-28}	NiS	3.0×10^{-21}
$CaCO_3$	3.8×10^{-9}	$AgC_2H_3O_2$	2.3×10^{-3}
CaF_2	4.0×10^{-11}	Ag_2CO_3	8.2×10^{-12}
$CaSO_4$	2.4×10^{-4}	$AgCl$	1.8×10^{-10}
$Ca_3(PO_4)_2$	1.0×10^{-26}	$AgBr$	5.0×10^{-13}
CuS	6.0×10^{-36}	AgI	8.5×10^{-17}
$Cu(OH)_2$	2.6×10^{-19}	Ag_2CrO_4	1.1×10^{-12}
$Fe(OH)_2$	8.0×10^{-16}	$AgCN$	1.6×10^{-14}
$Fe(OH)_3$	2.6×10^{-39}	Ag_2S	6.0×10^{-50}
FeS	6.0×10^{-18}	$Sn(OH)_2$	5.0×10^{-26}
$PbCl_2$	1.6×10^{-5}	SnS	1.0×10^{-26}
$PbCrO_4$	1.8×10^{-14}	$SrCO_3$	9.3×10^{-10}
$PbSO_4$	1.7×10^{-8}	$SrSO_4$	2.5×10^{-7}
PbS	2.5×10^{-27}	$Zn(OH)_2$	2.1×10^{-16}
PbI_2	6.9×10^{-9}	ZnS	1.2×10^{-23}

17.1.1 Calculation of solubility product from solubility data

The solubility product of a compound can be calculated from solubility data. This will be explained with the help of few worked out examples.

Example 17.1: The solubility of silver chloride, $AgCl$, is $1.92 \times 10^{-3}\ g\ L^{-1}$ at 25 °C. Calculate the solubility product of $AgCl$ at this temperature.

Solution: In solution $AgCl\,(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$$\text{Solubility in } mol\ L^{-1} = \frac{1.92\times10^{-3}}{143.5} = 1.34\times10^{-5}$$

{relative formula mass of $AgCl = 143.5$}

The concentration of each of the ions is equal to the solubility of the salt.

$$\begin{aligned}[Ag^+] &= [Cl^-] = 1.34\times10^{-5}\\ K_{sp} &= [Ag^+]\,[Cl^-] = (1.34\times10^{-5})^2\\ &= 1.8\times10^{-10}\end{aligned}$$

Example 17.2: At 25°C the solubility of lead iodide, PbI_2, is found to be $1.2\times10^{-3}\ mol\ L^{-1}$. Calculate the solubility product, K_{sp}, of lead iodide.

Solution: In solution $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$

The concentration, i.e. solubility, of the salt is equal to the concentration of Pb^{2+} ions. It can be seen that the concentration of iodide ion, I^-, is double that of lead ion, Pb^{2+}

$$\begin{aligned}[Pb^{2+}] &= 1.2\times10^{-3}\ mol\ L^{-1}\\ [I^-] &= 2\,[Pb^{2+}] = 2\times1.2\times10^{-3}\\ &= 2.4\times10^{-3}\ mol\ L^{-1}\\ K_{sp} &= [Pb^{2+}]\,[I^-]^2 = (1.2\times10^{-3})(2.4\times10^{-3})^2\\ &= 6.9\times10^{-9}\end{aligned}$$

Example 17.3: The solubility of calcium phosphate, $Ca_3(PO_4)_2$, is $2.47\times10^{-6}\ mol\ L^{-1}$ at 25°C. Calculate the solubility product of calcium phosphate.

Solution: In solution $Ca_3(PO_4)_2\,(s) \rightleftharpoons 3\,Ca^{2+}(aq) + 2\,PO_4^{3-}(aq)$

$[Ca^{2+}]$ is equal to 3 times the solubility of the salt and $[PO_4^{3-}]$ is 2 times the solubility of the salt.

$$\begin{aligned}[Ca^{2+}] &= 3\times2.47\times10^{-6}\ mol\ L^{-1} = 7.41\times10^{-6}\ mol\ L^{-1}\\ \text{and}\quad [PO_4^{3-}] &= 2\times2.47\times10^{-6}\ mol\ L^{-1} = 4.94\times10^{-6}\ mol\ L^{-1}\\ K_{sp} &= [Ca^{2+}]^3[PO_4^{3-}]^2 = (7.41\times10^{-6})^3\,(4.94\times10^{-6})^2\\ &= 9.93\times10^{-27}\end{aligned}$$

17.1.2 Calculation of solubility from K_{sp} values

Alternatively, the solubility can be calculated from K_{sp} data. Few examples are given below:

Example 17.4: The K_{sp} of $BaSO_4$ at 25°C is 1.1×10^{-10}. Calculate the solubility of $BaSO_4$ at this temperature.

Solution: In solution $BaSO_4\,(s) \rightleftharpoons Ba^{2+}\,(aq) + SO_4^{2-}\,(aq)$

Since one formula unit of $BaSO_4$ gives one Ba^{2+} ion and one SO_4^{2-} ion, we get

$$[Ba^{2+}] = [SO_4^{2-}]$$

The solubility of the salt is the same as the concentration of each of the ions.
Let concentration of each of these ions be $x\ mol\ L^{-1}$

$$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}] = x^2 = 1.1\times10^{-10}$$

Hence solubility $x=\sqrt{1.1\times10^{-10}} = 1.05\times10^{-5}\ mol\ L^{-1}$

Example 17.5: The solubility product of silver chromate, Ag_2CrO_4, at 25°C is 1.1×10^{-12}. Calculate its solubility at this temperature.

Solution: In solution $Ag_2CrO_4\,(s) \rightleftharpoons 2Ag^{+}(aq) + CrO_4^{2-}\,(aq)$

It can be seen that the concentration of CrO_4^{2-} ion is equal to the solubility of Ag_2CrO_4 as one formula unit of the salt gives one CrO_4^{2-} ion. The concentration of Ag^+ ion is twice that of CrO_4^{2-}.

Let $[CrO_4^{2-}] = x\ mol\ L^{-1}$

Then $[Ag^+] = 2x\ mol\ L^{-1}$

$$K_{sp} = [Ag^+]^2\,[CrO_4^{2-}] = (2x)^2.\,x$$
$$= 4x^3 = 1.1\times10^{-12}$$

Hence, $x = 6.5\times10^{-5}\ mol\ L^{-1}$

17.2 Solubility and Common Ion Effect

It has been shown (*Section 16.12*) that the dissociation of a weak acid is depressed when an electrolyte with an ion common to the ions formed by the acid is added to its solution. This happens because the added ion shifts the equilibrium to the side of the undissociated acid. A similar situation arises when an electrolyte with an ion common to a sparingly soluble salt is added to the saturated solution of the salt. The addition of the electrolyte decreases the solubility of the sparingly soluble salt. For example, if to a saturated solution of Ag_2CrO_4 some $AgNO_3$ is added the solubility of Ag_2CrO_4 decreases. The effect, as in the case of weak acid, is known as *the common ion effect* discussed in *Section 16.12*. Let us consider the equilibrium condition for a saturated solution of *Pb(II)* chromate:

$$PbCrO_4(s) + \mathrm{aq} \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}\,(\mathrm{aq})$$

The K_{sp} for this ionic equilibrium has been found to be 1.8×10^{-14} at 25^0C. At a particular temperature, the K_{sp} of this equilibrium depends only on the product of the concentrations of the constituent ions, i.e. $[Pb^{2+}][CrO_4^{2-}]$. If, however, the concentration of either of the ions is increased at equilibrium, the concentration of the other must decrease correspondingly to maintain the constant value of K_{sp}. Suppose we add a soluble salt Na_2CrO_4 to the saturated solution of $PbCrO_4(s)$. As a result the concentration of the common ion CrO_4^{2-} increases in the solution, and a portion of it will react with Pb^{2+} to form more solid $PbCrO_4(s)$. The equilibrium will, therefore, shift to the left as shown below:

$$PbCrO_4(s) + aq) \quad \rightleftharpoons \quad Pb^{2+}(aq) + CrO_4^{2-}\text{(aq)}$$

In effect the solubility of $PbCrO_4(s)$ will be reduced. The same conclusions can be drawn if, in stead of Na_2CrO_4, we add a soluble lead salt $Pb(NO_3)_2$. The added Pb^{2+} ions will combine with some CrO_4^{2-} (aq) to decrease the amount of dissolved $PbCrO_4$.

Example 17.6: The solubility of $Mg(OH)_2$ in pure water at 15°C is 1.3×10^{-4} *mol* L^{-1}. What will be its solubility in 0.05 *mol* L^{-1} *NaOH*? The solubility product of $Mg(OH)_2$ is 1.8×10^{-11}.

Solution: Let x = solubility of $Mg(OH)_2$ in 0.05 *mol* L^{-1} *NaOH*. x *mol* L^{-1} of $Mg(OH)_2$ in solution will give x *mol* L^{-1} of Mg^{2+} ions and $2x$ *mol* L^{-1} of OH^- ions. Since the solution has 0.05 *mol* L^{-1} of OH^- ions from *NaOH*, the equilibrium concentrations are

$$[Mg^{2+}] = x \text{ mol } L^{-1} \quad \text{and} \quad [OH^-] = (2x + 0.05) \text{ mol } L^{-1}$$

$2x$ may be considered too small compared to 0.05. So one can write

$$[OH^-] \approx 0.05 \text{ mol } L^{-1}$$

So that
$$[Mg^{2+}]\,[OH^-]^2 = x\ (0.05)^2 = 1.8 \times 10^{-11}$$

Hence
$$x = \frac{1.8\times10^{-11}}{(0.05)^2} = 7.2 \times 10^{-9} \text{ mol } L^{-1}$$

That is, the solubility of $Mg(OH)_2$ has decreased from 1.3×10^{-4} *mol* L^{-1} to 7.2×10^{-9} *mol* L^{-1} in presence of 0.05 *mol* L^{-1} *NaOH*.

Example 17.7: Calculate the solubility of PbI_2 in *mol* L^{-1} in a $Pb(NO_3)_2$ solution of concentration 0.10 *mol* L^{-1}. The K_{sp} of lead iodide = 6.9×10^{-9}.

Solution: In the solution of $Pb(NO_3)_2$ the concentration of Pb^{2+}, i.e.

$$[Pb^{2+}] = 0.10 \text{ mol } L^{-1}.$$

In this solution let the solubility of PbI_2 be x *mol* L^{-1}. The contribution of PbI_2 to the total concentration of Pb^{2+} ions will be x *mol* L^{-1} and. Hence in presence of $Pb(NO_3)_2$ the concentration of Pb^{2+} ion, $[Pb^{2+}] = (0.10 + x)\ mol\ L^{-1}$ the concentration of I^- ion, $[I^-] = 2x\ mol\ L^{-1}$.

$$K_{sp} \text{ of } PbI_2 = [Pb^{2+}][I^-]^2 = (0.10 + x)(2x)^2 = 6.9 \times 10^{-9}$$

As the solubility decreases in presence of a common ion x can be considered negligible in comparison to 0.10. With this assumption we get

$$(4x^2)(0.10) = 6.9 \times 10^{-9}$$

$$4x^2 = 6.9 \times 10^{-8}$$

Hence $x = 1.31 \times 10^{-4}$

The solubility of PbI_2 in the solution of $Pb(NO_3)_2$ is $1.31 \times 10^{-4}\ mol\ L^{-1}$

17.3 Effect of pH on Solubility

When one or more of the ions in a solubility equilibrium is derived from a weak acid or a weak base, the solubility of the compound is profoundly affected by *pH*. For example let us consider the case of $Mg(OH)_2$. The solubility equilibrium for this hydroxide is

$$Mg(OH)_2 + aq \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

The value of K_{sp} for $Mg(OH)_2$ is 1.8×10^{-11}. Suppose that solid $Mg(OH)_2$ is placed in a buffer solution of $pH = 9$. The solution has a pOH of 5, i.e. in the solution $[OH^-] = 1 \times 10^{-5}$. Inserting this value of $[OH^-]$ in the expression for the solubility product

$$K_{sp} = [Mg^{2+}][OH^-]^2 = 1.8 \times 10^{-11}$$

$$[Mg^{2+}](1 \times 10^{-5})^2 = 1.8 \times 10^{-11}$$

$$[Mg^{2+}] = 1.8 \times 10^{-1} = 0.18\ mol\ L^{-1}$$

Thus $Mg(OH)_2$ is quite soluble in slightly alkaline solution. If the solution was made more acidic the $[OH^-]$ will decrease and the solubility will increase, because the $[Mg^{2+}]$ has to increase in order to maintain equilibrium.

On the contrary, addition of H_3O^+ to a saturated solution of a compound with an anion of strong acid, will have no effect on the equilibrium position. As an example, let us consider the following equilibrium:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

Here, Cl^- ion, a conjugate base of a strong acid, HCl, can co-exist in solution with high H_3O^+. The Cl^- ion does not leave the solution, so equilibrium position is not effected.

17.3 Predicting Precipitation

It is known that when a solution of silver nitrate is added to a solution of sodium chloride or any other chloride a precipitate of silver chloride is formed. In fact this is a test for the presence of chloride ion in solution. Similarly the presence of sulphate ion in a solution is indicated by the formation of precipitate on addition of barium chloride solution to the test solution. It has been found, however, that if the solutions are extremely dilute precipitation may not occur. The solubility product value of the sparingly salt which forms the precipitate may be used to predict whether precipitation will occur or not.

Suppose, for example, we want to find out if a precipitate will form when a solution of lead nitrate of a certain concentration will form a precipitate of lead sulphate when a solution of sodium sulphate is added to it. First of all we have to consider the equilibrium

$$PbSO_4\,(s) + aq \rightleftharpoons Pb^{2+(}aq) + SO_4^{2-}(aq)$$

The solubility product of lead sulphate is given by

$$K_{sp} = [Pb^{2+}]\,[SO_4^{2-}] = 1.7 \times 10^{-8} \quad \text{at } 25^\circ\text{C}$$

In a solution of lead sulphate as long as the quantity on the right hand side of the solubility product expression, i.e. $[Pb^{2+}]\,[SO_4^{2-}]$ is less than 1.7×10^{-8} there will be no precipitation. If $[Pb^{2+}][SO_4^{2-}]$ is equal to or greater than $K_{sp} = 1.7 \times 10^{-8}$ precipitation occurs.

For any sparingly soluble salt the expression written for K_{sp} is also known as the *reaction quotient or ion product*. For example, for $Mg(OH)_2$ the reaction quotient is $[Mg^{2+}][OH^-]^2$ and for $Ca_3(PO_4)_2$ the reaction quotient is $[Ca^{2+}]^3[PO_4^{3-}]^2$. If the reaction quotient, which is designated as Q_c, is less than K_{sp} there will be no precipitation. If, however, Q_c is equal to or greater that K_{sp} precipitation occurs.

Example 17.8: 0.015 g of $CaCl_2$ is dissolved in water to make one litre of solution. To this is added 0.010 g of NaF. Will there be a precipitation of CaF_2? CaF_2 is a sparingly soluble salt and its K_{sp} is 4.0×10^{-11}.

Solution: RFM of $CaCl_2 = 111\ g\ mol^{-1}$ and RFM of $NaF = 42\ g\ mol^{-1}$

$$[Ca^{2+}] \text{ ion in the solution } = \frac{0.015}{111} = 1.35 \times 10^{-4}\ mol\ L^{-1}$$

$$[F^-] \text{ ion in the solution } = \frac{0.010}{42} = 2.38 \times 10^{-4}\ mol\ L^{-1}$$

$$Q_c \text{ for } CaF_2 = [Ca^{2+}][F^-]^2 = (1.35 \times 10^{-4})\,(2.38 \times 10^{-4})^2$$

$$= 7.65 \times 10^{-12}$$

The value of Q_c is less than K_{sp} (4.0×10^{-11}). So there will be no precipitation.
If the concentration of NaF is raised to 6.0×10^{-4} *mol L* $^{-1}$ then Q_c will exceed K_{sp} and precipitation will occur.

In general

If	$Q_c > K_{sp}$	*precipitation occurs*
Until	$Q_c = K_{sp}$	*faint precipitation occurs*
But if	$Q_c < K_{sp}$	*precipitation does not occur*

Example 17.9: 50.0 *mL* of 0.0010 *mol* $L^{-1}$of $BaCl_2$ solution is added to 50.0 *mL* of Na_2SO_4 solution of concentration 0.00010 *mol* L^{-1}. Will any precipitation be seen? The K_{sp} of $BaSO_4$ is 1.1×10^{-10}.

Solution: Moles of Ba^{2+} in the 50.0 *mL* $BaCl_2$ solution = $\frac{0.0010 \times 50.0}{1000} = 5 \times 10^{-5}$

Moles of SO_4^{2-} in 50.0 *mL* of Na_2SO_4 solution $= \frac{0.00010 \times 50}{1000} = 5 \times 10^{-6}$

Total volume of solution = 50.0 *mL* + 50.0 *mL* = 100.0 *mL* = 0.1 *L*

$$[Ba^{2+}] = \frac{5 \times 10^{-5}}{0.1} = 5 \times 10^{-4} \ mol\ L^{-1}$$

$$[SO_4^{2-}] = \frac{5 \times 10^{-6}}{0.1} = 5 \times 10^{-5} \ mol\ L^{-1}$$

The ion product, $Q_c = [Ba^{2+}][SO_4^{2-}] = (5 \times 10^{-4})(5 \times 10^{-5}) = 2.5 \times 10^{-8}$
This is greater than K_{sp}. Hence precipitation will take place.

17.4 Applications of Solubility Product Principle

Qualitative analysis is mainly based on precipitating out the metal ions from a solution by the addition of a suitable reagent. A salt will be precipitated if the conditions are created such that Q_c values exceed their solubility products. For example, metal ions in Group II of the general analytical Table are precipitated as sulphide by passing H_2S gas through the acidic solution of their salts.

As the solubility products of the sulphides of these metals are very low their sulphides are precipitated most easily, whereas those of the other metals remain in solution under the condition created.

Example 17.10: What will be the maximum concentration of Cd^{2+} ions and Mn^{2+} ions that will remain in solution after precipitation by excess H_2S in 0.25 *mol* L^{-1} HCl? Solubility products of CdS and MnS are 1.4×10^{-28} and 1.4×10^{-15} respectively and $[S^{2-}]$ in the solution is 1.7×10^{-22} *mol* L^{-1}.

Solution: In a solution containing S^{2-} of concentration 1.7×10^{-22} $mol\ L^{-1}$

$$[Cd^{2+}] = \frac{1.4 \times 10^{-28}}{1.3 \times 10^{-8}} \qquad \text{as } [Cd^{2+}][S^{2-}] = 1.4 \times 10^{-28}$$

$$= 1.1 \times 10^{-20}\ mol\ L^{-1}$$

while

$$[Mn^{2+}] = \frac{1.4 \times 10^{-15}}{1.3 \times 10^{-8}} \qquad \text{as } [Mn^{2+}][S^{2-}] = 1.4 \times 10^{-15}$$

$$= 1.1 \times 10^{-7}\ mol\ L^{-1}$$

It may be seen that the concentration of Cd^{2+}ion is practically nil compared to the concentration of Mn^{2+} ions, i.e., Cd^{2+} will be almost completely precipitated out on passing H_2S in acidic solution while Mn^{2+} will remain in solution.

17.5 Equilibria of Complex Ions

Most transition elements and some non-transition metals are able to combine with neutral molecules or ions to form complex species. In many cases complex ions are formed. Examples are $Ag(NH_3)_2^+$, $Cu(NH_3)_4{}^{2+}$, HgI_4^- , $Zn(NH_3)_4^{2+}$. The formation of complexes increases the solubility of certain sparingly soluble salts.. For example, $AgCl$ dissolves in excess ammonia solution, $Cu(OH)_2$ is easily soluble in excess ammonia solution, mercuric iodide dissolves in excess potassium iodide solution, $Zn(OH)_2$ dissolves in excess ammonia. As the metal ions form part of an anion or cation they lose their individual property and cannot usually be detected by qualitative tests, particularly if the complex ion is a stable one.

In a solution containing the complex ion there is an equilibrium between the complex ion and the simple ions or molecules. Thus

$$Ag(NH_3)_2^+ + \quad (aq) \rightleftharpoons Ag^+\ (aq) + 2NH_3(aq)$$

and the equilibrium constant, using concentration is

$$K_{inst} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)]_2^+} \tag{17.6}$$

This equilibrium represents the dissociation of the complex and the constant is called the ***instability constant***. The reciprocal of K_{inst} i.e., the equilibrium constant of the reaction

$$Ag^+ + 2NH_3 \rightleftharpoons Ag\ (NH_3)_2^+$$

is called the ***stability constant or formation constant***. The stability constant gives a measure of the stability of the complex, since the higher its value, the greater the degree of formation, and hence the greater the stability of the complex ion.

Example 17.11: Calculate the concentration of Ag^+ present in a solution at equilibrium when concentrated ammonia is added to a 0.10 $mol\ L^{-1}$ solution of $AgNO_3$ until the ammonia concentration is 0.20 $mol\ L^{-1}$.

The instability constant of $Ag\,(NH_3)_2^+ = 5.8 \times 10^{-8}$

Solution: If we consider the equilibrium

$$Ag(NH_3)_2{}^+ + \quad (aq) \rightleftharpoons Ag^+\,(aq) + 2NH_3(aq)$$

We can write

$$K_{inst} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)]_2^+} = 5.8 \times 10^{-8}$$

This value is very small so that the stability constant is very high. If it is assumed that all of the Ag^+ forms the complex, the concentration of the complex ion $Ag(NH_3)_2^+$ will be 0.01 $mol\ L^{-1}$. Now suppose x moles in 1.0 L dissociates at equilibrium. Then $2x$ moles of NH_3 will be formed and we can write as follows:

	$Ag(NH_3)_2^+ + \quad (aq) \rightleftharpoons$	$Ag^+\,(aq)$ +	$2NH_3(aq)$
Initial concentration	0.01	0	0.20
Equilibrium concentration	$(0.01 - x)$	x	$(0.20 + 2x)$

Since the stability of the complex is high the value of x may be considered very small compared to 0.01 or 0.20. Substituting in the equilibrium expression, we obtain

$$\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)]_2^+} = \frac{(x)\,(0.20)^2}{(0.01)^2} = 5.8 \times 10^{-8}$$

Solving for x we get

$$[Ag^+] = x = 1.4 \times 10^{-8}$$

We can see that because of the formation of the complex ion the concentration of Ag^+ in the solution is very small.

The ability of metal ions to form complexes has important applications in biology, chemical analysis, photography, metallurgy and other areas.

QUESTIONS AND PROBLEMS

1. The solubility of $PbCO_3$ at 25 °C is 1.8×10^{-7} $mol\ L^{-1}$. What is K_{sp} for $PbCO_3$?
2. The solubility of MgF_2 at 298 K is 7.6×10^{-2} $g\ L^{-1}$. Calculate its solubility product.
3. The pH of a saturated solution of $Ni(OH)_2$ is 8.83. Calculate the K_{sp} for $Ni(OH)_2$.
4. Using the data in Table 17.1 calculate the solubility of the following compounds in water at 25°C:
   (i) PbS;
   (ii) $Fe(OH)_3$;
   (iii) Hg_2Cl_2 (which gives Hg_2^{2+} and $2Cl^-$ ions);
   (iv)Ag_2CO_3 .
5. Calculate the pH of a saturated solution of $Cu(OH)_2$.
6. What volume of saturated solution of HgS contains a single Hg^{2+} ion?
7. Calculate the solubility of $CaCO_3$ in $mol\ L^{-1}$ *in* a solution of 0.025 $mol\ L^{-1}$ Na_2CO_3.
8. How many moles of Ag_2CrO_4 will dissolve in 1.0 L of 0.10 $mol\ L^{-1}$ $AgNO_3$?
9. How many moles of Ag_2CrO_4 will dissolve in 1.0 L of 0.10 $mol\ L^{-1}$ Na_2CrO_4?
10. Would a precipitate form in the following solutions?
    (a) 5.0×10^{-2} mol of $AgNO_3$ and 1.0×10^{-3} mol of $NaC_2H_3O_2$ dissolved in 1.0 L of solution.
    (b) 1.0×10^{-2} mol of $Ba(NO_3)_2$ and 2.0×10^{-2} mol NaF dissolved in 1.0 L of solution.
    (c) 500 mL of 1.5×10^{-2} $CaCl_2$ and 250 mL of 0.10 $mol\ L^{-1}$ Na_2SO_4 are mixed to give a solution of final volume 750 mL.
11. Which will precipitate first when solid Na_2CrO_4 is gradually added to a solution containing 0.010 $mol\ L^{-1}$ Pb^{2+} ion and 0.010 $mol\ L^{-1}$ Ba^{2+} ?
12. The formation constant of $Ag(NH_3)_2{}^+$ is 1.7×10^7 . What is the concentration of Ag^+ in a solution that is initially 0.15 $mol\ L^{-1}$ in Ag^+ and 1.0 $mol\ L^{-1}$ in NH_3?

18 SURFACE CHEMISTRY

The chemistry of surfaces is an important branch of physical sciences. The study of the chemistry of surfaces and its associated phenomenon play important roles in many industrial and biological fields. One such example is in the field of heterogeneous catalysis. Surfaces of solids or liquids have certain properties and characteristics that make them different from the bulk of matter. Although there is no chemical distinction between the molecules or atoms on the surface and the molecules or atoms in the bulk, energy considerations lead to quite dissimilar properties. In this chapter we will discuss these properties.

18.1 The Nature of Surfaces

The atoms or molecules on a surface of a liquid or solid are subjected to *unbalanced forces* due to their positions. A molecule in the interior of a solid body or a liquid experiences *intermolecular force* of equal magnitude in all directions. The resultant force on this particular molecule is, therefore, zero. But the condition of the molecules on the surface is different as they are pulled downwards and sideways but no *forces** act on them from above as shown in Figure 18.1. As a result there remains a residual field of force acting only on the surface. These unbalanced forces on the surface molecules give rise to surface tension in liquids which has been discussed in *Section* 3.7.

In solids, due to rather fixed positions of the molecules or atoms, the exact nature and magnitude of the unbalanced forces are different from those in liquids, thus imparting some special properties to solid surfaces. The unsatisfied combining capacities associated with surface atoms or molecules render them particularly reactive towards any other material body, specially liquids and gases, when the latter happen to come near the field of force. At the first available opportunity these surface atoms or molecules will try to satisfy the *'unsaturation'* by *'capturing'* other molecules or atoms.

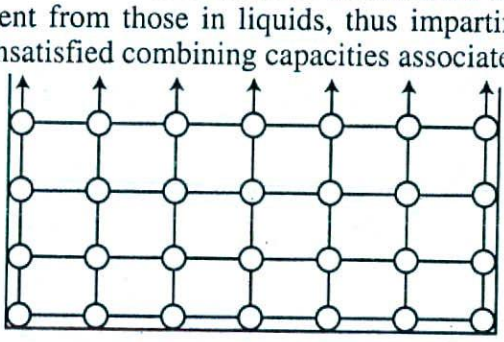

Figure 18.1 Surface unsaturation

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* *The term 'force' is vague; it includes forces of physical nature like van der Waals force and forces of chemical origin involving valence bonds and forces involved in intermetallic bonds; in addition other forces are involved. We shall, however, use the vague term 'force' for the sake of simplicity.*

The extent of such *capture or adsorption* will depend on, (i) the nature of the surface forces, (ii) the nature of the molecules captured and (iii) the temperature. The temperature of the system will have an effect since the *'escaping tendency'* of the captured molecules will be greatly influenced by the thermal motion. The concentration or the pressure of a gas will modify the amount of adsorbed gas because of the change in the number of molecules per unit volume with change of pressure. If the adsorption is exothermic (i.e., evolution of heat) rise of temperature will reduce the amount of adsorbed species as in physical adsorption. If, however, there is chemical interaction, rise of temperature will increase adsorption. This is according to the principle of mobile equilibrium as discussed in *Section 10.12*. In practice both the processes are exothermic but the quantity of heat involved varies widely. As a matter of fact, this thermal effect is utilized to differentiate between different types of adsorption.

18.2 Definition of Terms

Adsorption: Adsorption on the surface of a material may be defined *'as a process in which the concentration of a chemical species is greater on the surface than in the bulk resulting from inelastic collision suffered by molecules on the surface'*. The species that is adsorbed is called *adsorbate* and the material of the surface on which adsorption takes place is called *adsorbent*. Adsorption strictly refers to accumulation of adsorbate on the surface only due to residual field of force. An *adsorbent* attracts an *adsorbate* or *adsorbed phase* by van der Waals type of relatively weak forces. Two examples of adsorption are given below:

(a) *Adsorption of ethanoic acid by charcoal:* If powdered charcoal is added to a solution of ethanoic acid and the solution allowed to stand for sometime, it is found that the concentration of the acid in the solution has decreased. This is because some of the acid is adsorbed by the charcoal on its surface.

(b) *Adsorption of a gas by a solid:* In an enclosed vessel containing SO_2 or NH_3 gas some powdered charcoal is added and the pressure measured before and after addition of the solid. It is found that the pressure of the gas has decreased. This is attributed to adsorption of the gas by the charcoal.

Absorption: *Absorption refers to the accumulation and penetration of the particle through the surface inside the bulk of the absorbent*. An example is the uptake of water by a sponge in which water is found throughout the sample of sponge. ***Adsorption*** must not be confused with ***absorption.***

Sorption: McBain suggested a non-committal term "*sorption*" to describe both adsorption and absorption. However, in current literature the word "sorption" is not used any more.

The uptake of water vapour, alcohol vapour etc. by certain substances such as zeolites, is neither adsorption nor absorption. Water or alcohol vapours simply get into the vacant spaces in the crystal lattice and are retained there, the vacant spaces being created by dehydration of zeolites. This type of uptake has been termed *'persorption'*. Persorption may occur in other solids also. *'Desorption'* is the process of removing the adsorbed molecules from the surface. In gas-solid system desorption is carried out by continued evacuation of the system at low pressures ($10^{-2} - 10^{-6}$ mm of Hg) and at elevated temperatures. In case of adsorption from solutions, desorption is generally carried out by dilution, and addition of suitable chemical reagents.

18.3 Nature of Adsorption

Commonsense suggests that if adsorption results from purely physical forces like van der Waals forces it will have a pattern or nature quite different from the nature of adsorption caused by chemical forces, since physical forces and chemical forces are of different nature. Consequently, two limiting types of adsorption are recognized:

(a) *Physical adsorption:* When particle are held on the solid surface by purely physical forces like van der Waals forces, and

(b) *Chemical adsorption or Chemisorption: Chemisorption (also referred to as chemical adsorption) refers to a phenomenon in which there is chemical interaction between adsorbent and adsorbate.* In this case the binding force between adsorbent and adsorbate is relatively strong and it can be considered that a true covalent chemical bond is formed. Energy changes in chemisorption are much higher than in adsorption. The term *'activated adsorption'* is often used in place of chemisorption.

However, in many cases there may be partly physical adsorption and partly chemisorption, both occurring simultaneously on the surface. These cases are complicated and no attempt will be made to explain their behaviour.

When a gas molecule freely moving at random in all directions in the gas phase is adsorbed on a surface its translational freedom is lost or curtailed due to its adherence on the surface and its random motion is lost. If the adherence is strong it completely loses its translational motion and its vibrational and rotational energies are also modified. If the adherence is not strong it can at least move around within restricted areas of the surface but such motion must be less than the motion in gas phase. Consequently such adsorption must be accompanied by a rise of temperature, i.e., adsorption shall be exothermic. The part or whole of the translational kinetic energy is converted to heat energy. On the other hand, if adsorption is caused by chemical effects, the overall energy change will be governed by the nature and magnitude of chemical forces involved, plus the energy released due to loss of kinetic energy. No prediction from purely kinetic consideration can be made. Indeed chemisorption is quite complex and most of the discussions to follow will be confined mainly to physical adsorption. The following distinctions between the two types of adsorption may be used to better understand them.

	Physical adsorption		***Chemisorption***
(a)	Adsorption is rapid and equilibrium is quickly established.	(a)	Adsorption is rather slow and equilibrium is slowly established.
(b)	Adsorption usually takes place quickly at low temperature.	(b)	Adsorption usually takes place at low temperature.
(c)	Enthalpy of adsorption is low, usually 0 – 40 kJ mol^{-1}.	(c)	Enthalpy of adsorption is large, comparable to enthalpy of reaction.
(d)	Adsorption is exothermic, energy is released from the system due to loss of kinetic energy.	(d)	Energy release is not only due to the loss of kinetic energy, but also due to chemical interactions.
(e)	Temperature co-efficient is negative, i.e., amount of adsorption decreases due to rise of temperature.	(e)	Temperature co-efficient is positive, i.e., amount of adsorption increases due to rise of temperature.
(f)	Little or no activation energy is involved.	(f)	Activation energy is large.
(g)	The process is nearly reversible. On removing the surface the molecular species can be recovered.	(g)	The process is, in most cases, irreversible. The same molecular species cannot be completely recovered; they contain some reaction products.
(h)	Adsorption is not specific. Any solid surface can adsorb any gaseous substance. Adsorption is universal.	(h)	Adsorption is specific and not universal in character.
(i)	Physical adsorption is not associated with catalysis.	(i)	Chemisorption is associated with catalysis.

It should, however, be noted that for the same system a physical adsorption may change to chemisorption on increasing the temperature, as can be seen in Figure 18. 2. From *a* to *b* the adsorption is predominently physical in nature and from *c* to *d* it is mainly chemisorption. Between the temperature range from *b* to *c* both types are occurring simultaneously and temperature co-efficient is very low. However, it is impossible to say where exactly one process ends and the other begins because the change of one process to the other is not sharp.

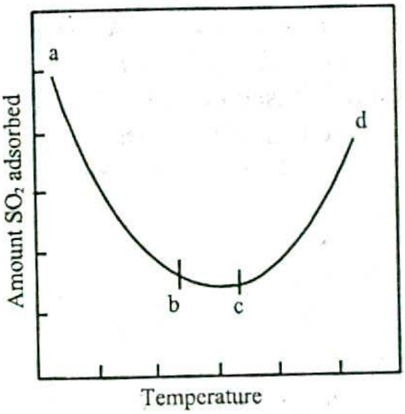

Figure 18.2 Adsorption of SO_2 on barium chromate (schematic).

Many other examples in which a change from physical adsorption to chemisorption takes place are known. The adsorption of oxygen on charcoal at liquid air temperature is purely physical in nature and the oxygen can be recovered by desorption. At room temperature the above adsorption is so strong that oxygen cannot be recovered fully. On prolonged evacuation of the system oxygen leaves the surface in combination with carbon as CO and CO_2.

18.4 Gas-Solid Systems: Langmuir Isotherm

Adsorption in gas – solid systems is relatively simple. Experiments showed that the volume of gas adsorbed on a solid increases with pressure rapidly at first and then slowly. Again at a particular pressure the volume of gas adsorbed decreases as the temperature is increased.

A plot of the volume of gas adsorbed against equilibrium pressure is shown in Figure 18.3. Initially the volume adsorbed rapidly rises with increase in pressure and then levels off showing that volume of gas adsorbed increases only very slightly with pressure. The three curves refer to experimental data at three temperatures, graph #1 is for the lowest temperature and the graph # 3 is for the highest of the three temperatures. Each of these curves is called an *isotherm*.

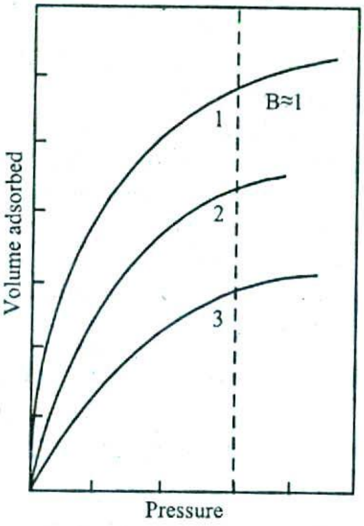

Figure 18.3 Schematic representation of isotherm (schematic) at different temperatures. 1, 2 and 3 are in increasing order of temperature.

Langmuir derived *a linear relation between gas pressure and the amount (volume) of the gas adsorbed at constant temperature. The relation is also called an* ***isotherm***. The derivation is based on the following assumptions:

(i) the adsorbed gas behaves ideally in the vapour phase
(ii) the adsorbed gas forms a unimolecular layer on the surface of the adsorbent
(iii) there is no lateral interaction between the adsorbate molecules
(iv) the adsorbed molecules are localized, that is, they do not move around on the surface
(v) the surface on which adsorption takes place is homogeneous, i.e. all points on the surface have equal and identical residual field of force.

Following the same argument as in *Section 12.27* at a particular temperature and pressure, let θ be the fraction of the surface covered as a result of adsorption so that the fraction which is bare (free) is $(1 - \theta)$. The adsorbed species may again be *desorbed* if the translational kinetic energy of the adsorbate species is sufficiently high to remove it from the surface. Thus, the process of adsorption and desorption will occur simultaneously and eventually a state of dynamic equilibrium between these two opposing processes will be established. This can be shown as

$$A\,(g) \;+\; W\,(surface) \;\rightleftharpoons\; AW \tag{18.1}$$

At this stage the rate of adsorption must be equal to the rate of desorption. Let k_a and k_d be the rate constants for adsorption and desorption respectively. The rate of adsorption is proportional to the pressure P_A of gas A, and the number of vacant (free) sites on the surface, $N\,(1-\theta)$, N being the total number of sites for adsorption. Therefore,

$$\text{The rate of adsorption} = k_a\,N\,(1-\theta)\,P_A \tag{18.2}$$

The rate of desorption is proportional to the number of adsorbed species,

$$= k_d\,N\,\theta \tag{10.3}$$

At equilibrium the two rates are equal.

$$k_a\,N\,(1-\theta)\,P_A = k_d\,N\,\theta \tag{18.4}$$

Solving for θ we have

$$\theta = \frac{(k_a P_A)}{(k_d + k_a P_A)}$$

$$= \frac{\left(\frac{k_a}{k_d}\right)P_A}{\left[1+\left(\frac{k_a}{k_d}\right)P_A\right]} \tag{18.5}$$

or

$$\theta = \frac{KP_A}{(1+KP_A)} \tag{18.6}$$

where K is equal to $\frac{k_a}{k_d}$

Equation (18.6) is known as the Langmuir isotherm. Equation (18.6) may also be written as

$$KP_A\,\theta + \theta = KP_A \tag{18.7}$$

Since the volume V of the gas adsorbed on the surface is proportional to θ (fraction of the surface covered by the adsorbed gas), we may write

$$\theta = \frac{V}{V_m} \tag{18.8}$$

where V_m is the volume of gas which will completely cover the surface of the adsorbent to form a monolayer on the adsorbent surface. Substituting this expression for θ in equation (18.7) and rearranging one obtains the linear form of the Langmuir isotherm.

$$\frac{P_A}{V} = \frac{1}{KV_m} + \frac{P_A}{V_m} \qquad (18.9)$$

A straight line would be obtained if $\frac{P_A}{V}$ is plotted against P_A. The slope of the line is $\frac{1}{V_m}$ from which V_m, the volume of the gas required to completely cover the surface of the adsorbent, can be calculated. If the area of cross section of a single gas molecule adsorbed on the surface is known, the total surface area of the adsorbent used may be calculated. A linear plot of $\frac{P_A}{V}$ against P_A is shown in Figure 18.4.

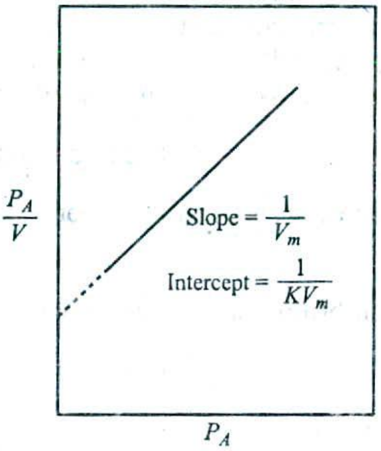

Figure 18.4 Linear plot of Langmuir isotherm (schematic)

Example 18.1: The volume of nitrogen gas (measured at 1 atm and 0°C) which completely covered the surface of a sample of silica gel with a unimolecular layer was found to be 112 $cm^3\ g^{-1}$ of gel. Calculate the surface area of the gel if each nitrogen molecule occupies $16.2 \times 10^{-20}\ m^2$.

Solution: The number of moles of gas adsorbed at STP = $\frac{112}{22400}$

The number molecules adsorbed = $\frac{112}{22400}(6.02 \times 10^{23})$

Area occupied by these molecules = Surface area of the adsorbent silica gel sample

$$= \frac{112}{22400}(6.02 \times 10^{23})(16.2 \times 10^{-20})\ m^2\ g^{-1}$$

$$= 488\ m^2\ g^{-1}$$

Many systems covering a wide range of temperature obey the Langmuir isotherm. As a matter of fact, deviation from linearity was ascribed to various other reasons which were not considered in the Langmuir theory. One typical Langmuir isotherm of the adsorption of sulphur dioxide on barium chromate is shown in Figure18.5. Strict obedience to Langmuir theory can be seen along the straight line *ab*. After the point *b* is reached deviation occurs. Langmuir isotherm is extensively used for the measurement of surface area or particle size of powdered material. From the slope and intercept of Langmuir plot the volume of the gas required to form a unimolecular layer on the surface of the powder is calculated. Since the area of the molecules of the absorbed gas is known the area of the surface of the solid can be easily calculated.

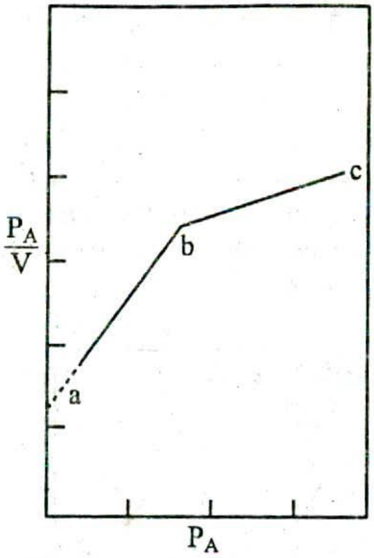

Figure 18.5 Langmuir plot

The results are expressed in terms of surface area in cm^2/g or m^2/g of the adsorbent. Surface area of such materials as paper, pulp, rayon, cotton, jute etc., can be determined by use of Langmuir equation as the method is equally applicable in case of adsorption from solution.

As mentioned earlier, adsorption is accompanied by energy change. The **enthalpy of adsorption** is defined as *the enthalpy change when one mole of gas measured at STP is adsorbed on the solid surface*. This quantity for a particular gas-solid system may be determined by use of the Clausius- Clapeyron equation in the form

$$\ln P_A = -\frac{\Delta H_{ads}}{RT} + constant \qquad (18.10)$$

P_A is the pressure at which one mole of gas is adsorbed on the same surface at different temperatures expressed in degree K. This is an equation of a straight line and the plot of $\ln P_A$ against $\frac{1}{T}$ yields a straight line, the slope of which will be $-\frac{\Delta H_{ads}}{R}$ from which the value of enthalpy of adsorption (ΔH_{ads}) can be calculated.

The similarity between this equation and equation (3.1) relating vapour pressure of a liquid with temperature may be noticed.

18.5 Deviations from Langmuir Isotherm

Deviations from Langmuir isotherm are quite common, particularly when the gas pressure is high. This deviation is thought to be due to the formation of multimolecular layer on the surface. Such multimolecular layers can be formed not only on the normal adsorption sites but also on the *bottle necks* or *capillaries* in the adsorbent (Figure 18.6). Langmuir assumption of uniform and homogeneous surface is a highly idealised concept. In practice surfaces are not homogeneous but there are peaks and cavities as shown in Figure 18.7. The residual field of force on such inhomogeneous surface cannot be identical; moreover, formation of multimolecular layer is much favoured in capillaries. These effects due to inhomogeneity are not usually observable at low prsssures but they markedly alter the isotherms at relatively higher pressure.

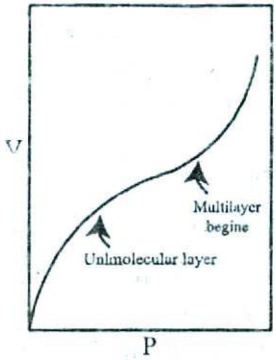

Figure 18.6 General isotherm

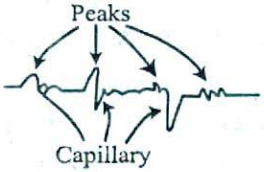

Figure 18.7 Surface inhomogeneity

18.6 BET (Brunauer, Emmet and Teller) Isotherm

In Figure 18.6 is shown a usual form of Langmuir isotherm at high pressures. After the unimolecular layer formation is completed, the multilayer begins to form and consequently the volume of the gas adsorbed rises instead of becoming nearly steady. This behaviour is reflected in the linear plot Figure 18.5 along *bc*. Brunauer, Emmet and Teller have developed, from kinetic considerations, an isotherm where provision is made for the formation of multilayer. This isotherm is known as *BET* isotherm. The *BET* equation, which is not mentioned here, is applicable when Langmuir equation fails due to multilayer formation. The BET equation is such that if only one layer of adsorbed molecules is considered, it reduces to the Langmuir equation. If capillary condensation is large the BET equation also fails. However, the *BET* isotherm and the Langmuir isotherm can explain a large number of cases. Mention should be made of a number of adsorption studies the result of which cannot be adequately explained by the two theories; the deviations mainly arise from chemisorption and formation of special types of surface compounds. A few examples have been given in *Section 18.3*. Deviations also occur due to the adsorption of a part of a molecule such as an atom of a molecule.

18.7 Gas-Liquid Interface: Surface Film and Surface Pressure

Mariners in early days used to calm sea waves by spreading oil on the ocean around their boats. It is not known whether they did it knowing the principles involved, but it appears that it was an accidental discovery. However, it is now known that the calming action of the oil was due to the formation of an insoluble layer of oil on water followed by a considerable lowering of surface tension. Scientific investigations of films at gas-liquid interface was probably first carried out by Miss Pockels (1891). Her findings, although not based on sound experimental observations, became the focal point of interest and the subject matter received attention of several investigators. Some of the conclusions she reached are still retained. It was, however, the simple but masterly experiments of Langmuir (1917) that has given us an insight into the nature of surface films and their structure and has widened the horizon of human knowledge in the two dimensional world of films*.

When a small quantity of a long chain fatty acid is added to a clean water surface the fatty acid spreads in a definite fashion. Due to their translational motion on the surface they can exert pressure on the sides of the containing vessel. The following experiment developed by Langmuir illustrates the film pressure.

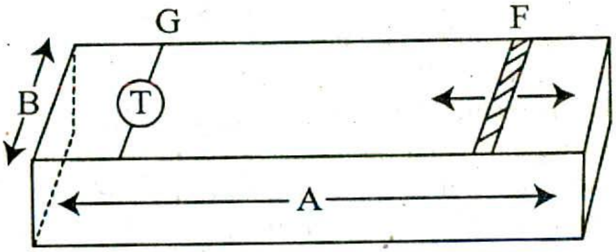

Figure 18.8 Langmuir trough (simplified); Surface balance

Clean water is contained in a trough. *F* is a movable barrier that can be moved right or left at will (Figure 18.8). *G* is a fixed barrier to which is coupled a torsion balance, *T*, so that any pressure exerted on the barrier, *G*, can be registered by the torsion balance. The trough has a fixed width, *B*, and the edge, *A*, is calibrated in *cm* and *mm*. Thus at any position of the movable barrier, *F*, a definite area is enclosed within *F* and G. A small quantity (0.05 to 0.1 mL of a benzene solution (0·01%) of a long chain fatty acid, say palmitic acid or stearic acid, is added gently to the clean water surface confined within the two barriers. The benzene quickly evaporates leaving behind a very small quantity of the fatty acid. The movable barrier, *F*, is slowly moved towards *G* in regular small successive steps. The pressure exerted on the barrier *G* is registered by the torsion balance. At each position of *F*, corresponding to a definite area available to the fatty acid molecules for their two dimensional translational motion, the pressure is read off. Several readings are thus taken and when they are plotted a curve of the nature shown in Figure 18.9 is obtained. The pressure-area ($P - A$) curve is shown by *pqrs*. Over the region *pq* the

---

* The molecules forming films can undergo translational motion in two planar directions on the surface only. They cannot move up and down.

pressure increases only slightly on decreasing the area. Between *qr* the change in pressure is more pronounced and between *rs* the curve is almost vertical and linear. On compressing the film beyond *s* the film ruptures and the pressure-area curve is no longer acceptable. This has been shown by a downward arrow. The film may, therefore, be divided into three types*. The molecules forming the film on the surface within *pq* area are almost lying on the surface and situated quite apart from each other.

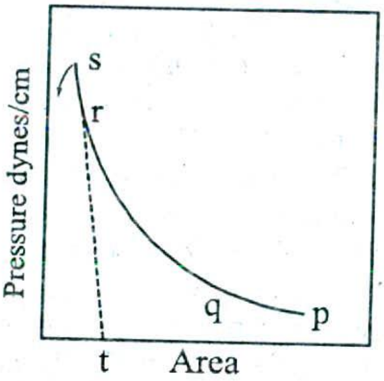

Figure 18.9 Pressure-Area curve

The film is said to be gaseous since they obey an equation, *PA =constant*, where *P* is the surface pressure and *A* is the area occupied. This equation is analogous to the ideal gas equation, *PV = constant*. Within the range *qr*, due to decrease in the available area, the molecules are close to each other and due to water-loving $-COOH$ group (*hydrophilic*) and the water-repelling (*hydrophobic*) *hydrocarbon tail*, the molecules are pushed up and assumes a semi-orderly state. The area occupied by the molecules is no longer small compared to the total available area. The film is now said to be a *liquid-expanded* film. An equation of the type, $P(A - Z) = constant$ is obeyed [compare van der Waals equation, $P(V - b) = constant$.]. When the film is sufficiently compressed the molecules are all tilted up and they are oriented in a definite fashion, the molecules touching each other. The film is said to be *liquid film* and the compressibility of the film is very low as shown by the portion *rs*. No satisfactory relation between pressure and area is known for this part of the curve. The behaviour is like a gaseous system at very high pressure. The pattern of films is diagrammatically shown in Figure 18.10.

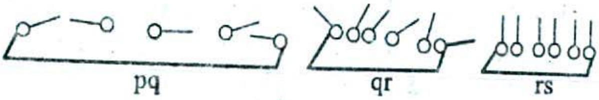

Figure 18.10 Structure of surface film —, hydrocarbon end O, carboxyl group

The portion *rs* is almost linear and gives the limiting area occupied by the molecules. If *rs* is extrapolated towards the area axis it cuts the area axis at *t*. This is the minimum area the molecules can occupy in a highly compressed and definitely oriented film. Since the mass of the fatty acid taken is known, the actual number of molecules present is easily calculated. The limiting area divided by the number of molecules gives the area occupied by a single molecule.

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* Note the unit of pressure of surface film, which is dynes/cm. The films may be divided into 5 to 6 types. For the present purpose only three subdivisions are thought sufficient.

This value for a number of long chain fatty acids is in the range of $(20 - 21) \times 10^{-16}$ cm^2 and the value is independent of chain length as long as a homologous series of compound is concerned. Measurements of surface areas of these molecules by independent methods confirm the values. These findings also indicate that the molecules on the surface are oriented in definite fashion as shown in Figure 18.10. Pressure-area curves of many other substances that form insoluble monolayer can be studied in an analogous manner.

Example 18.2: It is found that 0.106 *mg* of stearic acid covers 500 cm^2 of water surface at the point where the surface pressure just begins to rise sharply. Estimate the cross-sectional area *a* per stearic acid molecule and the thickness *t* of the film. Given: Molar mass of stearic acid = 284 $g\ mol^{-1}$ and its density = 0.85 $g(\mathrm{mL})^{-1}$

Solution: The number of stearic acid molecules in the sample

$$= \frac{0.106\times10^{-3}}{284}(6.02 \times 10^{23})$$

$$= 2.247 \times 10^{17}$$

Hence total area covered by the molecules $= a\,(2.247 \times 10^{17}) = 500\ cm^2$

Hence area covered by one molecule $= a = \dfrac{500}{2.247 \times 10^{17}} = 22 \times 10^{-16}\ cm^2$

Again $\quad (500)\,t = \dfrac{0.106\times10^{-3}}{0.85}$

Hence $\quad t = 25 \times 10^{-8}$ cm

18.8 Gibbs' Adsorption Equation

When alcohols, phenol, glycerol, fatty acids etc. are dissolved in water, the surface tension of water is reduced, the extent of reduction depending on the concentration of the solute. In such cases it is noticed that the concentration of the solute is more on the surface layer than in the bulk and the solute is said to be *positively adsorbed* on the surface. Ionic solids dissolved in a liquid cause the surface tension of the liquid to rise and the concentration of the solute is found to be less on the surface. In such cases the solute is said to be *negatively adsorbed.* Gibbs treated these phenomena from thermodynamic principles and derived the following relation:

$$\Gamma = -\frac{d\gamma}{dC}\cdot\frac{C}{RT} \qquad (18.11)$$

where γ is the surface tension of the solution, Γ, the excess concentration of the solute on the surface, C, the concentration of the solute in solution, R, the gas constant and T, temperature in K. *Excess surface concentration (Γ) means the concentration of the solute on the surface in excess of that in the bulk.* Consequently all substances that reduce surface tension must have a higher molecular concentration on the surface than in the bulk. As mentioned, electrolytes often have a lower concentration on the surface and they increase the surface tension of water. From a measurement of γ, the surface tension of a series of solutions of different concentrations, C, of a solute, say glycerol or phenol, a plot of γ vs C is drawn. The gradient of the graph, $d\gamma/dC$, is evaluated at various values of C as shown in Figure 18.11. Using the values of the gradient Γ may be calculated with the help of equation (18.11). The equation has been experimentally verified by determining Γ by actual chemical analysis of very thin sections of the surfaces of solutions.

The experiment can be carried out in any laboratory because no special or expensive instrument is required.

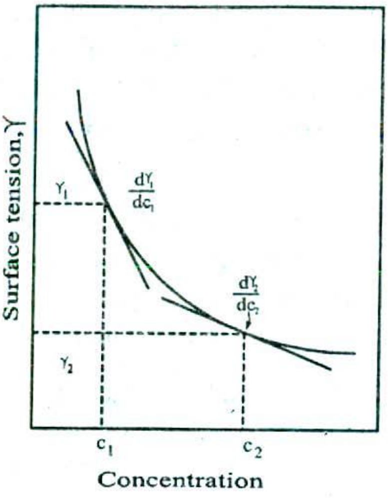

Figure 18.11 Surface tension as a function of concentration.

Example 18.3: The surface tensions of aqueous solutions of *n* - butyl alcohol have been measured at different concentrations. At $C = 0.1$ *mol* of alcohol in one *kg* of water the slope of the curve of the plot of γ *vs* C is $-0.103\ N\ m^{-1}$ at 298 K. What is the surface excess concentration of the alcohol, and what is the surface area per molecule?

Solution: Using equation (18.11)

$$\Gamma = -\frac{d\gamma}{dC}\cdot\frac{C}{RT} = -\frac{(-0.103)\,(0.1)}{(8.314)\,(298)}$$

$$= 4.16\times10^{-6}\ \text{mol m}^{-2}$$

Since there are 6.02×10^{23} molecules per mole, the area per molecule is

$$= \frac{1}{(4.16\times10^{-6})(6.02\times10^{23})}$$

$$= 3.99\times10^{-19}\ \text{m}^2$$

18.9 Adsorption from Solution

When a solid is placed into a solution adsorption takes place on the surface of the solid for the same reasons which cause adsorption in gas-solid system. There is, however, the presence of the solvent which may modify the adsorption. If the solute is a strong electrolyte, the cation and the anion are not likely to be equally adsorbed, particularly at low concentration. In general, one of the ions, depending on the nature of the adsorbent and concentration, is preferentially adsorbed and the particles will acquire electric charge. The present discussion will be confined to *adsorption of non-electrolytes or weak electrolytes.*

It is observed that at constant temperature the amount of adsorption depends on the concentration of the solute, the higher the concentration the greater the adsorption. The general pattern of the isotherm, as long as physical adsorption takes place, is the same as in gas-solid system shown in Figure 18.12. Deviations occur, as in gas-solid systems, due to multilayer formation or penetration through the surface. As a matter of fact the basic principles and mechanism in all adsorption processes are the same, the magnitude varies from system to system. In solution there is the probability of adsorption of the solvent molecules also. If the solute is adsorbed more than the solvent we get the usual positive adsorption and the solute concentration becomes less in the bulk of the solution. But if the solvent is more adsorbed than the solute then the solution becomes more concentrated with respect to the solute.

18.10 Freundlich Isotherm

The extent of adsorption from solution is related to concentration by an empirical expression known as Freundlich isotherm[*]

$$\frac{x}{m} = KC^{n} \tag{18.12}$$

where x is the amount of the solute adsorbed by m gram of the solid, C, the concentration and n and K are constants. This equation can be converted to a linear form by taking logarithms on both sides,

$$log \frac{x}{m} = log\ K + n\ log\ C \tag{18.13}$$

A plot of $log \frac{x}{m}$ vs $log\ C$ should give a straight line of slope n[*]. An example is shown in Figure 18.12. Many systems show agreement with this equation over limited range of concentrations, although the significance of n is not clearly understood; moreover, no useful or significant information can be obtained except establishing an empirical relation.

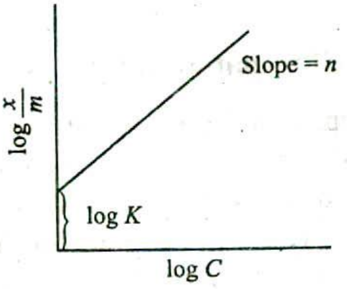

Figure 18.12 Freundlich isotherm

18.11 Langmuir Isotherm for Solid-Liquid Adsorption

Langmuir's theory of unimolecular layer can be extended in an exactly analogous manner to adsorption from solutions. The workable form is at once obtained by putting C in place of P and x/m in place of V, a quite justifiable procedure. The linear equation (18.9) then becomes

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[*] The same isotherm can be used in gas/solid systems but it has been left out of discussion for brevity and because it is a special form of Langmuir isotherm. No significant information can be obtained from it.

[*] In many texts the equation is given as $\frac{x}{m} = KC^{1/n}$ where n is a constant. The authors prefer to use n in place of $\frac{1}{n}$.

$$\frac{C}{x/m} = \frac{C}{k_1} + \frac{1}{k_2} \qquad (18.14)$$

so that a plot of $\frac{C}{x/m}$ *vs* C gives a straight line(k_1 and k_2 being constants).

Just as the equation is obeyed by many systems so also there are many cases which deviate from it. The deviation principally arises due to multilayer formation. In Figure 18.13 a linear plot of $\frac{C}{x/m}$ *vs* C is shown for adsorption on jute of iodine in CCl_4. Along *ab* Langmuir equation is obeyed; at *b* the available surface is fully covered with a monolayer of iodine and between *bc* multilayer is formed. The general pattern of Figure 18.13 is identical to the pattern as in Figure 18.5. It is possible to calculate the surface area of jute or any such adsorbent by using Langmuir isotherm. The necessary data are obtained from the slope and intercept of the linear portion *ab*.

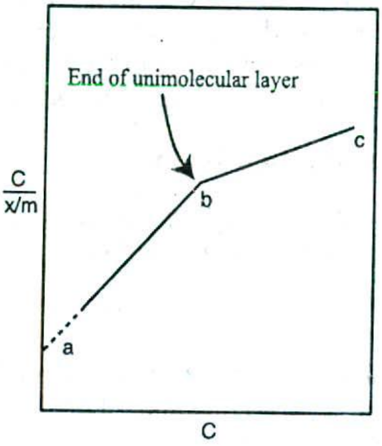

Figure 18.13 Adsorption of I_2 on jute in CCl_4 medium (schematic)

18.12 Chromatography

An important and useful application of adsorption is in chromatography. Chromatography may be roughly defined as a process by which several constituents in a homogeneous mixture can be separated and identified by preferential and selective adsorption. The method is of almost universal application and is one of the most powerful tools in an analytical laboratory. The following experiment will illustrate the point. A solution of, say, three coloured constituents *p, q* and *r* is taken. A small amount of this solution is poured into the chromatographic tube *A* generally known as column, as shown in Figure 18.14. The column is properly packed with a suitable adsorbing material, *e.g.*, Al_2O_3. A small amount of the solution is placed on top

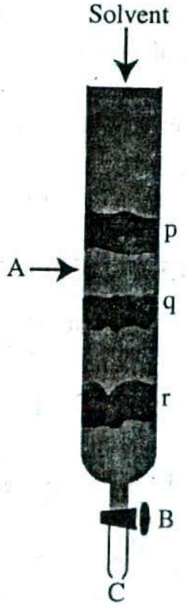

Figure 18.14 Column chromatography

of the packing when the coloured materials will be taken up at the upper part of the column material. Small amounts of the solvents are added gradually to the column. The process is called *elution*. The solvent while descending downwards will carry with it the solutes, but the extent to which it will be carried down will depend on the extent of adsorption of the solute by the column material. The species that has been most weakly adsorbed will be carried down more readily and, therefore, more rapidly; the species that has been adsorbed most strongly will be *eluted least* rapidly and, therefore, only very slightly. Thus on successive elution the different species will move downwards with different velocities and a separation will occur. The species p, q and r will occupy different places in the column as shown in Figure 18.14. The species can now be separated by removing the column material or by further elution by the solvent. In the latter case the species r will first come out in the solution through the outlet, T; next species q will follow and finally p can be removed. The three solutions so obtained, one containing r, one containing q and the other p, can be subjected to appropriate chemical analysis.

The method is so effective that only trace quantities of materials which defy separation by usual chemical means can be separated. If the species are coloured the whole column can be seen to contain several coloured bands standing at different heights. In fact, the word '*chromatography*' originally meant '*colour graph*', i.e., different colour separation. However, the method can be equally applied for colourless material but in such cases careful control of conditions and elaborate techniques are needed to satisfy the conditions of separation. This process of separation by use of a column is known as *column chromatography.*

An effective separation by chromatography requires a judicious choice of the adsorbing material and the solvent, and they are to be selected on the basis of the properties of the solutes. Excellent tables of solvents and column materials to meet different requirements are available.

In addition to using column for chromatographic separation simple filter paper strips can be used with good results, and in some cases with spectacular success. This is known as paper chromatography. In this method a small dot, usually of the size of a millimeter, is made with the solution containing different solutes near one end of a strip of chromatogrphic filter paper. The solvent is then allowed to flow along the paper strip slowly up to a definite length of the paper. The different solutes move with different speeds and a separation is affected. If the solutes are colourless they can be rendered visible by spraying the paper with suitable reagents that form coloured compounds. Alternatively in many cases, the solutes can be rendered luminescent and thus visible by irradiation with ultraviolet rays in a dark room. The luminescence is due to fluorescence. Ordinary blue-black fountain pen ink is a good sample for paper chromatography. Most of them contain three or four coloured materials and they become easily recognisable in a paper chromatogrm. If the dot is formed near the upper edge and the solvent is allowed to flow downwards, the method is called *descending chromatography* because the constituents descend; if the dot is formed near the lower end of the paper and the solvent moves upward by capillary action, the method is called *ascending chromatography*. In paper chromatography the adsorbing material is cellulose in all cases and, therefore, is of somewhat limited application, whereas in column chromatography there are some inherent difficulties. The limitations of both the methods are eliminated in *thin layer chromatography*. In this method a thin layer of a suitable adsorbing material is made on a rigid support and normal chromatographic techniques employed.

The principle of different adsorption is now-a-days extensively used in gas phase or *vapour phase chromatography*. The elution is done by an inert carrier gas, almost universally helium.

QUESTIONS AND PROBLEMS

1. What is meant by the term `adsorption'? Does absorption convey the same meaning as adsorption? If not, how do they differ?
2. Distinguish between physical adsorption and chemisorption. Discuss how physical adsorption may pass on to chemisorption in the same system on changing the temperature.
3. Write a short essay on the Langmuir theory of unimolecular layer in a gas-solid system.
4. Derive Langmuir isotherm and the linear form of the equation.
5. The data below are for the adsorption of CO on charcoal at 0oC. Show that the data fit the Langmuir isotherm in its linear form and find the surface area of the charcoal sample on which the adsorption took place;

p/ mm Hg	100	200	300	400	500	600	700
V/mL	10.2	18.6	25.5	31.4	36.9	41.6	46.1

Mass of adsorbent; 3 022 g. V has been corrected to 1 atm

6. How is the formation of the multilayer explained and how can it be detected from Langmuir isotherm?
7. What is meant by the heat of adsorption of a substance on a solid surface? The following are data on pressures at which a fixed amount of bromine vapour is adsorbed on a given quantity of charcoal at different temperatures:

t (°C)	58.0	79.0	100.0	117.5	138.0
P (mm Hg)	740	1340	2631	3881	5650

Draw a graph of ln P vs 1/T (T in oK). From the slope of the straight line calculate the heat of adsorption.

8. Draw a pressure-area curve for a surface film at a gas-liquid interface and discuss how many types of surface films can be formed.
9. Discuss the similarities between surface pressure and bulk gas pressure. What evidences can be put forward to explain the existence of oriented molecules in a liquid film?
10. What is the effect of solutes, electrolytes or other materials on the surface tension of water? Explain with the help of Gibb's adsorption isotherm.

19 COLLOIDS AND EMULSION

The term colloid, first used by Graham (1861), has been used for more than a century, but the art of preparing and processing colloids had been known for thousands of years. In fact, colloids, as we understand to-day, were known, prepared and used by man as early as our civilization itself. The various paints and varnishes used in early days, making of earthen wares from clay and its painting and glazing, preparation of butter and cheese from milk, the use of wood and timber for various purposes are only a few examples of man's use of colloids. Of course, these were done without any systematic knowledge of the principles involved. Man prepared and used colloids by mere 'hit and miss' method. In addition to manifold uses of colloids, man was puzzled to see many colloids formed in nature, such as clouds, fog and mist, smokes, dust storms etc., but they failed to recognize the common basis amongst them and tried to console their souls by assuming them to be purely of divine character.

Modern views of colloids and the tremendous development that has taken place in this branch of physical science owe a great deal to Graham although his classification of colloids is no longer fully acceptable. We are indebted to him not only for the term *colloid* but also for a number of other nomenclatures which are still used. The interest he created amongst the scientists is primarily responsible for subsequent developments.

19.1 Crystalloids and Colloids

Graham divided all substances in solution into two classes:

(i) *Crystalloids*, like sodium chloride, sugar etc. which diffused rapidly and easily, passed through animal membranes and formed a clear solution in water.

(ii) *Colloids*, which diffused slowly and passed through membranes very slowly and the system is not always transparent to light. Examples of this group were gum, glue etc.

The former class was given the name crystalloids as most of the substances which showed such properties were crystalline in shape. This classification by Graham is not valid any more as Graham's crystalloids could also be made to behave like colloids. For example, sodium chloride in fine dispersion in benzene or any such medium can exhibit colloidal properties. Moreover, smokes, emulsions, aerosols, or mists, fog etc. cannot be placed in any of the groups. In fact, all material bodies can be converted into colloid under appropriate conditions.

A colloid may be defined as a substance in a peculiarly fine state of subdivision dispersed in another continuous medium giving rise to a large increase in surface area of the dispersed phase.

Thus colloids are two-phase heterogeneous systems, the *dispersed phase* present being bounded by surface in a very fine state of subdivision in the *dispersion medium (continuous medium).* This definition puts no limitation as to the substances that can behave like a colloid. It, on the other hand, differentiates colloids from other states of matter in such a way that 'degree of fineness' of material bodies is the distinguishing feature between a colloid and a 'non-colloid'. The qualitative term 'fineness' can be expressed in a quantitative form. It is, in fact, the size of the particles of matter (liquid, solid or gas) which can be dispersed or maintained in another continuous medium that decides whether such a system can exhibit colloidal property or not. For the sake of simplicity particle size shall be expressed as the radius of the particle, assuming it to be spherical. This principle of classification is so successful that the colloidal properties associated with 'true solution' of high polymers can also be satisfactorily explained. It is indeed the size that counts, not the nature of the material. In Figure 19.1 the classification of material bodies according to their size in dispersion is shown. It is to be noted that no sharp division is possible between the states, one state overlaps the other. In general, it may be stated that colloids have a particle size from 1 to 1000 nm (nanometer); few colloids have somewhat smaller size.

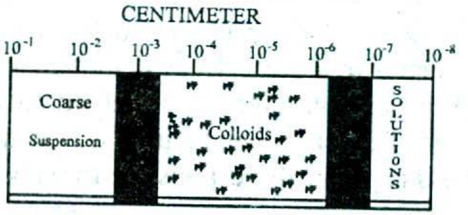

Figure 19.1 Particle size of matter, shaded area shows overlapping region

19.2 Disperse Phase and Dispersion Medium

The material body which is present in a state of fine discrete particles is called the *disperse phase* and the continuous medium in which the discrete particles are present is called the *dispersion medium.* For example, in potable gold (this is a suspension of gold particles in aqueous medium and is used in medicine), gold is present as discrete particles and constitutes the disperse phase, water is the dispersion medium. Yet another example is milk where small fat globules are present as discrete particles in water. Here the fat globules are the disperse phase and water the dispersion medium. In butter water is the disperse phase and fat the dispersion medium.

19.3 Types of Colloids

Depending on the dispersion medium and disperse phase colloidal systems have been grouped into different types. Table 19.1 lists some of these.

Table 19.1 Different types of colloids

Disperse phase	*Disperse medium*	*Type*	*Examples*
Gas	Liquid	Foam	Shaving cream Whipped cream
Gas	Solid	Solid foam	Foam rubber, pumice stone
Liquid	Gas	Aerosol	Fog, mist, clouds
Liquid	Liquid	Emulsion	Hair cream, milk
Liquid	Solid	Solid emulsion (gel)	Butter, cheese
Solid	Gas	Smoke	Dust, soot in air
Solid	Liquid	Sol	Ink, paint, prepared sol
Solid	Solid	Solid sol	Alloys, ruby glass

Our discussion will be mainly confined to colloidal systems consisting of solid substances dispersed in a liquid. Some of the types of colloids listed above are discussed in more details later in the chapter.

19.4 Sol and its Preparation

A sol is a dispersion of solid particles in a liquid medium. If the liquid is water it is called *hydrosol,* such as ferric hydroxide sol. If the liquid is alcohol it is called *alcosol.* If, however, the dispersion medium is air it is called *aerosol*, such as fog, mist, smoke. Thus the dispersion medium is shown as a prefix to sol. In all sols the continuous phase is a liquid or a gas, i.e. a fluid

No single method is known by which all types of colloids can be prepared. This is quite obvious from the diverse nature of the colloids, a state to which all matter can be brought by judicious choice of conditions. Preparation of some colloids are quite easy and simple and also inexpensive, requiring no special appliance or skill. On the other hand, some colloids are very difficult to prepare and requires the use of expensive appliance and great skill and rigid control of conditions. Basically, however, all methods of preparation can be divided into two groups:

(i) association or condensation method and

(ii) disintegration or dispersion method.

(i) ***Association method:*** In the association method the desired chemical species are formed by appropriate chemical reactions in solution. The molecules so formed undergo association or agglomeration and grows to colloidal dimension. The sol thus produced usually needs to be made from excess electrolyte which may be formed during chemical interaction. If appropriate control of the reaction rate and extent of reaction is not done, the colloid may form larger particles and separate out as precipitate. The initial

concentration of the reactants, temperature, volume, rate of addition of one of the reactants – are all important steps for a successful preparation of the sol. By this method many hydrosols, alcosols etc. can be prepared.

Arsenious sulphide sol (double decomposition): For the preparation of arsenious sulphide sol a saturated solution of pure arsenious oxide is made in clean water by boiling in a clean flask. The solution is cooled to about 50°C and the undissolved oxide is removed by filtration and it is diluted to about three times its volume with clean water. Purified H_2S is slowly passed through the clear solution. The H_2S reacts to form arsenious sulphide. The solution becomes yellow and almost all the arsenious sulphide remains in the colloidal state. If any precipitate is formed it should be removed by filtration through sintered crucible or glass wool and not through filter paper. Purified H_2 or CO_2 or N_2 is now slowly bubbled through the sol till the excess H_2S is removed. A clear, quite stable sol of arsenious sulphide can thus be prepared.

A still more convenient method is to add a small quantity of thioacetamide or thiourea to the original arsenious oxide solution in water. The thio compounds undergo slow hydrolysis forming H_2S which reacts to form arsenious sulphide. The sol thus produced contains arsenious sulphide particles even smaller than the sol prepared by direct bubbling of H_2S. While the sol made by the first process is yellow in colour, the sol obtained by the action of thio compound appears yellow with a bluish tinge in transmitted light. This shows that the particles of arsenious sulphide are at least $0.01\mu(10\ nm)$.

***Silver bromide sol (double decomposition)*:** A very dilute solution of silver nitrate is prepared in subdued light and any suspended impurity is carefully removed by filtration. If to this solution is added a very dilute clean solution of potassium bromide turbidity does not appear immediately. After a while a silver bromide sol is formed which looks bluish-white in transmitted light, indicating very small particles of silver bromide. Even without any dialysis the sol is stable for quite sometime.

Ferric hydroxide sol (hydrolysis): A freshly prepared nearly saturated solution of ferric chloride is first made. About 10 to 12 *mL* of the ferric chloride solution is then added *drop wise* to about 800 *mL* of boiling water. A few minutes interval is kept between successive drops. A brilliant dark red sol is produced by the hydrolysis of ferric chloride forming ferric hydroxide and hydrochloric acid. The sol needs immediate dialysis against hot water to remove the hydrochloric acid, otherwise the sol would be coagulated. Many sols of heavy metal hydroxides can be prepared in this way.

Gold sol (reduction): This sol is of particular interest since it is the earliest sol prepared and studied. It was known well before Graham's definition of colloid. The celebrated *purple of cassius* was known as early as 1663 A.D. Quite a number of methods are known by which this sol is prepared. All of these methods are based on the reduction of a gold compound in solution by a suitable reducing agent. The reducing agents used are carbon monoxide, hydrogen, phosphine, hydrazine, formaldehyde, phosphorus, phenyl hydrazine, glucose etc. These reducing agents do not form any strong electrolyte and consequently dialysis is not required. If, however, stannous chloride is used as the reducing agent dialysis is necessary.

About 10-15 *mg* of gold chloride is dissolved in about 100 *mL* of clean water. To this is added about 30-40 *mg* of potassium carbonate. A dilute ethereal solution of phosphorus is made and about 0.5 *mL* of it is mixed with the gold chloride solution. A bright red gold sol is then produced by the reduction of the chloride. A similar gold sol can be prepared using formaldehyde as the reducing agent, other steps being nearly identical.

Sulphur sol (oxidation): Sulphur sols can be prepared by the oxidation of H_2S in solution. The oxidation can be carried out either by oxygen of the air or by a solution of SO_2. There is no need of dialysis since no electrolytes are formed. Sulphur sol can also be prepared by the action of a strong acid, say, sulphuric acid, to a concentrated solution of sodium thiosulphate.

Many sols can be prepared by similar principle of condensation or agglomeration but without any chemical reaction. Thus if a concentrated solution of a substance is poured into another liquid in which the solubility of the substance is less, it will be thrown out of the solution due to supersaturation and a colloid may result. If an alcoholic solution of phosphorus is poured into water, the phosphorus is thrown out of the solution and under appropriate conditions passes on to colloidal state. Several modifications of the method have been made and these can be used for preparation of sols.

(ii) Disintegration or Dispersion method : Whatever may be the technique the method consists in disintegrating or pulverizing a large form of the substance to colloidal dimension, and then dispersing it in an appropriate medium in presence of a suitable stabilizer. The disintegration method may be of two types:

(a) Mechanical disintegration

(b) Electrical disintegration

(a) Mechanical disintegration: In this process the substance is reduced to particles of colloidal dimension by purely mechanical device, such as a colloid mill. The substance is generally placed between the annular gap of swiftly revolving discs or cylinders. Under the extremely powerful shearing force created by the oppositely rotating discs or cylinders the substance is broken down to fine particles. Coarse particles are removed and the pulverized material is dispersed in a liquid containing a stabilizer. The method is not of general applicability.

(b) Electrical disintegration: Bredig was the originator of disintegrating metals into sols by means of an electric arc. Two metallic electrodes dipped in water, as shown in Figure 19.2 are connected to a D.C. source. A rheostat and an ammeter are connected in series for controlling current. On passing the current an arc is produced near the ends of the electrodes and a metal sol results.

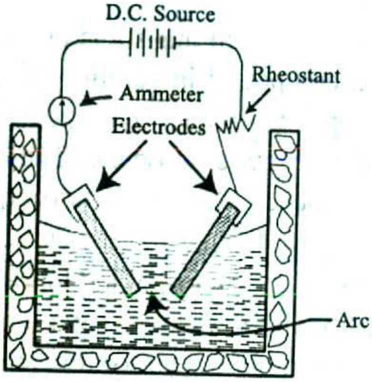

Figure 19.2 Bredig's method of electrical disintegration

A small quantity of sodium hydroxide is added to water. The sol thus produced consists of metal in case of noble metals like gold, platinum, but the sol is mainly oxide or hydrous oxide, in case of metals like zinc, aluminum, chromium, iron etc. Svedberg improved the technique by using an A.C. source and working at high current densities. He succeeded in preparing not only hydrosols but also organosols. It is thought that under the influence of the high temperature of arc the metal is first vaporised and the colloidal particles formed later by condensation.

A special class of colloid can be prepared by simply heating the substance with the dispersion medium. These are molecular colloids i.e., substances of high molecular mass but the molecules attain colloidal dimension due to their largeness. Solutions of high polymers like proteins, cellulose etc. fall under this category.

The two general methods given for preparation of colloids are not to be taken as the last word. The preparation of each different colloid needs special conditions and each system must be separately studied. What is good for one system need not necessarily be good for the other. Each individual colloid needs individual attention and quite often the control of conditions is to be rigid. Even then for some unknown reasons, one attempt fails and the other succeeds. It is not too much to say that preparation of colloids is as much science as it is art.

19.5 Purification of Colloids: Dialysis and Electrodialysis

After the preparation of the colloid, say, by a precipitation technique, it becomes necessary to remove the excess electrolyte from the sol to impart stability to the sol. One could think of filtering the colloidal system, wash the colloid and re-disperse. But even the finest filter paper will retain little or none of the colloid. Electrolytes or other soluble materials in sols are removed by putting the sol in a membrane of cellophane or parchment surrounded by water as shown in Figure 19.3. The salts can pass through the membrane of parchment and are gradually washed away by the running water whereas the colloid is left inside the vessel. This process of separation of colloid and Graham's 'crystalloid' is called dialysis. Graham himself insisted on the importance of dialysis. The assembly in which the *dialysis* is carried out is called a *dialyser*.

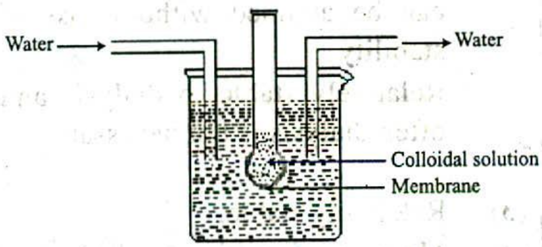

Figure 19.3 A simple dialyser

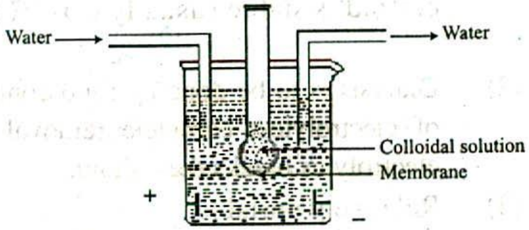

Figure 19.4 Electrodialyser

The membrane through which dialysis is carried out serves as a sieve of extremely fine pore size so that only the small molecules or ions can pass but not the relatively larger colloidal particles or large molecules of high polymers. The membrane also controls such selective retention and passage due to difference in diffusion and absorption. The dialysis can be frequently improved and made faster if the assembly is subjected to a suitable electric field. The migration of the ion of the electrolytes through the membrane becomes quite fast in the electric field and makes the process rapid. This is known as *electrodialysis.*

19.6 Lyophobic and Lyophilic Sols

A rough classification of sols, based on their methods of preparation, is sometimes made, e.g., association or condensation colloid, dispersion colloid and molecular colloid. But it is not a suitable classification because disintegration or dispersion colloid in its properties is not different from association colloid. The final products are the same, only the method of preparation is different. However, molecular colloids have some distinguishing properties. So, only two types of colloids are generally recognized.

The association or dispersion colloids are considered to be *lyophobic* or solvent hating whereas the molecular colloids are *lyophilic* or solvent loving. The colloidal electrolytes, although in many cases are similar in their properties to lyophilic colloids, constitute a separate class. We have thus three types of colloids :

(i) Lyophobic,
(ii) Lyophilic, and
(iii) Colloidal electrolytes.

Colloidal electrolytes have been discussed in *Section 19.14*. The properties of lyophobic and lyophilic colloids are summarized below:

Table 19.2 Points of difference between Lyophobic and Lyophilic colloid

Lyophobic colloid	*Lyophilic colloid*
(1) Only low concentration of the colloid is stable (usually 0.1-1%).	(1) Relatively higher concentration can be attained without loss of stability.
(2) Dialysis is to be done by rigid control of electrolytes; complete removal of electrolytes breaks the colloid.	(2) Relatively stable to dialysis and often dialysis is not necessary.
(3) Relatively unstable.	(3) Relatively stable.
(4) Very sensitive to electrolyte concentration and coagulation is very easy.	(4) Much less sensitive to electrolyte concentration; separation may occur at high electrolyte concentration.
(5) After phase separation by coagulation, re-dispersion of the coagulum is difficult and needs special treatment.	(5) Re-dispersion of the separated phase is quite easy.
(6) The coagulum consists of discrete aggregated particles.	(6) Coagulation is often followed by `*gel*' formation.
(7) Exhibits marked light scattering and strong Tyndall effect.	(7) Light scattering is low and little or no Tyndall effect.
(8) Most of the colloids are visible under high power microscope or ultramicroscope.	(8) Most of the colloids are invisible even under ultramicroscope.
(9) Surface tension very close or similar to that of the dispersion medium.	(9) Surface tension is usually lower than that of the dispersion medium.
(10) Viscosity is only slightly higher than that of the medium.	(10) Viscosity is markedly increased.
(11) Exhibits no solution properties, such as the colligative properties. The colloid is a two phase mixture.	(11) Exhibits properties of solution, such as colligative properties; only the molecules are of colloidal dimension.
(12) Refractive index of the colloid does not follow any definite pattern.	(12) Refractive index in most cases follow definite pattern like that of true solutions.

Many colloids have properties intermediate between the two classes just outlined. The two types described are only extreme cases.

19.7 Properties of Colloids

All colloids exhibit a number of properties, many of which are characteristic of colloids only. Some of their properties have been briefly outlined above. A few important general properties of colloids are given below:

19.7.1 Optical property

Colloids have some distinctive optical properties. The Tyndall phenomenon, named after Tyndall who extensively studied it, is attributed to scattering of light. If a narrow beam of sun's rays is allowed to enter into a dark or semi-dark room the small dust particles floating in air become visible when viewed at right angle to the incident ray. One can easily see that the particles look like bright spots against the dark background of the room.

This brightness of the particles is due to scattering of light by the dust and they act as secondary sources of radiation. The phenomenon is known as *Tyndall effect.* This property of lyophobic colloids is utilised in the ultramicroscope, first advanced by Siedentop and Zsigmondy. The principle of the ultramicroscope is illustrated in Figure 19.5.

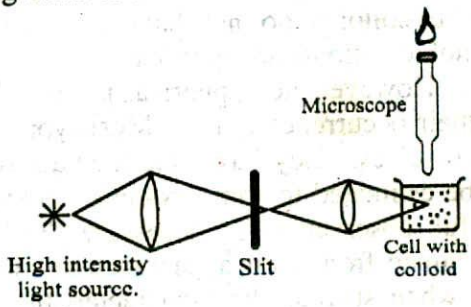

Figure 19.5 Principle of an ultramicroscope

From an intense light source the rays are passed through suitable lenses and a narrow slit. By a second set of convergent lenses the rays are converged inside the colloid which is contained in an optical cell. The microscope is focused somewhere inside the cell in such a way that the rays scattered by the particles at right angle to the direction of incident ray can enter the microscope and reach the eye of the observer. The particles of lyophobic colloid appear as bright spots to the observer's eye against a dark background. If a clean true solution or a clean liquid is placed in the cell, nothing can be observed since particles large enough to scatter light are not present. Due to this scattering the resolution of the microscope is increased many fold. In an ordinary high power microscope the visibility limit is about 0.2μ (200 *nm*) whereas in an ultramicroscope particles as small as 0·01μ (10 *nm*) are visible. The ultramicroscope is a powerful tool for studying lyophobic colloids. Approximate idea about particle shape and size can be made from the observations in the ultramicroscope. Zsigmondy confirmed the Brownian movement (*Section 2.40*) by observing gold sol in his ultramicroscope. The colloidal particles executing intense Brownian motion appear like twinkling stars in the microscope field.

A somewhat modified apparatus, where there is provision for measuring the weak intensity of scattered rays by lyophilic colloids, is used for measurement of molecular masses of high polymers. The method is known as the *light scattering* method.

19.7.2 Colour

The colour of a lyophobic colloid depends not only on the colour of the disperse phase but also considerably on the particle size. The same colloid system may appear to have different colours in white light depending on the size. A reasonable estimate of particle size can be made from the colour of the sol in transmitted light and reflected light. Thus a sulphur sol may be bright yellow, light yellow or even white depending on the size. Arsenious sulphide sol, which is normally bright yellow in transmitted and reflected light, may appear bluish yellow in reflected light depending on the particle size. The difference in the refractive index of the dispersion medium and disperse phase also greatly controls the colour.

19.7.3 Shape of colloidal particles

The colloids do not have any definite and uniform shape. A large number of lyophobic colloids are spherical or nearly spherical as can be seen in a high power microscope. However, non-spherical particles like rods or discs are also sometimes observed but their occurrence is rare. Most lyophobic colloids are not perfect spheres, ellipsoids, rods or discs. They have intermediate shapes. For sub-microscopic particles, the shape can be estimated to some extent from the twinkle of the particles in an ultramicroscope. Careful observation is necessary. The shape of some colloids can be fairly well ascertained from their appearance in stirred and unstirred conditions. Thus a number of sols, when stirred, show characteristic `silky' appearance. This is only possible if the particles are rod-like or disc-shaped. Vanadium pentoxide sol is an example. Association colloids have definite shapes for a particular system but disintegration colloids may vary widely in shape. They are often of irregular shape. However, for many theoretical treatments it becomes necessary to assume a definite geometrical shape, usually a sphere, for the sake of simplicity. Molecular colloids also have no definite shape in solution. Some are almost spherical while some are rod-like. Many linear high polymers have a rod-like shape. Several proteins also are of similar shape. The shape of high polymers may vary with the molecular mass. Thus a stiff rod-like molecule may become deformed due to increase in flexibility on increase of molecular mass and may behave like a random coil. One of the principal objects of the physical chemists working in the high polymer field is to ascertain the shape of the macromolecules. The practical application of colloids in many fields depends on their shape, and whether the colloid is lyophobic or lyophilic. Thus the final finish of a surface coated with paint or varnish will depend on the shape of the particles. Only linear high polymers are suitable for textile purposes whereas plastic type of materials is best made of non-linear cross-linked polymers.

19.7.4 Size of colloids

The particles of colloids are not of uniform size. They vary over a wide range. Lyophobic colloids, irrespective of the method of preparation, show often wide divergence in their size – some are small, some are relatively big. Accurate measurement of particle shape and size and drawing up of reliable size distribution curve is still a challenging problem to physical chemists. The complexity of the problem further increases due to different values of particle size of the same colloid obtained by different methods. The molecular colloids are still more complex. They cover a very wide range of molecular mass. It does not matter whether the polymer is natural, like cellulose or rubber, or man-made like polystyrene or nylon. For the same sample in the same solution the molecular mass range may be from a few thousands to a few hundred thousands. Moreover, for the same solution the molecular masses determined by different methods may widely differ. Thus all colloids are polydisperse in character.

Particles of lyophobic colloids undergo quite intense Brownian motion. They move at random in all directions executing zigzag irregular motion. For a short distance interval the motion is linear. Lyophilic colloids must also have Brownian motion but this cannot be observed due to their small size. Colloids, therefore, have linear translational motion.

19.7.5 Viscosity

Although the viscosity of dilute lyophobic colloids is slightly greater than the viscosity of the dispersion medium, concentrated lyophobic colloids can have quite high viscosity. For the same volume fraction* (**Volume of the disperse phase divided by the volume of the disperse phase plus volume of the dispersion medium*) of different lyophobic colloids, the viscosity can be markedly changed due to particle shape. Again, for the same colloid having the same volume fraction the viscosity may change, particularly for concentrated colloids, with shear rate. These are non-Newtonian systems. This non-Newtonian behaviour finds wide application in the use of modern paints and varnishes. Molecular colloids have quite characteristic flow behaviour and for the same solvent-solute pair the viscosity depends on the molecular mass of the polymer. A very common and widely used method for the measurement of molecular mass is the viscosity method. The study of viscosity of both lyophobic and lyophilic colloids is of great theoretical and practical importance.

19.7.6 Colligative properties

All molecular colloids in solution exhibit colligative properties. Since most of these colloids have high molecular masses the depression of freezing point, elevation of boiling point or lowering of vapour pressure is so small that these methods fail. They can at best be used up to molecular mass of a few thousand. The osmotic pressure, however, is quite marked for even high molecular mass polymers and this method finds wide use for the determination of molecular masses of a variety of polymers like proteins, cellulose and its derivatives, rubber, and a host of man-made polymers. The simple van't Hoff equation as discussed in *Section 9.15* is, however, not applicable. Modified osmotic pressure equation is used and the molecular mass is calculated from the intercept of a linear plot of π/C *vs* C as shown in *Section 9.16*. The extrapolation of the straight line is carried to zero concentration of the solution [π is the measured osmotic pressure and C is the concentration expressed in $g\ L^{-1}$ of solution].

For osmotic pressure measurements the colloid must be completely free from any electrolyte or any low molecular mass non-polymeric material to obtain any reliable value.

19.7.7 Electrical properties: Electrokinetic phenomenon

If a hydrophobic sol or a protein solution is placed in an electrical field then it is observed that the colloidal particles migrate either to the cathode or to the anode depending on the nature of the sol. This indicates that the particles are electrically charged. *The movement of the colloid particles under the influence of an electrical field is known as **electrophoresis***. If a potential difference is applied to the electrodes dipping into an electrolyte solution on opposite sides of a porous diaphragm or capillary tube, a flow of solution takes place from one side to the other. This is known as ***electro-osmosis***. On the other hand, if a liquid is forced through a membrane by the application of pressure an e.m.f. is found to develop, and this e.m.f. is called ***streaming potential.*** Analogous to these phenomena is the ***Dorn effect*** or the ***sedimentation potential***, which is the potential difference developed when the colloidal suspension is allowed to sediment. These four closely associated phenomena are called the ***electrokinetic phenomena***. Of these the phenomenon of electrophoresis has been extensively studied and used.

19.7.7.1 Electrophoresis

We have already defined electrophoresis (*Section 19.7.7*). A simple experiment may be carried out in order to firmly establish that colloid particles are electrically charged. Some arsenious sulphide sol are taken in a U-tube as shown in Figure 19.6. Two platinum electrodes are dipped into the sol in the two limbs of the U -tube and an e.m.f. is applied. It will be observed that the arsenious sulphide particles migrate towards the anode like negatively charged ions. If the e.m.f. is applied for a sufficient length of time a clear liquid free of the sol can be seen around the cathode.

It is found that the sols of metallic oxides and hydroxides, e.g., ferric hydroxide, and basic dyestuffs carry positive charges, while sols of metals, metallic sulphides, acid dyestuff carry negative charges.

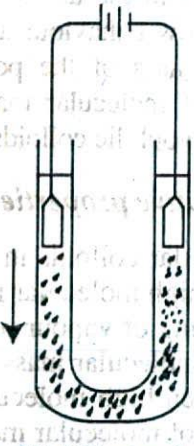

Figure 19.6 Electrophoresis

In the case of lyophilic colloids like proteins the magnitude of the charge, measured by the rate of movement of the colloid particles of the same substance depends on the *pH* of the solution. ***Isoelectric point** of a protein solution is the pH at which the colloid particles show no movement under an electric field, i.e. the particles carry no charge*. In solutions more acidic than the isoelectric point the particles move to the anode while in less acidic solutions they move to the cathode.

19.7.7.2 The electrical double layer

The electrical properties of the colloidal state of matter and other associated phenomena may be explained in terms of the existence of an *electrical double layer* at the interface between two phases. The concept of the electrical double layer arises from the question of the origin of the electrical charge on colloidal particles as evidenced by the *electrokinetic phenomena*. The charge on the colloidal particles is supposed to be derived by adsorption of ions of electrolytes from the solution, as it is found that in the absence of traces of electrolytes most lyophobic colloids are unstable. In the case of lyophilic colloids the charge is formed by the ionization of ionizable groups present in the colloidal particle. Whether the colloidal particle will adsorb positive or negative ions will depend on the nature of surface of the particles and sometimes on the concentration of the electrolytes.

Let us consider a colloidal particle carrying a positive charge. A layer of positive ions from the electrolyte will be strongly adsorbed on the surface. As the surface as a whole is electrically neutral there will be present in the vicinity of the surface negative charges (*counter ions or gegen ions*) as shown in Figure 19.7. The concentration of the negative charges gradually decreases as the distance from the surface increases. The layer of positive charges on the particle and the negative charges in the suspension medium constitute what is known as *an electrical double layer*.

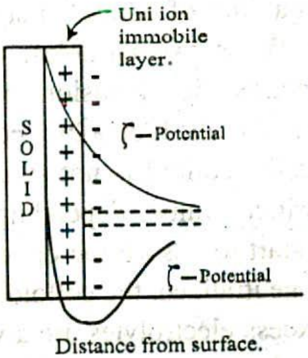

Figure 19.7 Electrical double layer and electrokinetic potential

The potential difference between the surface layer and the solution is known as *electrokinetic potential or zeta potential* (Figure 19.7). The magnitude of this potential depends not only on the nature and extent of adsorption but also on the distance from the surface of the particle .The zeta potential may be modified by changing the nature and concentration of the electrolyte as shown in Figure 19.8. Zeta potential should be clearly distinguished from *thermodynamic potential* (Chapter 12). The thermodynamic potential represents the total potential between the solid phase and the liquid phase.

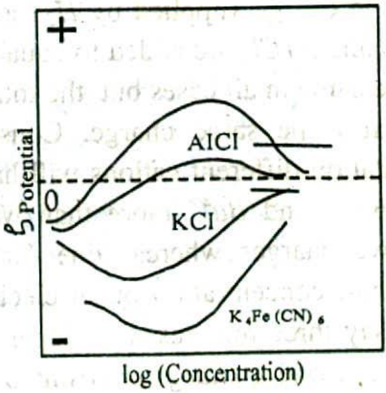

Figure 19.8 Effect of electrolyte on zeta potential

19.8 Stability of Colloids

The stability of colloids, particularly of lyophobic colloids, is dependent on the adsorption of cations or anions by the dispersed phase. If a sol is treated with excess of electrolyte the discrete particles undergo aggregation, i.e. they join together and grow larger in size. Ultimately they may separate from the dispersion medium. The colloid is said to be *coagulated.* The aggregated material is called a *coagulum.* Thus *coagulation is a process of joining of colloid particles to form particles of much larger size with separation of solid phase.* The coagulation results from neutralization of the charges of the colloid particles with ions of opposite charges. Other types of colloids may also undergo coagulation. Sometimes a colloid may form a coagulum on standing and is thus unstable.

The stability of colloids may be explained in terms of charge carried by the colloid particles. When two particles, which are similarly charged electrically, approach each other electrostatic repulsion between the particles takes place and coagulation is prevented. In all lyophobic colloids some amount of electrolyte must be present, otherwise the colloid is not stable. If, however; the electrolyte concentration exceeds a certain critical value, depending on the charge carried by the ion on the colloid, the particles start to adsorb the oppositely charged ions and at appropriate concentration the charge is neutralized, the colloid becomes unstable and undergoes rapid coagulation. This is why excess electrolytes are always added to break the colloidal state. The coagulation will depend not only on the concentration of the electrolyte but also on the charge carried by the cation or the anion.

Let us start with an arsenious sulphide sol. The stability of the colloid is due to the negative charge supplied by H_2S as sulphide* ion. If equimolecular quantities of $NaCl$, $BaCl_2$ and $AlCl_3$ are added to equal volumes of the same sol, the total number of cations are the same in all cases but the total charge is different since Na^+, Ba^{2+} and Al^{3+} ions do not carry the same charge. Consequently for charge neutralisation and subsequent coagulation different cations will have different effects, i.e., Al^{3+} will be more effective than Ba^{2+}, and Ba^{2+} more than Na^+. If one Al^{3+} is adsorbed it will neutralise three negative charges whereas one Ba^{2+} will neutralise two and Na^+ ion one. Thus the minimum concentration of an electrolyte to bring about coagulation within a specified time, say three minutes, will depend on the ionic charge. It is, therefore, the *valency of the ion, carrying charge opposite to the charge of the sol, which is the dominating factor.* Thus cationic charge is important for negatively charged colloid like arsenious sulphide and the anionic charge for the positively charged sol like ferric hydroxide. Instead of addition of an electrolyte, a colloid carrying an opposite charge may be used for coagulation since the two colloids having opposite charges will neutralise each other.

19.9 Peptization**

Peptization is the process by which a coagulum or a precipitate is dispersed to a colloidal state. It is the reverse process of coagulation. If a freshly prepared precipitate of silver bromide is washed in a controlled way, the precipitate can be easily dispersed in water to give a sol. Several sulphides, notably of arsenic and cadmium, are easily peptized by a further treatment of H_2S. Small but appropriate amount of electrolytes, weak or strong, is essential for peptization and subsequent stability of the sol.

19.10 Gel

If the sol is concentrated and the discrete particles are present in a state of bridged or cross-linked structure the system is called a *gel*. Gel is mechanically stable and possesses elasticity. Ordinary jelly or jello is an example of gel. *All gels are basically sols but all sols are not necessarily gels.* There are cases in which sol-gel transformation and vice versa are possible. The main distinction between sol and gel lies in the pseudo-regular structure of particles in a gel whereas in a sol the particles are wide apart in a completely irregular fashion. Moreover, in a gel the liquid entrapped within the bridged or cross-linked structure is immobilised, i.e., this liquid is not available for free flow but moves along with the whole gel as if it is an integral part of the whole structure. This is shown in Figure 19.10.

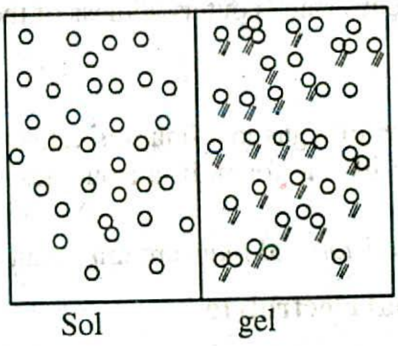

Figure 19.10 Schematic representation of sol-gel structure (shaded portion shows immobilized dispersion medium)

Many gels, simply by vigorous agitation, can become fluid again, giving a *sol*, but on standing reverts back to gel structure. For example, if a concentrated ferric hydroxide sol is allowed to stand undisturbed in a test tube it will set to a gel. The gel will not fall even when the test tube is inverted; if it falls at all, the whole gel will fall like a plug. But if the test tube is shaken vigorously and then inverted, the mass will undergo flow indicating that gel structure is broken and sol has been formed.

19.11 Syneresis

Many gels, if allowed to stand, are found to exude some water or the dispersion medium and the gel undergoes contraction, i.e., the gel shrinks and some of the

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* The case is complex.

** The word peptization comes from peptic digestion in which large solid particles of food are disintegrated to small ones prior to absorption and metabolism.

immobilised medium is given out. The phenomenon, observed by Graham himself, is known as *syneresis*. Concentrated gels of silicic acid or dilute gels of agar-agar exhibit the phenomenon. There is no net change of volume of the gel, i.e., the volume change undergone by shrinkage is equal to the volume of the medium given out.

19.12 Imbibition and Swelling

If some gelatin or agar is placed in water it first swells considerably and then either passes on to dispersion or remains as a gel, depending on the concentration of salt, pH or temperature. A similar behaviour is found with many natural and man made polymers in organic solvents. This uptake of the dispersion medium is followed by tremendous increase of pressure and some increase in volume. This increase in volume due to uptake of the continuous medium is called *swelling*. In some other cases of colloids, such as silica gel, the liquid is absorbed without any marked swelling. The absorption of a liquid by a colloid is sometimes called *imbibition*. Imbibition may or may not be accompanied by swelling. If the material that undergoes swelling can be confined in some way, then tremendous swelling pressure may be developed. The use of wooden wedges to split rocks in early days stands out as witness of the large swelling pressure.

19.13 Foam

A dispersion of a gas in a liquid is called a *foam*. Ordinary soap solutions form lather which behave like a foam if air-bubbles entrapped into it is reduced to colloidal dimension.

Sol, *gel*, *emulsion* and *foam* are important colloids which find uses in our daily life.

19.14 Colloidal electrolyte

If a very small quantity of soap, say sodium oleate, is dissolved in water, the solution will behave like a solution of electrolyte since the soap is a salt. If the concentration of the soap is gradually increased a certain critical concentration is reached beyond which the undissociated molecules and anion of the soap form aggregates and assume colloidal dimension. These *micelles*, as they are called, strongly adsorb ions from the solution and become electrically charged. Some unadsorbed ions are always left in the solution. The micelles behave both like a colloid and an electrolyte. They are, therefore, called *colloidal electrolytes*. The critical concentration above which the micelles are formed is called the *critical micelle concentration (CMC)*. This can be determined from either the electrical conductivity or surface tension measurements of the solutions. Not only soaps but many other substances with an ionizable group and a long hydrocarbon chain or similar tail behave in the same way. Alkyl sulphonates, sulphates etc. belong to this class. Several dyes with ionizable end, such as congo red, are colloidal electrolytes.

19.15 Emulsion

Emulsion is a dispersion of one liquid into another liquid in the form of small globules. Milk is a well known emulsion. Many oils of animal or vegetable origin are used in medicine in the form of emulsions. Since in almost all cases water is one of the liquids and the other is an organic liquid, emulsions are classified as

(i) Oil in water (O/W), where fat globules are dispersed in water.

(ii) Water in oil (W/O) emulsions, where water globules are dispersed in oil.

Milk is a common example of emulsion of the type O/W, where fat globules are dispersed in aqueous phase. Butter, on the other hand, is a W/O type emulsion. The term oil is an unfortunate choice but it is still being used to represent the organic phase. In general, the liquid droplets at rest or even during flow or stirred condition (except at very high field of shear) will remain spherical. Thus although emulsions are lyophobic colloids they have some distinctive properties.

If an emulsion is made simply by shaking two liquids like benzene and water or chloroform and water, the emulsion on standing will quickly break and the two liquids will separate into two layers. This breaking of emulsion is due to *coalescence* of the droplets. When two liquid drops touch each other, they combine to form a bigger drop, each individual droplet losing its identity completely. This is known as *coalescence*, to distinguish it from *coagulation* in which the solid colloid particles undergo aggregation. Coalescence must be prevented by some means to obtain a stable emulsion. Addition of traces of electrolytes, as in sols, cannot prevent coalescence and special reagents, called *emulsifiers*, are used to give them stability.

Emulsifiers are substances which not only reduce the interfacial tension (interfacial tension may be termed as surface tension between two liquid phases) between the two liquids but form a stable coherent film around the globules and thereby prevent coalescence (Figure 19.10). When two globules have protective films around them they cannot undergo coalescence until the film is broken.

Figure 19.10 Coalescence and its prevention

Various types of emulsifiers are now available. They are all long chain molecules with a hydrophilic group or lyophilic group so that one end of the molecule may be strongly adsorbed and form a strong and coherent film of the lyophobic group around the droplets. The emulsifiers may be ionic if they are soap-like materials, or they may be non-ionic if they are esters etc. All ionic types of emulsifiers will impart electrical charge to the emulsion.

19.15.1 Preparation of Emulsion

Emulsions are generally prepared by dispersion methods. Most emulsions are prepared by mixing the two liquids along with a suitable emulsifier and then passing the mixture through a colloid mill or a similar appliance. One of the liquids, mainly decided by the emulsifier, is broken down by the shearing forces into small globules and an emulsion results. In other methods the liquid to be dispersed is forced through a narrow capillary and injected directly into the dispersion medium containing the emulsifier as shown in Figure 19.11.

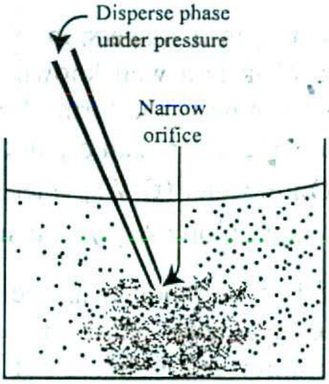


Figure 19.11 Injection method for preparation of emulsion

Under the pressure in the nozzle, the dispersed phase is broken down into small globules giving rise to an emulsion. The emulsifier could also be dissolved in the dispersed phase. The most common example of emulsion is milk where small fat globules are dispersed in water, protein being the principal stabilizer.

19.16 Importance of Colloids

The study of colloids, lyophobic, lyophilic, molecular or colloidal electrolytes is important not only for the satisfaction of an inquisitive mind, but also from practical point of view. There is hardly any field where these little particles, with their electric charge and incessant zigzag motion, do not show their influence and importance. The human body with all its intricacies is principally composed of colloids. Blood is a dispersion colloid where corpuscles are dispersed in a liquid medium known as blood serum. The serum itself is a colloidal solution of a number of molecular colloids of proteins. Thus blood is a colloidal suspension in another molecular colloid. Digestion of most food we eat are caused by enzymes, again a colloid; the food particles are broken down to colloidal dimension before dissolution or absorption in the body. Even the food we take are mostly colloids, notable amongst them are the proteins which are associated with the very process of our life. No less important is milk, butter and cheese. The garments we wear to protect ourselves are made of colloids, whether it is made of cotton or dacron, wool or nylon, rayon or silk. The paints and varnishes that decorate a multitude of things and protect materials against corrosion are colloids. The entire family of cosmetics is colloids of different types and finds a variety of use. The paper we write on, the ink we write with, the ink we print with, are only a few of many colloids we use every day. Around us we have our atmosphere, which is an aerosol, below us we have soil and clay which are also colloids. Thus we ourselves are colloids, we live on colloids.

QUESTIONS AND PROBLEMS

1. Classify the various states of matter which constitute colloids. What are molecular colloids, dispersion colloids and association colloids?
2. Write a short essay on the methods used for preparation of colloids in general. Specially describe the preparation of arsenious sulphide sol.
3. How does a sol differ from a gel? Explain your answer with a suitable diagram.
4. What are emulsions, foams and aerosols? Describe briefly one method for preparation of emulsions.
5. Discuss the role played by an emulsifier in the process of emulsification.
6. What is coagulation and peptization? Give suitable examples and discuss the role of electrolyte on coagulation.
7. Explain dialysis and electrodialysis.
8. Classify the colloids into different groups with special reference to their 'affinity' towards the dispersion medium.
9. Explain the principle of ultramicroscope. What is Tyndall effect?
10. Write a short essay on the shape and size of colloids.
11. Explain electrophoresis, electro-osmosis, streaming potential and Dorn effect.
12. How can you prove that colloidal particles are electrically charged? How do the colloidal particles acquire electrical charge? What is isoeletric point?
13. What is your concept of an `electrical double layer'? What is zeta potential? What is the effect of electrolyte concentration on zeta potential? What is the difference between zeta potential and thermodynamic potential?
14. Write an essay on the application and importance of colloids in our daily life?
15. Write notes on electrophoresis of colloidal systems and coagulation of colloids.
16. Write short notes on: Brownian movement, cataphoresis and dialysis.
17. Write explanatory notes on the following: (a) Tyndall phenomenon, (b) isoelectric point, (c) coagulation.
18. Write explanatory notes on lyophilic colloids, coagulation, sol and gel.
19. Write explanatory notes on Dialysis, Electropheresis, Emulsions.
20. Explain the following: (i) lyophilic colloid and (ii) peptization.
21. What is an emulsion? What are different types of emulsion? How can you prepare stable emulsion? Discuss the applications of emulsions.

20 PHYSICAL PROPERTIES AND MOLECULAR STRUCTURE

Physical properties of compounds can provide useful insight into the structure of the molecules. These properties can be broadly classified into two groups:

(a) Additive and
(b) Constitutive

An additive property is considered to be the sum of the properties of the constituent atoms or groups of atoms present in the molecule. Molecular mass is an additive property, because it is given by the sum of the masses of individual atomic masses. Molar volume is another example of additive property.

The constitutive property depends on the arrangement of the atoms and bonding structure in the molecule. Optical properties, viscosity, surface tension are constitutive properties.

Many physical properties may be partly additive and partly constitutive.

A study of the physical properties described in the following pages is valuable in many respects. More direct and valuable information are now-a-days obtainable from the use of the different types of spectroscopic measurements.

20.1 Molar Volume

The molar volume of any substance is the volume occupied by one mole of the substance. This quantity is easily determined by dividing the molecular mass by the density of the compound. According to Avogadro's hypothesis the molar volume of all gases at S. T. P. is 22,414 *mL*. As Avogadro's hypothesis is not strictly applicable to all gases slight variations from this value are likely to be observed.

The molar volumes of all liquids, however, show marked additivity when measured at their respective boiling points under atmospheric pressure. These observations led Kopp (1842) to state that the *molar volume of a liquid at its boiling point is equal to the sum of the atomic volume of its constituent atoms.* This is known as *Kopp's law.* Kopp's measurements showed that the molar volumes of two members of a homologous series of organic liquids differ by about 22 *mL* for each CH_2 group. Kopp calculated the volume equivalent of each element by a simple arithmetic means. For example, in a hydrocarbon of the formula C_nH_{2n+2} there are n numbers of CH_2 groups and two hydrogen atoms. Subtraction of $n \times 22$ *mL* from the molar volume of a liquid hydrocarbon gives the volume equivalent of 2 *H* atoms. The mean value of the difference comes to 11.0 *mL* so that the volume equivalent of each hydrogen atom is 5.5 *mL*. This leaves the volume equivalent of carbon as 11.0 *mL*. From these values and molar volumes, the volume equivalents of many atoms were calculated. The values of volume equivalents were taken as atomic volumes by Kopp.

This law was found to be only approximately correct as deviations are numerous. This is particularly obvious in the case of isomers which, according to Kopp's law, should have the same molar volume. In a large number of such cases the difference between the molar volumes of isomers were marked. This may be attributed to structural effects on the molar volume. In spite of its approximate nature the law has been useful in estimating molar volumes.

20.2 Parachor

An empirical relation between surface tension of a liquid (γ), its density (*D*) and that of the vapour (*d*) was established by Macleod (1923). The relation, known as Macleod equation, is

$$\gamma = C(D-d)^4 \qquad (20.1)$$

where C is a constant, the densities and the surface tensions being measured at the same temperature. The constant C was found to be independent of temperature and the equation was valid over a wide range of temperature. Equation (20.1) was modified by Sugden (1924) by multiplying both sides of equation (20.1) by the molecular mass (M) of the liquid.

$$M\gamma = MC\,(D-d)^4 \qquad (20.2)$$

Equation (20.2) upon rearrangement gives

$$\frac{M\gamma^{\frac{1}{4}}}{D-d} = MC = [P] \qquad (20.3)$$

The quantity *[P]* was found to be constant for a liquid, and Sugden named it as *Parachor*. If it is assumed that the density of vapour (*d*) is negligible compared to the density of the liquid at the same temperature, equation (20.3) may be written as

$$\frac{M\gamma^{\frac{1}{4}}}{D} = MC = [P] \qquad (20.4)$$

or

$$[P] = V_m\gamma^{\frac{1}{4}} \qquad (20.5)$$

where V_m is the *molar volume* of the liquid. At the temperature when surface tension is ity *parachor* becomes equal to the molar volume. In other words, *the parachor gives a* *ure of the molar volume at temperatures at which different liquids have the same* *tension.*

According to Kopp's law the molar volumes are additive, so parachor should also be additive. This was shown to be essentially correct by Sugden. He also showed that parachor is constitutive. From the data for isomeric substances and members of different homologous series Sugden was able to calculate the parachor equivalent for a number of elements and for some structural factors, such as double bond, triple bond, ring structure etc. Table 20.1 gives some of the values of parachor equivalent.

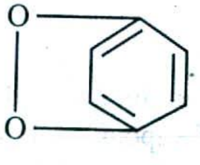
Table 20.1 Parachor equivalents

Atom	[P]	Structural factor	[P]
H	17.1	Double bond	23.2
C	4.8	Triple bond	46.6
N	12.5	5-membered ring	8.5
O	20.0	6-membered ring	6.1
S	48.5	Naphthalene	12.2
Cl	53.8		
Br	68.0		

20.2.1 Applications of the parachor

The parachor has been used to determine the structure of a number of substances. An important example is *p*-benzoquinone for which the following two alternative structures were suggested:

A



B

The parachor of structure A and B were calculated according to the data given in Table 20.1 and found to be 230 and 206.9 respectively. The experimental value is 236.8, indicating that structure A is correct. A number of other structural controversies have been settled with the help of parachor values.

It should be pointed out that anomalies in the parachor values have been noticed in a number of cases, *viz.*, organometallic compounds. Since the advent of spectroscopic methods which give better results the parachor is not used to any great extent in recent times.

20.3 Refractive Index and Molar Refraction

Refractive index is the ratio of the velocity of light in a vacuum to its velocity in a specified medium. The refractive index of liquids depends on the density, but is independent of temperature. Based on purely theoretical consideration from the electromagnetic and wave theories of light H.A. Lorenz and L. Lorenz deduced the expression

$$r = \frac{(n^2 - 1)}{(n^2 + 2)} \cdot \frac{1}{d} \tag{20.6}$$

for the specific refraction, r, where n is the refractive index and d is the density of liquid. They defined molar refraction, M_r, as *equal to the specific refraction multiplied by molecular mass*. Mathematically it is given by

$$M_r = \frac{(n^2 - 1)}{(n^2 + 2)} \cdot \frac{M}{d} \tag{20.7}$$

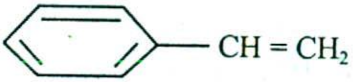
The value of the molar refraction calculated according to the expression of Lorenz and Lorenz was found to be independent of temperature and pressure but dependent on the wave-length of light used to measure the refractive index. Refractive index is usually measured with a refractometer, the commonly used ones being Abbe refractometer and the Pulfrich's refractometer. For description of the instrument and the method of measurement a book on practical physical chemistry should be consulted. For comparison purposes refractive index is measured with light of definite wave-length, usually the sodium-D line.

Molar refraction has been found to be an additive as well as a constitutive property, and in the same way as for volume equivalent and parachor equivalent it has been possible to calculate the refraction equivalent of the elements and for structural factors like double bond, triple bond etc. Table 20.2 gives some refraction equivalent values.

Table 20.2 Refraction equivalents of elements and structural factors (Sodium-D line)

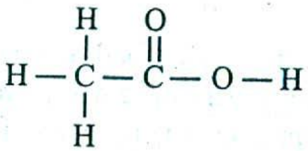
Atom	R.E.	Structural Factor	R. E.
C	*2.418*	*C − C*	*1.2*
H	*1.100*	*C = C*	2.79
Cl	*5.967*	*C ≡ C*	4.79
Br	*8.865*	*C− H*	1.67
I	*13.900*	*4 C ring*	0.32
O (carbonyl)	*2.211*	*5 C ring*	− 0. 10
O (ether)	*1.643*	*6 C ring*	− 0.15
O (hydroxyl)	*1.525*		

Unlike parachor, ring formation has little effect on molar refraction. Although, in general, the molar refraction may be calculated with the help of refraction equivalents, some anomalies are observed, particularly with open chain compounds containing conjugated double bonds and with compounds in which the conjugated double bond is partly in the ring and partly in the side chain, as in styrene.



Structure of styrene

Nevertheless, the refraction equivalents have been useful in some cases in deciding between possible alternative structures of compounds. Let us take an example. The accepted structure of ethanoic acid has been shown to be



$$\mathrm{H-\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-H}$$

Structure of ethanoic acid

The molar refraction for ethanoic acid may be computed from the data presented in Table 20.3.

$2C$	$2 \times 2.418 = 4.836$
$6H$	$4 \times 1.100 = 4.400$
$1\ O$ (in $O-H$)	$1 \times 1.525 = 1.525$
$1\ O$ (in $C = O$)	$1 \times 2.211 = 2.211$
	Total M_r = 12.972 $mL\ mol^{-1}$

The experimentally determined value of M_r for ethanoic acid is 13.300 $mL\ mol^{-1}$. This is in good agreement with the calculated value. This confirms the structure of ethanoic acid as shown above.

20.4 Optical Activity

A substance is said to be optically active if it can rotate the plane polarization of *polarized light*. Ordinary light is believed to consist of electromagnetic waves, the oscillation taking place in all planes perpendicular to the direction of propagation. If, however, the light is passed through a Nicol prism the oscillations take place in a single plane and the light is said to be *plane polarized* and the plane in which oscillations take place is called the *plane of polarization*. A schematic diagram of the plane polarized light and its rotation is shown in Figure 20.1. When solutions of substances like sucrose, glucose etc. are placed in a beam of plane polarized light, the plane of polarization is found to be rotated either to the right or to the left. If it is rotated to the right the substance is said to be *dextro-rotatory*, while if the plane is rotated to the left the substance is *laevo-rotatory*. The extent of rotation is measured in angles and is determined with a polarimeter. Descriptions and the method of using a polarimeter will be found in books on Practical Physical Chemistry. The property of rotation of the plane of polarization is also shown by pure solids and liquids.

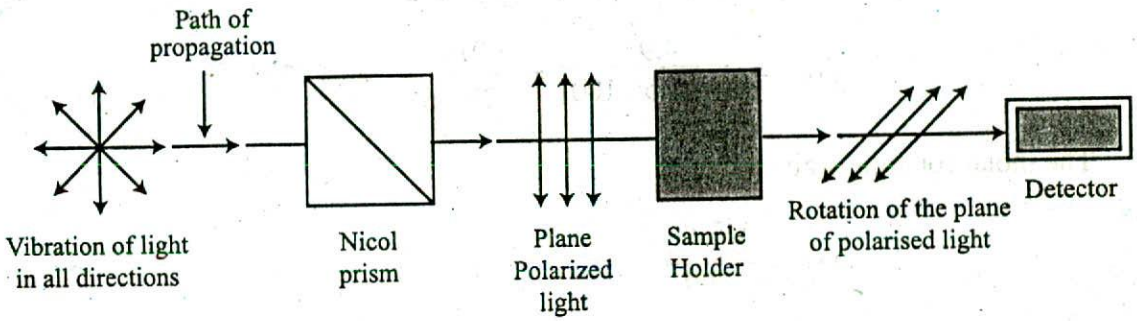


Figure 20.1 Schematic diagram of polarization of light and its rotation

The extent of the optical rotation of a substance depends on a number of factors, viz., the wave-length of light, the temperature, the length of the column through which the light passes, the concentration, if the substance is in solution. The optical activity of a pure substance is usually expressed in terms of *specific rotation*, *[α]*, given by the relation

$$[\alpha]_D^t = \frac{\alpha}{l\rho} \tag{20.8}$$

where the subscript *D* and superscript *t* on α represent the wave-length (sodium-D line) of light used and temperature respectively. α is the angle of rotation when the light passes through a column of length *l* (expressed in decimetre*) of the liquid of density *ρ*, in $g\ (mL)^{-1}$. For a solution the relationship is written as

$$[\alpha]_D^t = \frac{\alpha}{l.c} \tag{20.9}$$

where *c* is the concentration in $g\ (mL)^{-1}$ of solution. If $l = 1.0\ dm$ and $c = 1.0\ g\ (mL)^{-1}$, equation (20.9) can be written as

$$[\alpha]_D^t = \alpha \tag{20.10}$$

Thus the specific rotation may be defined as

The angle through which the plane of polarization of polarized light is rotated when one gram of substance is dissolved in 1.0 mL of solution and the length of the solution through which the light passes is 1.0 dm.

The specific rotation is a characteristics property of a substance. For example, the specific rotation of glucose is 66.5 degree at 25°C when measured with sodium-D light.

Example 20.1: An optically active substance containing 1.56 *g* in 100 *mL* of solution rotated the plane of polarization of polarized sodium-D light by 4.91° when placed in a cell of length 2 *dm*. Calculate the specific rotation of the compound.

Solution: Given, $c = 1.56$ *g* per 100 *mL* of solution, $\alpha = 4.91^\circ$ and $l = 2$ *dm*. Substituting these data in equation (20.9) we get the specific rotation as

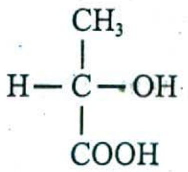
$$[\alpha]_D^t = \frac{4.91}{2 \times (1.56/100)} = \frac{4.91 \times 100}{2 \times 1.56} = 157.37^0$$

The molar rotation is given by

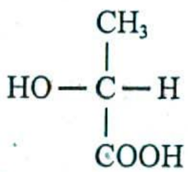
$$[M]_D^t = \frac{M[\alpha]_D^t}{100} \tag{20.11}$$

20.4.1 Optical activity and chemical structure

Optical activity is exhibited by a large number of organic compounds, some inorganic complex salts, quartz and some inorganic compounds. A general characteristic of all these compounds is that there is an element of asymmetry either in the arrangement of atoms or groups of atoms in the molecule or in the arrangement of molecules in the crystal, as in quartz. J. H. van't Hoff (1874) suggested that in the case of organic compounds if a carbon atom is bonded to four different atoms or groups of atoms the molecule as a whole will be asymmetric and will show optical activity. This observation of van't Hoff was found to be valid not only for organic compounds but also for inorganic complexes where the central metal atom is bonded to different atoms or groups of atoms. The simplest example is lactic acid which exists in the dextro and laevo forms, which are mirror images of each other. A mixture of equal quantities of dextro and laevo forms is optically inactive.



$$\begin{array}{c} CH_3 \\ | \\ H-C-OH \\ | \\ COOH \end{array}$$



$$\begin{array}{c} CH_3 \\ | \\ HO-C-H \\ | \\ COOH \end{array}$$

There are examples of compounds where one part of the molecule is the mirror image of the other so that the molecule is internally compensated and is optically inactive. One example is tartaric acid, the internally compensated form being known as the *meso* form. Optical activity is shown by many simple carbohydrates.

20.5 Dipole Moment and Molecular Structure

In diatomic molecules formed by atoms of the same elements, e.g. H_2, O_2, Cl_2 the bonding electrons forming the covalent bond are equally attracted by the two atoms joined by the bond. If in a diatomic molecule the bonding electron pair is unequally attracted the by the two atoms, namely in HF, then there is separation of charge in the molecule, the bonding electrons spending more time near the fluorine atom. This happens because of the difference in the electronegativity of the two atoms joined by the bond. As a result in the HF molecule the more electronegative fluorine atom acquires partial negative charge, $\delta-$, and the hydrogen atom acquires an equal amount of positive, $\delta+$, charge as shown below.

$$\overset{\delta^+}{H} - \overset{\delta^-}{F}$$

Or, more precisely it can be shown as

$$\overset{\delta^+}{H} \; \overset{\delta^-}{:F}$$

Such a bond where there is separation of charge between the two atoms is called a polar bond and the diatomic molecule is said to be a polar molecule.

The shift of electron density is represented by placing a cross arrow (⇸) above the Lewis '*dot structure*' to indicate the direction of the shift. For HF this can be represented as

$$\overset{⇸}{H \;:\; F}$$

As the polar molecule has two electric charge of equal magnitude of opposite sign and separated by a distance it acts as a dipole.

The magnitude of polarity of the bond is measured by a quantity known as ***dipole moment*** represented by μ. The dipole moment is a vector quantity with a magnitude and direction. The direction of the vector is from positive end to the negative as indicated above. Dipole moment is defined as follows:

Dipole moment of a dipole is the product of the charge ***q*** *and the distance* ***d*** *between the cenres of the two opposite and equal charges.*

In other words,

$$\mu = d \times q \tag{20.12}$$

For a non- polar molecule $q = 0$, and so $\mu = 0$. The dipole moment of a polar bond is called **bond moment**.

Unit of dipole moment

The unit of dipole moment is e.s.u.cm, the charge being expressed in electrostatic unit (e.s.u.) and the distance in cm, and dipole moment is usually expressed in Debye.

$$1 \text{ Debye} = 10^{-18} \text{ e.s.u.cm}$$

since the charge on one end is usually of the order of 10^{-10} e.s.u. and the distance between the centers of two atoms is of the order of 10^{-8} cm.

20.5.1 Applications of dipole moment measurements

Some applications of dipole measurements in determining structure of the molecule are mentioned below. The dipole moment values are useful in choosing the correct shape or structure from two or more possible alternatives.

(i) Predicting shapes of molecules

Diatomic molecules like hydrogen, nitrogen, chlorine etc. are linear as two atoms can combine only in a straight line. The electron pair/pairs forming bonds between the combining atoms are equally shared by atoms. The dipole moments (which are actually bond moments) of these molecules are found to be zero.

In a polyatomic molecule all bonds between two atoms may or may not be bipolar. As a consequence the molecule as a whole may or may not be polar depending on the arrangement in space of the bonds in the molecule because the dipole moment of the molecule is the vector sum of the moment of each polar bond. For example, a triatomic molecule like carbon dioxide has zero dipole moment and the molecule is found to be linear from X-ray investigation of solid carbon dioxide. This is explained in the following way: in carbon dioxide each carbon – oxygen bond has a polarity in which the more electronegative oxygen atom has a partial negative (δ^-) charge as shown below:

$$\overset{\delta^-}{O} = \overset{2\delta^+}{C} = \overset{\delta^-}{O}$$

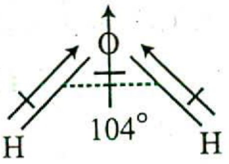
The dipole moment contribution from each bond (bond dipole) may be represented as

$$O \overset{\leftarrow\!\!\!+}{=} C \overset{+\!\!\!\rightarrow}{=} O$$

As can be seen the two $C = O$ bond moments in carbon dioxide are equal and opposite. They cancel each other and the dipole moment of carbon dioxide molecule is zero, i.e. $\mu = 0$. This gives carbon dioxide molecule its linear shape. If the bond moment did not cancel each other, as would happen if the molecule was bent or V - shaped, then there would be a resultant dipole moment of the molecule. Similar arguments and facts lead to the conclusion that CS_2 molecule is also linear as $C - S$ bond moments cancel as shown below:

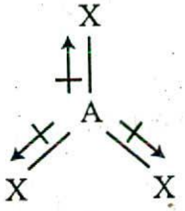
$$S \overset{\leftarrow\!\!\!+}{=} C \overset{+\!\!\!\rightarrow}{=} S$$

On the other hand water, H_2O, has high dipole moment indicating that the molecule is not linear and the bonds make an angle with each other. As a result the two bond moments do not cancel each other. According to the principle of vector addition there will be a resultant bond moment as indicated below. The molecule has a dipole moment of 1.84 D.

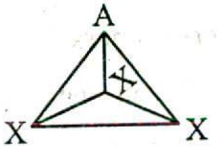


Similarly H_2S and SO_2 have non - zero dipole moments, and the molecules have *V*-shape as in the case of H_2O.

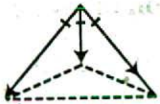
If the molecule is of the type AX_3 there may be two possible structures **(I)** and **(II)** : The direction of bond moments in AX_3 can be shown in **(III)**.



(I)



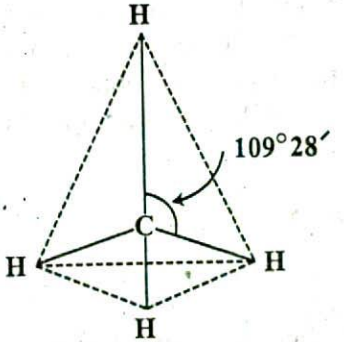
(II)

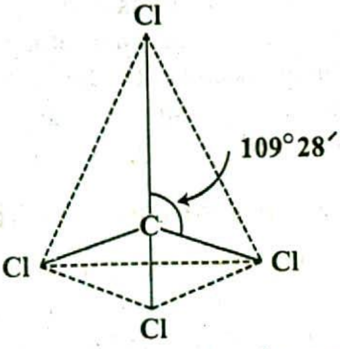


(III)

Molecules with structure **(I)** will be non-polar but those with structure **(II)** will be polar. A molecule of BF_3 has a zero dipole moment, and has structure like **(I)**. All four atoms in BF_3 lie in one plane in such a way that the $F-B-F$ bond angles between them are equal. A molecule of BF_3 has *planar trigonal* shape. NH_3 has a high dipole moment (1.46D) indicating that the bond moments do not cancel. This value of the dipole moment is consistent with an arrangement such that the direction of bond moments are shown as in **(III)** above. As a result a molecule of NH_3 has triangular *pyramidal* shape. PH_3, AsH_3, *and* SbH_3 have similar shapes.

The pentatomic molecules CH_4, CCl_4, $SiCl_4$, $SnCl_4$ etc. have zero dipole moments. This suggests that the bond moments are symmetrically arranged around the central atom (*C, Si or Sn*) in such a way that the four bonds *tetrahedrally* arranged around them as shown below:

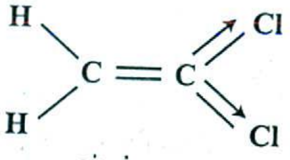




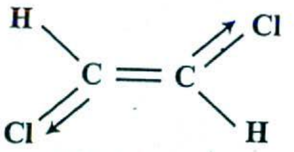
With such an arrangement the bond moments cancel each other and the molecules are non polar. If any of the four atoms is substituted by another atom of different electronegativity the molecule will become polar.

(ii) Differentiation between *cis*- and *trans*-isomers

Measurement of dipole moments of *cis*- and *trans*- isomers of 1,2-dichlorethylene helps to determine their configurations. The configurations are shown below:



cis-isomer

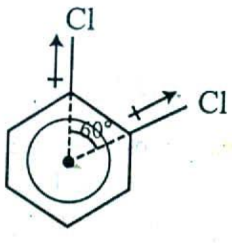


trans-isomers

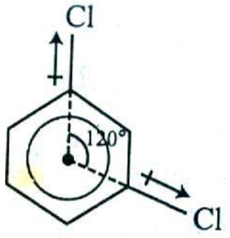
As can be seen the dipole moment of *trans*- form will has zero value, since the $C-Cl$ bond dipoles are directed in the opposite directions. The bond moments cancel each other. On the other hand the *cis*- form has a dipole moment of 1.90 D.

(iii) Differentiation of *o*- , *p*- and *m*- isomers

The *o*-, *p*- and *m*- isomers of dichlorobenzene are shown below:



$\mu = 2.6$ D



$\mu = 1.5$ D

$\mu = 0$

The dipole moments of *o*-, *m*-, and *p*- forms of dichlorobenzene have been experimentally found to be 2.60, 1.50 and 0.00 D respectively. The *p*- isomer of dichlcrobenzene is expected to have zero dipole moment, because the two $C-Cl$ bond moments cancel each other. However, the dipole moment of *o*- isomer is higher than *m*-isomer, because the angle between the two $C-Cl$ bond moments in *o*- isomer is higher than the corresponding angle in *m*-isomer. Vector addition of bond moments in these two cases will give higher value in *o*- isomer.

20.6 Spectroscopy and Molecular Structure

The determination of the structure of organic compounds has become simpler and much less time consuming by the applications of instrumental techniques which have found wide use in the analytical laboratory. Some of these techniques are also used in industry, medicine and other fields. The discussion here will be on Mass spectrometry (*MS*), Infra - red spectroscopy (*IR*) and Nuclear Magnetic Resonance spectroscopy (*NMR*) and the sort of information each of these techniques provide.

Mass spectrometry	Molecular mass and formula
Infra red spectroscopy	Functional groups in a molecule
Nuclear magnetic resonance spectroscopy	Carbon – hydrogen framework in the molecule

A spectrum is a display of component parts of a mixture of particles of different masses, or dispersion of the components of radiation. In a NMR spectrum different carbon-hydrogen components in a molecule is elucidated.

20.6.1 Mass spectrometry

The mass spectrometer was devised by F.W. Aston (1813) and was first applied in the determination of isotopic masses and the relative abundances of isotopes. Later on the technique has found wide application in the determination of molecular masses of compounds and elucidation of their structures.

20.6.1.1 How a mass spectrometer works

The essential parts of a mass spectrometer are shown in Figure 20.2. A gaseous sample (a liquid or solid is vaporized) of the substance under investigation is introduced into an ionization chamber where low pressure is maintained. Here the sample is bombarded with high energy electrons when electrons are knocked out of the sample particles forming positively charged ions. These are mainly singly charged ions, although ions with more than one charge may be formed. If molecules are bombarded with very high energy electrons the molecules may break up into atoms or groups of atoms with +ve charge which may be described as *fragments* of the molecules.

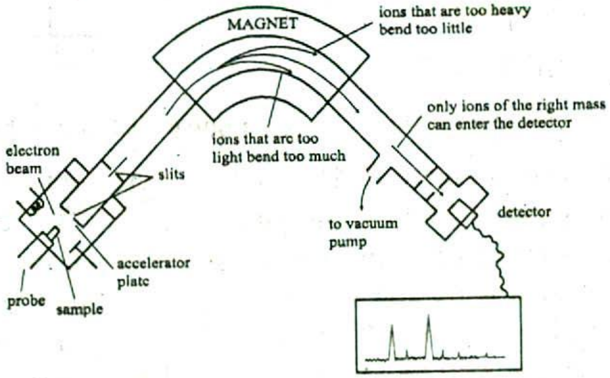


Figure 20.2 Diagram showing the essential parts of a mass spectrometer

The positively charged ions are then accelerated by the application of a negative electric field towards a curved tube where it is subjected to a strong magnetic field. The magnetic field deflects the positively charged particles according to their *mass to charge* *ratio* (m/z^+), particles with lower m/z^+ value being deflected more than particles with higher m/z^+ value. The particles then fall on a detector where the intensity of the ion beam is detected electrically, amplified and recorded as peaks at the various m/z^+ ratios. Particles with different m/z^+ ratios are brought to focus on the detector by gradually changing the strength of the magnetic field. Since the number of charge z on each ion is usually 1, the value of m/z^+ for each ion is simply its mass m.

The mass spectrum of a substance is usually presented as a stick diagram with m/z^+ values on the x – axis and the intensity (number of ions of a particular m/z^+ value) or relative abundance on the y – axis.

20.6.1.2 Applications of mass spectrometry

A mass spectrometric analysis of a monatomic element reveals the isotopic composition of the element. When calibrated using ^{12}C isotope the relative isotopic masses can be read directly from the stick diagram. Such analysis shows that Neon has three isotopes, ^{20}Ne, ^{21}Ne and ^{22}Ne with relative abundances in the ratio 114:0.2:11.2. This is shown in the form of a stick diagram in Figure 20.3.

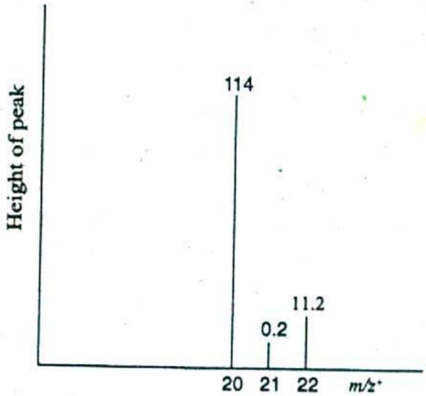


Figure 20.3 Mass spectrum of neon

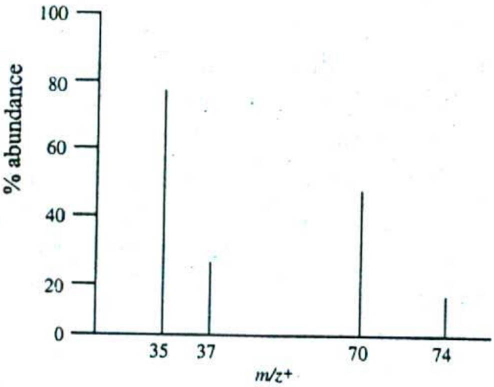
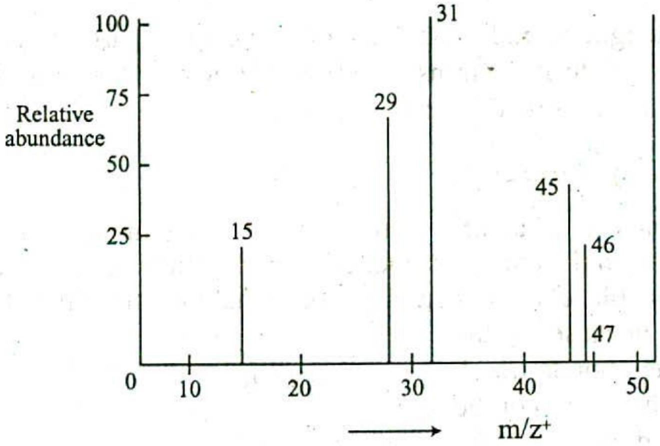


Figure 20.4 Mass spectrum of chlorine

A mass spectrum given in Figure 20.4 shows that there are two isotopes of chlorine ^{35}Cl and ^{37}Cl and three types of chlorine molecules, $^{35}Cl^{35}Cl$, $^{35}Cl^{37}Cl$ and $^{37}Cl^{37}Cl$.

When a compound is investigated in the mass spectrometer one can obtain the peak for the molecular ion, which is the ion formed when an electron is knocked out of the molecule, and singly charged fragments into which the molecules may be broken into. Some times the molecular ion may be so unstable as to break up into fragments in which case the molecular ion may not be detected. As an example the mass spectrum of CH_3CH_2OH shown in Figure 20.5 may be considered. It shows peaks at m/z^+ values of 15, 29, 31, 45, 46. The molecular mass of the compound is 46. Hence the peak at 46 must be for the molecular ion $CH_3CH_2OH^+$. The other peaks may be attributed to the presence of the ions CH_3^+, $C_2H_5^+$, CH_2OH^+, $CH_3CH_2O^+$ respectively.



Mass spectrum of ethanol

Figure 20.5 Fragmentation of the ethanol molecule

Masses of the fragments yield valuable information about the structure of the molecule. For example, it is possible to differentiate between propanaldehyde and acetone. Propan- aldehyde gives peaks at 48, 43 and 29 whereas acetone gives peaks at 48, 43 and 28.

20.6.2 Spectroscopy and electromagnetic spectra

Infrared, ultraviolet and nuclear magnetic resonance spectroscopy involve interaction of molecules/atoms with electromagnetic radiation and thus differ from mass spectrometry where high energy electron beam is used to ionize the sample particles.

Visible light, infrared and ultraviolet (*uv*) radiation, X–rays, microwaves, radio waves are all different kinds of electromagnetic radiation. The wave lengths of the different kinds of radiation are shown in Figure 20.6.

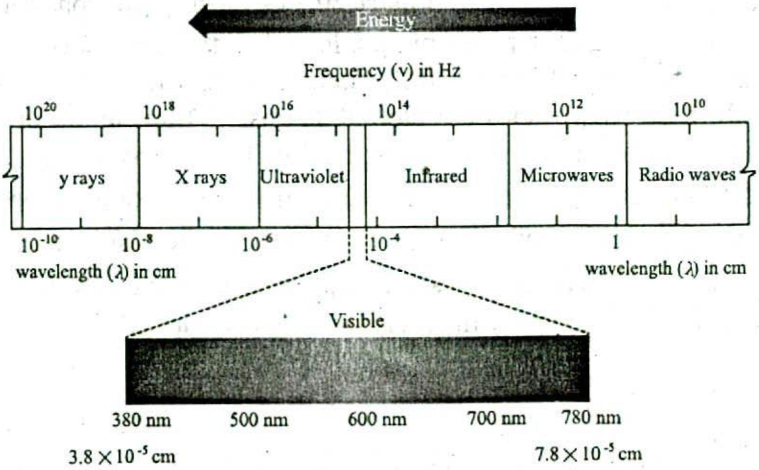


Figure 20.6 The electromagnetic spectrum

When electromagnetic radiation falls on a sample, part of the radiation may be absorbed, part may go through (transmitted) or diffracted. Our interest will be on the part of the radiation that is absorbed by the sample.

20.6.2.1 Infra-red spectroscopy

It was mentioned in Chapter 1 that molecules containing two or more atoms may execute vibrational and rotational motions in addition to translational motion, i.e. movement from one place to another. The vibrational motion of the atoms with respect to each other arises because of the fact that the covalent bonds which keep atoms together can not be considered as rigid as these are formed by the sharing of electrons. Rather these are considered as two atoms or point masses joined by a spring (Figure 20.7). The springs represent the bonds between atoms. These bonds may undergo stretching or bending vibrations as shown in the diagram below. The frequencies of these vibrations have been calculated to be of magnitude of the order of the frequency of electromagnetic radiation in the infra red (*IR*) region of the spectrum.

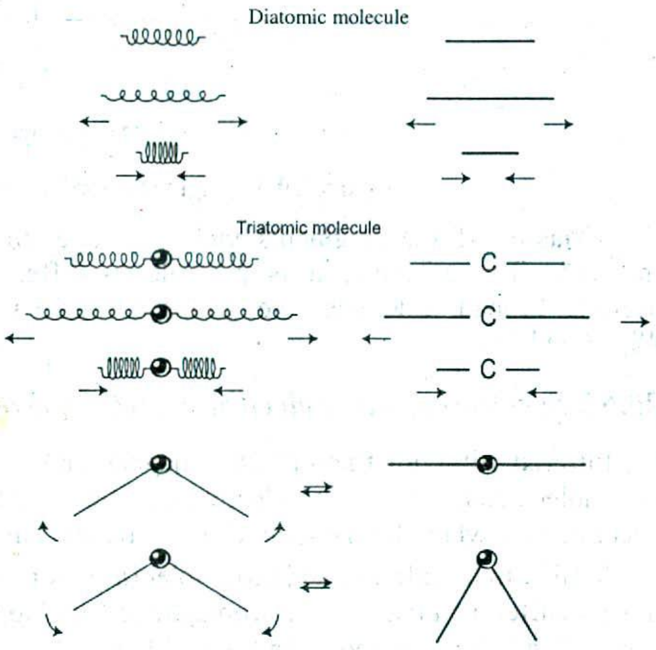


Figure 20.7 Covalent bonds considered as springs

If a beam of electromagnetic radiation is allowed to fall on an organic compound the molecules absorb radiation of certain frequencies and radiation of other frequencies is transmitted. If all these frequencies are plotted against % transmitted or % absorbed, we get the infra – red spectrum of the compound. Usually the wave length (λ) or the wave number ($\bar{\nu}$) is plotted against either % of radiation transmitted or absorbed.

The wave lengths of infra-red radiation of interest to chemists range from 2.5×10^{-4} cm to 2.5×10^{-3} cm. The frequencies are expressed in wave numbers ($\bar{\nu}$). The wave number expressed in cm^{-1} is simply the reciprocal of wave length (λ).

$$\text{Wave number} \quad \bar{\nu}\ (\text{cm}^{-1}) = \frac{1}{\lambda}$$

Thus, the useful *IR* region is from 4000 cm^{-1} to 400 cm^{-1}

When a beam of electromagnetic radiation strikes a molecule, radiation of frequency equal to the frequency of vibration of a bond is absorbed. It has been observed that molecules of different compounds having the same bond between the same two atoms absorb radiation of the same frequency; that is to say that the frequency absorbed is characteristic of the bond between the two atoms. Such absorption is indicated by a peak in the *IR* spectrum. A schematic diagram of the essential parts of an infra-red spectrophotometer is shown in Figure 20.8.

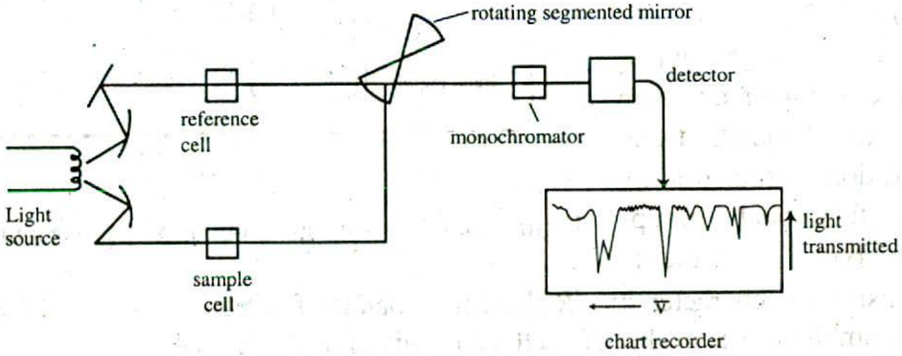


Figure 20.8 Schematic diagram of the essential parts of an infra-red spectrophotometer

A beam of light from a source is divided into two parts with the help of a set of mirrors. One beam passes through the sample cell which holds the sample under investigation as thin film or dissolved in a solvent and the other beam passes through a reference cell which contains only the solvent. A rotating mirror alternately allows light from each of the beams to enter the monochromator. The monochromator uses a prism or diffraction gratings to allow light of only one frequency to pass to the detector at a time. A range of infra-red radiation of different wave lengths goes to the detector. The detector measures intensity of the light of each frequency which has passed through the sample (after correction for the absorption by the solvent). The detector is connected to a recorder which plots per cent transmission against wave length (or wave number) of radiation. (Smaller the absorption greater is the transmission).

Observation of the peaks in the spectrum has been used to identify the presence of particular bond types in molecules. For example, the IR spectrum would show if a molecule has a $C-H$ bond, $C-C$ bond, $C=O$ group or an $O-H$ group. Such groups absorb radiation with wave numbers in the range from 1300 cm^{-1} to 3500 cm^{-1}. Specific absorption peaks indicate the presence of these groups in the molecule. This part of the spectrum is known as the ***band region***. The part of the *IR* spectrum with wave numbers in the region 1300 cm^{-1} to 600 cm^{-1} characterize the whole molecule and is called the ***fingerprint region*** since it can be used to distinguish between molecules with the same functional group. For example, acetone, CH_3COCH_3 (propanone), and methyl ethyl ketone (butanone), $CH_3COCH_2CH_3$, give the same spectra in the band region but in the fingerprint region the peaks differ sufficiently to enable one to distinguish between the two compounds (Figure 20.9).

If two compounds have the same *IR* spectra, they are almost certainly identical compounds. Again by learning where characteristic functional groups occur it is possible to get structural information from the *IR* spectra. A very large number of organic compounds were subjected to *IR* radiation and the absorption of radiation by different functional groups analyzed. Based on these results a list of the characteristic *IR* absorption bands of some common functional groups has been compiled. A short list of such data is given in Table 20.4.

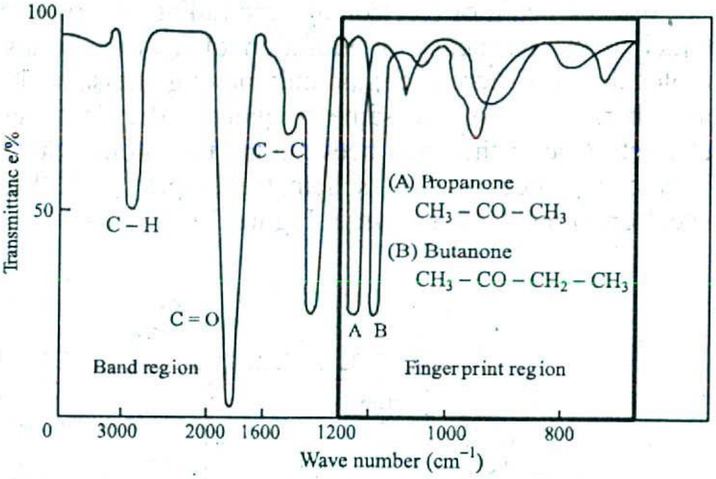


Figure 20.9 Infra-red spectrum of propanone and butanone

Table 20.4 Characteristic *IR* absorption of some functional groups

Functional group	Compound type	Vibration type	Band position (cm^{-1})	Intensity of
$C - H$	Alkanes	Stretch Bend	2850 – 2960 1350 – 1470	Medium to Strong
$C - H$	Alkanes	Bend	1350 – 1470	
$= C - H$	Alkenes	Stretch Bend	3020 – 3100 700 – 1000	Medium Medium
$- C = C -$	Alkenes	Stretch	1640 – 1680	Medium
$\equiv C - H$	Alkynes	Stretch	3300	Strong
$- C \equiv C -$	Alkynes	Stretch	2100 – 2260	Medium
$- O - H$	Alcohol, monomeric	Stretch	3610 – 3640	Strong
$- O - H$	Alcohol,hydrogen bonded	Stretch	3400 – 3650	Strong, broad
$- O - H$	Carboxylic acids	Stretch	2500 – 3000	Strong, broad
$- C - O$	Alcohols, ethers, esters, carboxylic acids	Stretch	1050 –1150	Strong, broad
$C = O$	Aldehydes, ketones, carboxylic acids esters	Stretch	1680 – 1750	Strong

Using this list one can detect the presence of a particular functional group in a compound. Some *IR* spectra are given in Figures 20.10, 20.11, 20.12

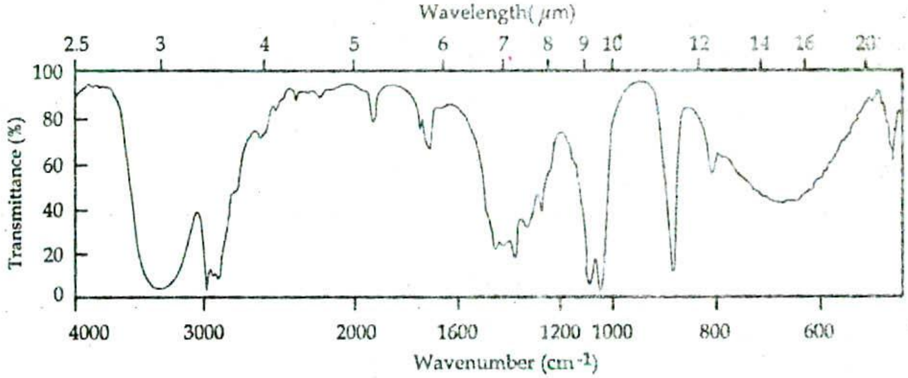


Figure 20.10 The infra-red spectrum of ethanol. Note the band around 3300 cm^{-1}. It is due to stretching of the $O-H$ bond (strong and broad because of hydrogen bonding).

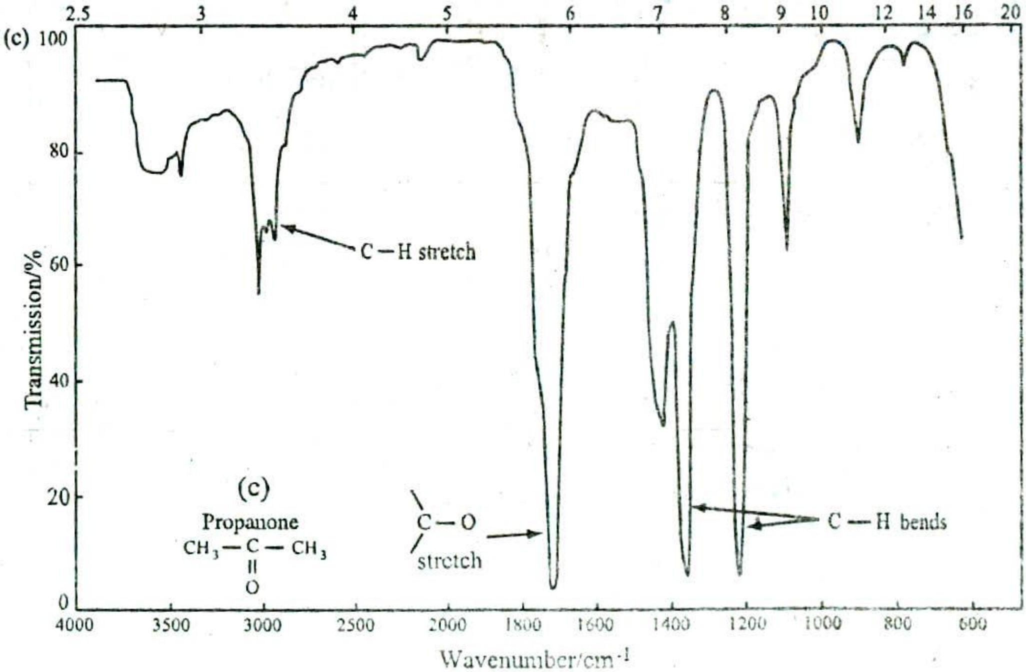
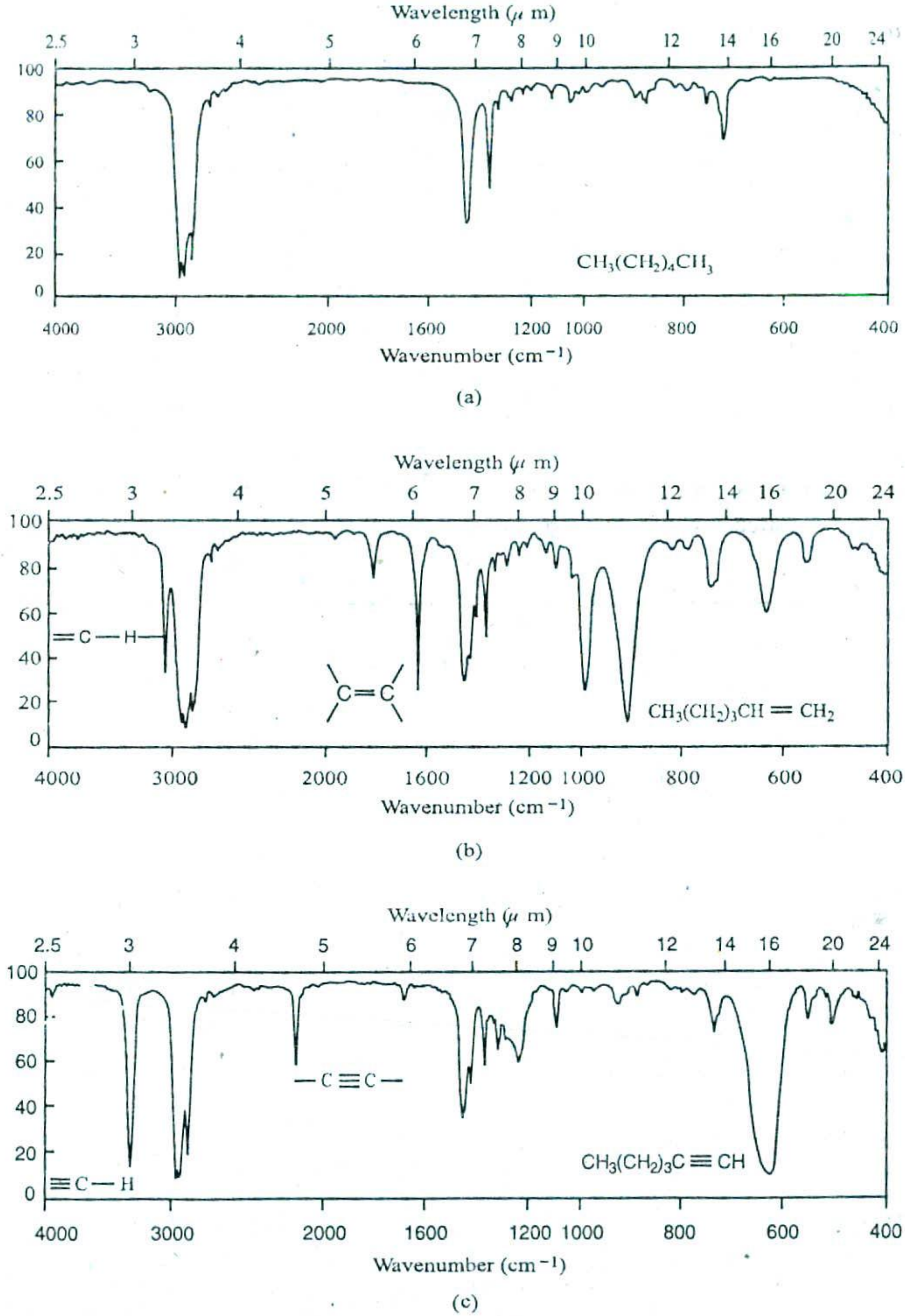


Figure 20.11 *IR* spectrum of acetone. Note the strong absorption at around 1700 cm^{-1} characteristic of $C=O$ bond.



(a)

(b)

(c)

Figure 20.12 Infra-red spectra of (a) hexane, (b) hexene and (c) hexyne. Note the characteristic absorption for different groups.

20.6.3 *Nuclear magnetic resonance (NMR) spectroscopy*

The phenomenon of spinning electron is familiar in connection with the study of atomic structure and electron configuration of atoms. The nuclei of certain atoms are also considered to spin as shown in Figure 20.13. One such nucleus is that of hydrogen atom, i.e. a proton.

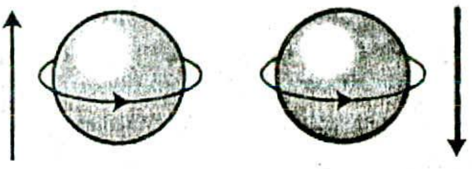
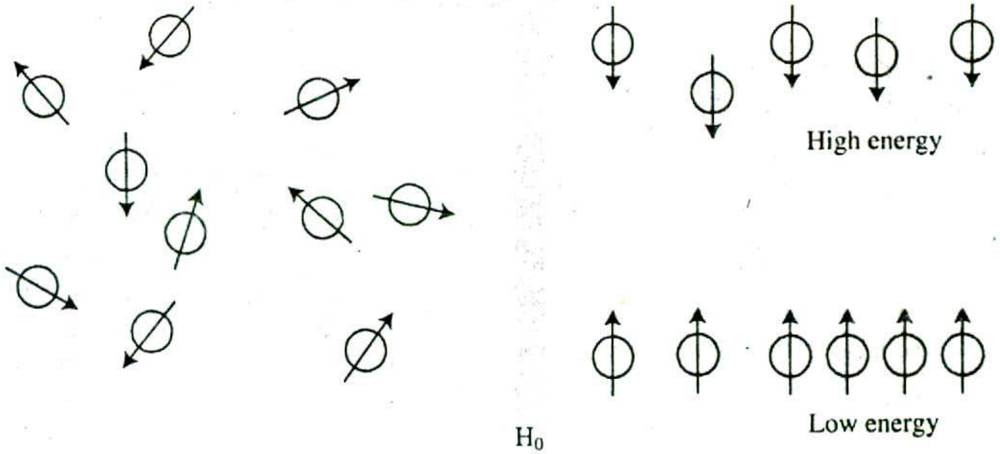


Figure 20.13 Opposite spins of protons

Since protons have positive charge, the spinning charges (protons) act like tiny magnets.

Ordinarily, i.e. in the absence of an external magnetic field, the nuclear spins are randomly oriented. If these are placed in an external magnetic field, according to quantum mechanics the tiny magnets can align themselves either with (parallel) or against (anti-parallel to) the external field. The two orientations do not have the same energy and, therefore, are not equally likely. Alignment with the field is more stable. The situation is shown in Figure 20.14.



(a) (b)

Figure 20.14 (a) Nuclear spins are oriented randomly in the absence of a magnetic field; (b) In the presence of a magnetic field they have specific orientation

If the oriented nuclei are now subjected to electromagnetic radiation of the right frequency, energy absorption occurs and the protons with lower energy 'flips' to the higher energy state. When this spin flips occur the nuclei are said to be in resonance with the absorbed radiation, and hence the name *nuclear magnetic resonance*. Nuclei of other atoms can show this property. The description in the following pages will be confined to the behaviour of protons. These will be *proton magnetic resonance*.

The frequency of radiation absorbed in such cases depends on the strength of the magnetic field (H_0). It has been observed that the radiation necessary to cause flipping of the hydrogen nuclei falls in the radiofrequency range, 60 to 300 MHz (1×10^6 Hz). This corresponds to 2.4×10^{-5} kJ mol^{-1} to 12×10^{-5} kJ mol^{-1}. The frequencies of such radiation are much smaller than those of infra-red radiation (the wave lengths of radiation absorbed are much larger than those of *IR* radiation).

In practice radiofrequency radiation of appropriate frequency is allowed to fall on a sample and the strength of the magnetic field gradually changed. At some value of the magnetic field strength the energy required to flip the proton matches the frequency of radiation, absorption of the radiation occurs, and a signal is observed in the detector. A schematic diagram of a *NMR* spectrometer is given in Figure 20.15.

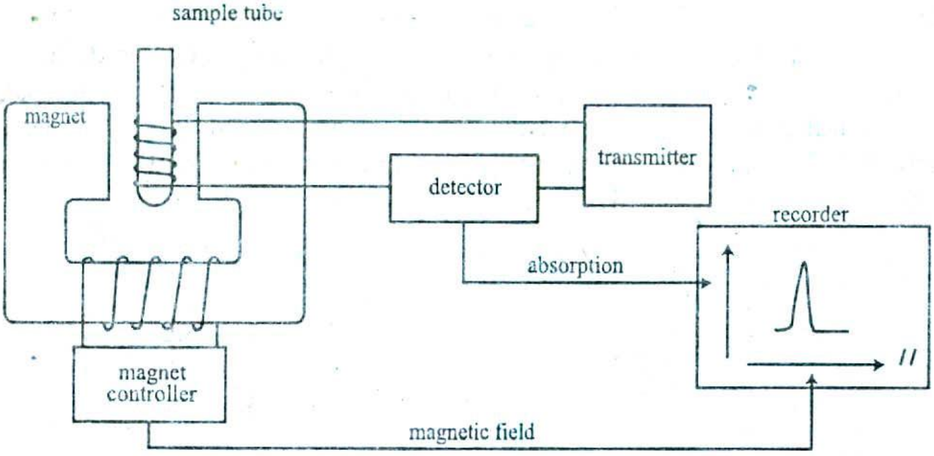


Figure 20.15 A schematic diagram showing the essential parts of a nuclear magnetic resonance spectrometer

As shown, the *NMR* spectrometer consists of four basic parts :

1. A strong electromagnet with a sensitive controller to produce a precise magnetic field
2. A radiofrequency (*RF*) transmitter capable of emitting a precise frequency of radiation
3. A detector to measure the absorption of *RF* energy by the sample
4. A recorder to plot the output from the detector against the applied magnetic field.

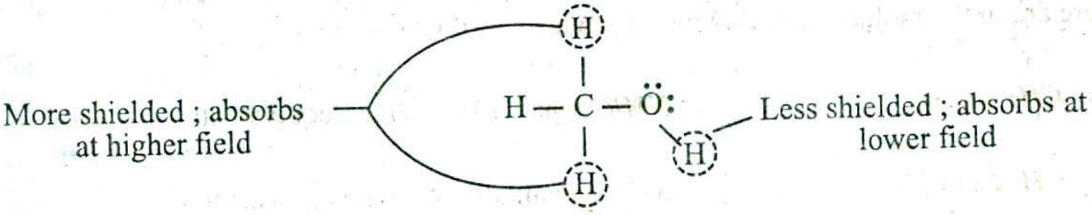
The recorder prints a graph of absorption (on the y-axis) as a function of the magnetic field strength (on the x-axis). Higher values of the magnetic field are toward the right (upfield) and lower values are on the left (downfield). The absorption of more shielded protons appears on the right and those with less shielding appear on the left of the graph (Figure 20.17).

From what has been said above one might think that all proton (^1H) nuclei in a molecule absorb at the same combination of radiofrequency (*RF*) and magnetic field strength. If this were so, one would observe a single *NMR* signal in the instrument. In fact at a particular frequency absorption does not occur at the same magnetic field strength for all protons in a molecule.

All nuclei in a molecule are surrounded by electrons. When an external magnetic field is applied to a molecule, the tiny magnetic fields of the electrons (themselves having spins) act against the applied field so that the effective field (experienced by a proton) is slightly smaller than the applied field.

$$H_{effective} = H_{applied} - H_{local}$$

As a result the nuclei are said to be *shielded* from the full effect of the applied field by the circulating electrons around them. Since each specific nucleus in a molecule is in a slightly different electronic environment, each nucleus is shielded to a slightly different extent, and the effective magnetic field experienced is not the same for all ^1H nuclei. A sensitive instrument is able to detect the differences in the magnetic field experienced by different nuclei, and we can see distinct *NMR* signal for each ^1H with different electronic environment. More shielded the nuclei are, the stronger has to be the magnetic field at which resonance (absorption) will occur. One can say that there are different 'kinds' of protons in a molecule. The protons in methanol, CH_3OH, can be taken as example. The strongly electromagnetic oxygen atom withdraws electrons towards it reducing the electron density on the ^1H atom of the *OH* group. Consequently the hydroxyl ^1H is not shielded as much as the methyl protons (said to be *deshielded*), so the hydroxyl proton absorbs at a lower magnetic field (downfield) than methyl protons.



A careful study of the *NMR* spectrum of a compound provides us with valuable information mentioned below about the protons (protons in different electronic environments) in the molecule:

1. the number of signals show how many different 'kinds' of protons are in the molecule,
2. the positions of the signals tell us something about the electronic environment of each kind of proton
3. the relative extents of absorption tell us about the number of protons of each kind in a molecule of the compound.

Absorption peaks of all 'kinds' of protons in the molecule form the *NMR* spectrum of the compound shown in Figure 20.16.

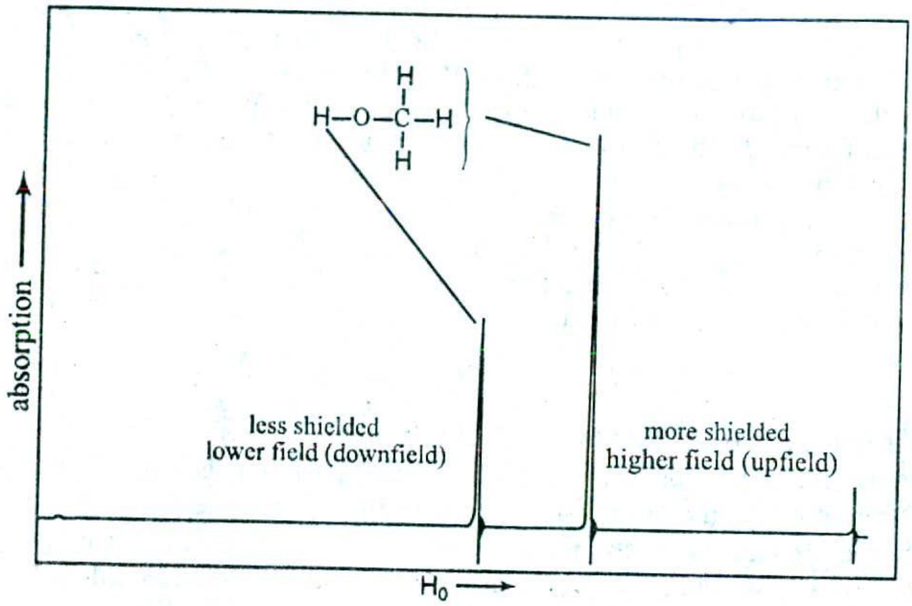


Figure 20.16 Proton *NMR* spectrum of methanol showing peaks for two types of protons

20.6.3.1 NMR: number of signals; equivalent and non-equivalent protons

Protons with the same electronic environment in a molecule absorb at the same (applied) field strength. These protons are said to be equivalent. Protons with different electronic environments absorb at different (applied) magnetic fields and will show a number of signals in the *NMR* spectrum. Such protons are said to be non-equivalent. The number of signals in a *NMR* spectrum tells us how many different 'kinds' of protons there are in the molecule. Following examples will illustrate the point:

(1) $\overset{x}{CH_3} - \overset{x}{CH_3}$ 1 *NMR* signal; all six ^1H are equivalent

(2) $\overset{x}{CH_3}\ CO\ \overset{x}{CH_3}$ 1 *NMR* signal; all six ^1H are equivalent

(3) $\overset{x}{CH_3}\ \overset{y}{CH_2}\ \overset{x}{CH_3}$ 2 *NMR* signals; CH_3 protons are different from CH_2 protons

(4) $\overset{x}{CH_3}\ \overset{y}{CH_2}\ \overset{z}{CH_2}Cl$ 3 *NMR* signals; 3 types *x, y* and *z*

(5) $(CH_3)_2\,C = C(CH_3)_2$ 1 *NMR* signal; all 12 protons are equivalent

20.6.3.2 Chemical shifts: Position of signals

In a *NMR* spectrum of a compound, protons of different 'kinds' show signals at different positions as the applied magnetic field is increasing from left to right in the chart. This is because of shielding and deshielding by electrons. Such shifts in the position of signals are called *chemical shifts*. To define the position of the signals the chart is calibrated and a reference point is used. The reference point from which chemical shifts are measured is the signal from tetramethylsilane (*TMS*), $(CH_3)_4Si$. Since all ^1H in this molecule are equivalent there is only one signal. In actual experiments a small amount of *TMS* is added to the sample under investigation, and the instrument measures the difference in the magnetic field where the protons in the sample absorb and where the *TMS* absorbs. For each type of proton in the sample, this difference is the chemical shift.

By convention, the chemical shift of *TMS* is set at zero and other absorptions occur downfield (to the left of the chart). *NMR* charts are usually calibrated using an arbitrary scale, called the delta (δ) scale. Delta unit (δ) is expressed in parts per million (ppm). The position of the trimethylsilane signal is taken as 0.0 ppm. Most chemical shifts have δ values between 0 and 10. A small δ value indicates a small downfield shift, and a large δ value indicates a large downfield shift.

The chemical shift is measured in terms of frequency units. The frequency is related to the magnetic field strength as follows:

$$\nu = \frac{\gamma H_o}{2\pi}$$

ν = frequency, in Hertz (Hz)

H_o = strength of the magnetic field, in gauss

γ = a nuclear constant, the gyro*magnetic ratio*, and is 26 570 for the proton

(*Gyromagnetic ratio* is a constant that depends on the magnetic moment of the nucleus)

The chemical shift is the frequency equivalent of the magnetic field strength at which absorption takes place divided by the frequency at which the spectrometer operates. A simple *NMR* spectrometer operates at a frequency of 60 *MHz* (60×10^6 *Hz*). For such an instrument the chemical shift is given by

$$\text{Chemical shift, } \delta = \frac{\text{(Observed shift downfield, } Hz)}{NMR \text{ frequency (60 MHz)}}$$

As the chemical shift is determined by the electronic environment of the proton, in a given molecule protons in different environments (non-equivalent protons) will have different chemical shifts. It has been observed that a proton with a particular environment shows almost the same chemical shift irrespective of the molecule it is present in. Data on chemical shift have been collected for protons in many compounds and in different environments. Table 20.5 shows a list of chemical shift of some of the 'kinds' of protons in different environment.

Table 20.5 Some characteristic ^1H chemical shifts

Type of ^1H	Chemical shift, δ (ppm)	Type of ^1H	Chemical shift, δ (ppm)
Reference, $(CH_3)_4Si$	0.0	Aromatic (Ar) $Ar - H$	6.0 – 8.5
Alkane $-CH_3$ $-CH_2-$ $-CH-$	 0.9 1.3 1.5	Aromatic methyl $Ar - CH_3$	2.5 – 2.7
Halogenoalkane $R - CH_2 - X$ (X = halogen)	3 – 4	Methyl ketone $-\overset{\overset{O}{\parallel}}{C}-CH_3$	2.1 – 2.4
Alkenes $-C = C - H$	4.6 – 5.9	Aldehyde $R-\overset{\overset{H}{\vert}}{C}=O$	9.0 – 10
Alkynes $-C \equiv C - H$ Alcohols $-C-O-H$	 2 – 3 2.5 – 5.0 (variable)	Carboxylic acids $R-\overset{\overset{O}{\parallel}}{C}-O-H$	11.0 – 12.0

Figure 20.17 and Figure 20.18 show peaks for equivalent protons. Note the chemical shifts for different kinds of protons.

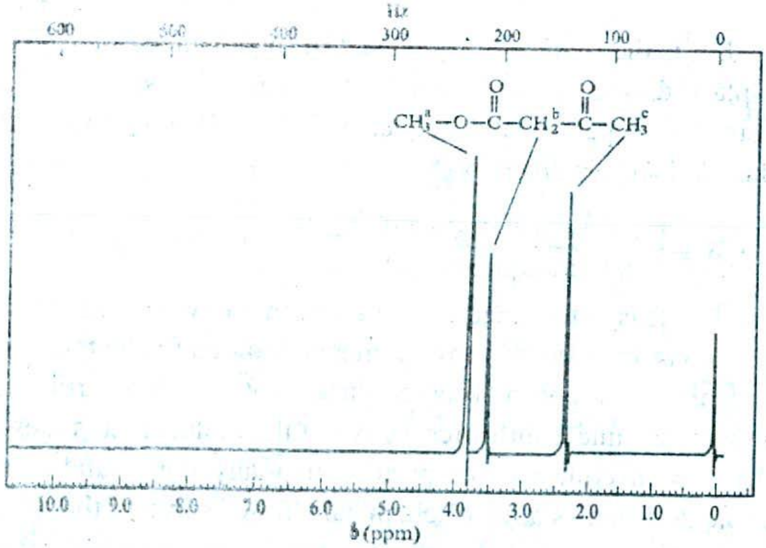


Figure 20.17 *NMR* spectrum of methyl acetoacetate. There are three types of protons giving three *NMR* signals

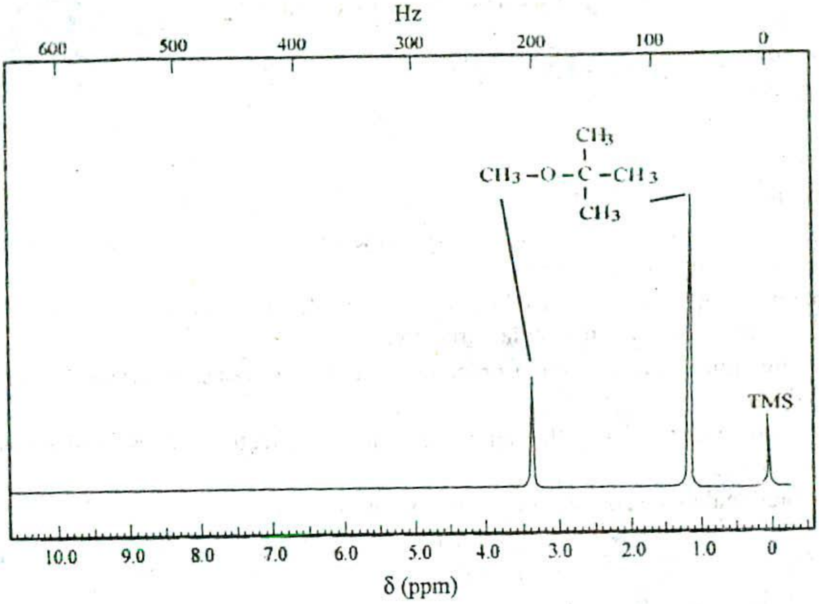


Figure 20.18 *NMR* spectrum of methyl t-butyl ether. There are two kinds of protons in the ratio of 1: 4 as shown by the relative peaks heights.

20.6.3.3 Proton counting

The relative number of different 'kinds' of protons in a molecule may be determined from the ratio of the areas under each peak. The areas are determined electronically by an integrator connected to the detected. The numbers in the simplest ratio gives the number of each kind of proton in the molecule. This can be seen in Figures 20.17 and 20.18.

20.6.3.4 More about NMR spectra

The descriptions given above are for low resolution ^{1}H *NMR* spectra where an instrument with a 60 *MHz* magnetic field strength is used. Instruments using stronger magnetic field, such as 100 *MHz* or 300 *MHz*, give more detailed information about the molecules.

In addition to ^{1}H nucleus other nuclei, such as ^{13}C, ^{14}N, ^{19}F, ^{31}P, with odd number of protons have been found to show magnetic properties. Of these ^{13}C has also found wide application in the determination of structure of organic molecules.

Nuclear magnetic resonance is being used extensively in the field of medicine in what is called ***MRI*** (magnetic resonance imaging). The principle of measurement is the same as described. However, the magnets are strong and the gap between the magnetic poles is also large so that parts of the human body may be placed between the poles. The ***MRI*** technique takes advantage of the magnetic properties of the protons, which are present in abundance in the body fluids, and of the signals emitted when these are exposed to radiofrequency energy. Powerful computers and data processing techniques enable the physician to diagnose large number different types of abnormalities in the body.

QUESTIONS AND PROBLEMS

1. Explain the following terms :
   (i) Specific rotation,
   (ii) Parachor,
   (iii) Dipole moment,
   (iv) Molar volume.
2. What is parachor and how it can be measured experimentally? Show how parachor values can be used for ascertaining molecular structure.
3. Explain dipole moment. What is induced dipole moment? Give an example when dipole moment can be successfully used to ascertain molecular structure.
4. What is meant by optical activity? What structural factors are responsible for optical activity? What is plane polarized light?
5. What is molar refraction? Show with example how molar refraction values can be used to ascertain molecular structures.
6. Describe the vibrational modes of the following molecules:
   (a) HBr
   (b) CO_2
   (c) H_2O
7. Describe the essential parts of a mass spectrometer. What important information about molecules may be derived from a mass spectrum?
8. Describe the principle of obtaining the infra-red spectrum of a substance. The infra-red spectra of three different compounds are shown below. One is an alcohol, one is a ketone and the other is an organic acid. Using the data in Table 20.6 identify the types of the compounds.
9. Explain the basic principle of proton nuclear magnetic resonance spectroscopy.
10. Using a low resolution NMR equipment state how many different 'kinds' of protons can be identified in the following molecules :
    (a) CH_3COOH
    (b) $CH_3CH_2CH_2CHO$
    (c) C_6H_6
    (d) H_2NCH_2COOH
11. Propose structures for compounds with the following formulas that show only one peak in their 1H NMR spectra. :
    (a) C_6H_6
    (b) C_5H_{12}
    (c) C_5H_{10}
    (d) $C_4H_8O_2$
    (e) C_3H_9N
12. How many kinds of nonequivalent protons are present in each of the following compounds?
    (a) CH_3CH_2Br
    (b) $CH_3CH_2CH_2NO_2$
    (c) $CH_3OCH_3CH(CH_3)_2$